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High-Pressure Spectroscopy of Selected Wide Bandgap Lithium Metal Oxides Doped with Transition Metal and Rare Earth Ions.

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Doctoral Thesis

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AUTHOR CONTRIBUTION

The primary responsibility of the doctoral candidate was to conduct high-pressure luminescence measurements on a variety of materials under diverse experimental conditions. The author independently performed all the luminescence and related experiments discussed in the thesis, including measurements at ambient, low-temperature, and high-pressure conditions. Additionally, he was responsible for sample preparation for high-pressure measurement, as well as the assembly and operation of the diamond anvil cell (DAC) for high-pressure experiments, data analysis, and results interpretation. He also actively participated in the preparation of the publications.

For comprehensive data interpretation and manuscript preparation, high-pressure luminescence measurements alone were insufficient; therefore, complementary characterisation techniques were employed with the assistance of collaborators. Raman spectroscopy was performed with the support of Damian Włodarczyk; EPR measurements with Yadhu Krishnan Edathumkandy and Hanka Przybylińska; SEM analysis with Anastasiia Lysak; XPS measurements with Anna Wolska; and SIMS analysis with Rafał Jakiela, all of whom are affiliated with the Institute of Physics, Polish Academy of Sciences (IPPAS), Poland. Furthermore, selected studies were conducted through national and international collaborations, including powder X-ray diffraction and mechanoluminescence measurements with Justyna Barzowska (University of Gdańsk, Poland); high-pressure XRD with Arpita Aparajitha (IGCAR, India); field-emission SEM with Manju Mohandas (MGU, India); thermally stimulated and cathodoluminescence studies with Ivo Romet and Eduard Feldbach (IPUT, Estonia); EXAFS measurements with Shusaku Hayama (Diamond Light Source, UK); Mössbauer spectroscopy with Agnieszka Grabias (Łukasiewicz–IMiF, Poland); and antimicrobial studies with Monika Trzaskowska and Marcin Kruk (SGGW, Poland).

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LIST OF PUBLICATIONS

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1. **Ajeesh Kumar Somakumar**, Lev-Ivan Bulyk, Volodymyr Tsiumra, Justyna Barzowska, Puxian Xiong, Anastasiia Lysak, Yaroslav Zhydachevskyy, and Andrzej Suchocki. "**High-Pressure Near-Infrared Luminescence Studies of Fe³⁺-Activated LiGaO₂.**" *Inorganic Chemistry* 62, no. 31 (2023): 12434-12444.
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Other publications

Journal articles

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4. Abhishek Mukherjee, Damian Wlodarczyk, **Ajeesh Kumar Somakumar**, Piotr Sybilski, Ryan Siebenaller, Rahul Rao, Michael A. Susner, Andrzej Suchocki, and Svetlana V. Boriskina. "**Synergistic Effects of Defects and Strain on Photoluminescence in Van der Waals Layered Crystal AgScP₂S₆.**" *Advanced Optical Materials* 12, no. 35 (2024): 2400481.
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Conference papers

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Popular science article

1. **Ajeesh Kumar Somakumar**, "Niewidzialna rewolucja lamp ledowych." *Delta Science Magazine*, Poland, pp.3.2022. (<https://www.deltami.edu.pl/2022/07/niewidzialna-rewolucja-lamp-ledowych/>).

LIST OF ATTENDED CONFERENCES AND SCHOOLS

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- Participated in and presented a poster at the **International Conference on Excited States of Transition Elements (ESTE 2023)**, 3-8 September 2023, Swieradow Zdroj, Poland. “High-Pressure Study of $\text{LiGaO}_2\text{:Fe}$ Near Infrared Phosphor for Biological Applications” Ajeesh Kumar Somakumar, Andrzej Suchocki.
- Participated and delivered a talk at the “**8th International Workshop on Advanced Spectroscopy and Optical Materials (IWASOM 2024)**”, 7-12 July 2024, Gdańsk, Poland “ Mn^{2+} luminescence in ZnS under high pressure”, Ajeesh Kumar Somakumar, Andrzej Suchocki.
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Schools

- Participated in ‘**Summer School on scintillation, dosimetric, and phosphor materials (LUMDETR 2021)**’ on 10-11 September 2021, in Bydgoszcz, Poland.
- Attended and delivered a talk on high-pressure research at the ‘**European School for Young Materials Scientists (ESYMS-2024)**’ on 4-5 November 2024, at Fraunhofer IKTS, Dresden, Germany.

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ABSTRACT

Lithium-based materials have recently attracted considerable interest because of their optical, mechanical, and electrical properties. In this PhD dissertation, the spectroscopic properties of three ternary lithium metal oxides (LMOs) doped with transition metal and rare-earth elements, particularly under high pressure in the gigapascal range, have been investigated. The research focuses on wide-bandgap lithium metal oxides doped with d^5 -configuration transition metals and selected rare-earth ions. Doping these LMOs with different metal ions gives them specific spectroscopic features, including luminescence spanning the visible to near-infrared range. Furthermore, their luminescence properties are extensively studied under different physical conditions, including low to room temperature, and pressure ranges from ambient to 25 GPa. The ambient-pressure optical properties of these materials doped with different luminescent activators have already been reported. In this thesis, we adopt an alternative approach to study these materials using high-pressure technique with a diamond anvil cell (DAC) and analysing the results using Tanabe-Sugano diagrams and crystal field theory. This approach allows not only the study of their spectroscopic features but also their structural properties, including pressure-induced phase-transition behaviours.

The main content of the PhD dissertation comprises 8 chapters, beginning with an introduction to lithium metal oxides and concluding with a summary of the work. The first chapter presents a brief literature review of lithium metal oxides, lists some of the lithium metal oxides studied using various high-pressure techniques, and provides basic information on the lithium metal oxides (LiGaO_2 , LiGa_5O_8 , and LiYO_2) studied in the thesis. The second chapter lists various luminescence phenomena and describes briefly the possible mechanisms leading to luminescence in condensed matter. It also provides a short introduction to the properties of luminescent ions discussed in the subsequent chapters. Chapters 3 and 4 introduce the different experimental techniques used in the research. Chapter 3 emphasises various high-pressure techniques, focusing on the high-pressure studies in DAC. Details of the experimental methods and sample preparation procedures used in high-pressure measurements are also described here. Chapter 4 discusses experimental techniques other than high-pressure used in the research. Some of these experiments were performed at synchrotrons and at foreign research institutions under collaborations.

Chapters 5 to 7 present the results of experimental research conducted during PhD studies, some of which have been published in peer-reviewed journals, but also incorporate unpublished data from those studies. Chapter 5 consists of two published papers. The first one covers the investigation of near-infrared luminescence in Fe^{3+} -doped LiGaO_2 at low temperatures and high pressures. The phosphor shows strong near-infrared luminescence at low temperatures and ambient pressure, which persists even after the phase transition from orthorhombic to the trigonal phase above 3 GPa. The luminescence is quenched when the applied pressure increases to 14 GPa, due to amorphisation of the material. The phosphor was also found to exhibit excellent near-infrared mechanoluminescence at ambient conditions. The second paper reports the study conducted as an extension to the experimental work described in the previous paper. It focuses on the issues not addressed in the previous one, such as multisite occupation of Fe^{3+} in LiGaO_2 powder. The Fe^{3+} luminescence centres in the LiGa_5O_8 impurity phase present in the phosphor were also analysed. To this aim, the LiGa_5O_8 impurity phase in the sample was purposefully increased by thermal annealing. Chapter 6 is devoted to the Mn^{2+} -doped LiGaO_2 phosphor synthesised using a vacuum-assisted method. Its luminescence was examined at low temperatures and high pressures. The sample also exhibited behaviour associated with multiple-site occupation of the dopant in the crystal lattice, similar to previously reported samples. Additionally, the Mn^{2+} luminescence in LiGaO_2 under pressure was compared with that observed in other materials with tetrahedral coordination of the Mn ions, such as ZnS and GaN . A particularly interesting result was obtained for $\text{GaN}:\text{Mn}^{2+}$, in which pressure-induced Mn^{2+} -related luminescence appeared above 15 GPa. This effect was attributed to the pressure increase of the GaN energy gap. Further studies on related topics are ongoing. Chapter 7 provides a comprehensive overview of high-pressure luminescence and XRD investigations of undoped, and Eu^{3+} and Gd^{3+} co-doped LiYO_2 . A previously unreported pressure-induced phase transition was observed in both doped and undoped LiYO_2 using high-pressure luminescence and XRD techniques. The high-pressure XRD studies were conducted at a synchrotron facility, and the results from this research work are currently progressing towards publication. Chapter 8 summarises the findings from the research work and concludes with a perspective on future developments in this field.

STRESZCZENIE

Materiały na bazie litu cieszą się ostatnio dużym zainteresowaniem ze względu na swoje właściwości optyczne, mechaniczne i elektryczne. W niniejszej pracy doktorskiej zbadano właściwości spektroskopowe różnych trójskładnikowych tlenków litowo-metalowych (LMO) domieszkowanych metalami przejściowymi i pierwiastkami ziem rzadkich, szczególnie pod wysokim ciśnieniem w zakresie gigapaskali. Badania koncentrują się na tlenkach litowo-metalowych o szerokiej przerwie energetycznej, domieszkowanych jonami metali przejściowych o konfiguracji d^5 i wybranymi jonami pierwiastków ziem rzadkich. Domieszkowanie tych LMO różnymi jonami metali nadaje im charakterystyczne właściwości spektroskopowe, m.in. luminescencję w zakresie od światła widzialnego do bliskiej podczerwieni. Ponadto ich właściwości luminescencyjne zostały dokładnie zbadane w różnych warunkach fizycznych, w tym w temperaturze od niskiej do pokojowej i w zakresie ciśnień od ciśnienia atmosferycznego do 25 GPa. Dotychczas opisano już niektóre właściwości optyczne tych materiałów w ciśnieniu atmosferycznym z różnymi aktywatorami luminescencji. W niniejszej pracy przyjęto alternatywne podejście do badania tych materiałów, wykorzystując technikę wysokociśnieniową z wykorzystaniem komory diamentowej (DAC) i analizując wyniki za pomocą diagramów Tanabe-Sugano oraz teorii pola krystalicznego. Podejście to pozwala nie tylko badać ich właściwości spektroskopowe, ale także właściwości strukturalne, w tym zachowania związane z przemianami fazowymi wywołanymi ciśnieniem.

Zasadnicza treść rozprawy doktorskiej składa się z 8 rozdziałów, zaczynających się od wprowadzenia do tlenków litowo-metalowych, a kończących się podsumowaniem pracy. W pierwszym rozdziale przedstawiono krótki przegląd literatury dotyczącej tlenków litowo-metalowych, wymieniono niektóre z badanych tlenków przy użyciu różnych technik wysokociśnieniowych oraz przedstawiono zarys tlenków litowo-metalowych takich jak LiGaO_2 , LiGa_5O_8 i LiYO_2 , badanych w pracy. Rozdział drugi poświęcony jest zjawisku luminescencji i omawia w skrócie mechanizmy luminescencji występujące w ciele stałym, a także zawiera krótkie wprowadzenie do własności jonów luminescencyjnych omawianych w kolejnych rozdziałach. Rozdziały 3 i 4 skupiają się głównie na różnych technikach eksperymentalnych wykorzystanych w naszych badaniach. W rozdziale 3 położono nacisk na różne techniki wysokociśnieniowe, w

tym wyjaśnienie, czym jest DAC. Opisano tu także szczegóły dotyczące metod eksperymentalnych i procedur przygotowania próbek stosowanych w pomiarach wysokociśnieniowych. W rozdziale 4 omówiono natomiast inne niż wysokociśnieniowe techniki eksperymentalne, wykorzystywane w badaniach. Niektóre z tych eksperymentów przeprowadzono na synchrotronach i w zagranicznych instytucjach badawczych w ramach współpracy.

Rozdziały od 5 do 7 przedstawiają wyniki badań eksperymentalnych przeprowadzonych podczas studiów doktoranckich, które zostały opublikowane w recenzowanych czasopismach, a także zawierają niektóre niepublikowane dane z tych badań. Rozdział 5 składa się z dwóch opublikowanych artykułów. Pierwszy z nich dotyczy badań luminescencji LiGaO_2 domieszkowanego Fe^{3+} w bliskiej podczerwieni, w niskich temperaturach i wysokich ciśnieniach. Fosfor ten wykazuje silną luminescencję w bliskiej podczerwieni zarówno w niskich temperaturach, jak i w temperaturze pokojowej, nawet po przejściu z fazy ortorombowej do trygonalnej pod ciśnieniem 3 GPa. Luminescencja ta zanika gdy przyłożone ciśnienie wzrasta do 14 GPa, ze względu na amorfizację materiału. Ponadto materiał ten wykazuje doskonałą mechanoluminescencję w bliskiej podczerwieni. Drugi artykuł przedstawia wyniki badań przeprowadzonych w ramach rozszerzenia prac eksperymentalnych opisanych w poprzednim artykule. Koncentruje się on na zagadnieniach nieomówionych w poprzednim artykule, takich jak zajmowanie przez jony Fe^{3+} wielu miejsc w sieci krystalicznej proszku LiGaO_2 . Przeanalizowano również centra luminescencyjne Fe^{3+} w fazie domieszkowej LiGa_5O_8 obecnej w luminoforze. W celu przeprowadzenia dalszych badań celowo zwiększono fazę domieszkową LiGa_5O_8 w próbce poprzez wygrzanie termiczne. Rozdział 6 jest poświęcony luminoforowi LiGaO_2 z domieszką Mn^{2+} otrzymanemu w próżni. Zbadano jego luminescencję w niskich temperaturach i pod wysokim ciśnieniem. Próbką wykazywała również zachowanie związane z obsadzaniem przez jony domieszki wielu miejsc w sieci krystalicznej, podobne do próbek opisanych wcześniej. Dodatkowo porównano luminescencję Mn^{2+} w LiGaO_2 pod ciśnieniem z luminescencją obserwowaną w innych materiałach o tetraedrycznej koordynacji jonów manganu, takich jak ZnS i GaN . Szczególnie interesujący wynik uzyskano dla $\text{GaN}:\text{Mn}^{2+}$, w którym zaobserwowano wywołaną ciśnieniem luminescencję związaną z Mn^{2+} powyżej 15 GPa. Efekt ten przypisano zwiększeniu przerwy energetycznej GaN pod wpływem ciśnienia. Trwają dalsze badania dotyczące podobnej tematyki. Rozdział 7 zawiera kompleksowy przegląd wysokociśnieniowych

badan luminescencji i XRD niedomieszkowanego LiYO_2 oraz LiYO_2 z domieszkami Eu^{3+} i Gd^{3+} . Za pomocą technik luminescencji wysokociśnieniowej i XRD zaobserwowano nieraportowane wcześniej przejście fazowe wywołane ciśnieniem zarówno w domieszkowanym, jak i niedomieszkowanym LiYO_2 . Badania XRD pod wysokim ciśnieniem przeprowadzono przy użyciu promieniowania synchrotronowego, a wyniki tych badań są obecnie przygotowywane do publikacji. Rozdział 8 zawiera podsumowanie wyników badań i kończy się wnioskami dotyczącymi perspektyw przyszłych osiągnięć w tej dziedzinie.

LIST OF ABBREVIATIONS

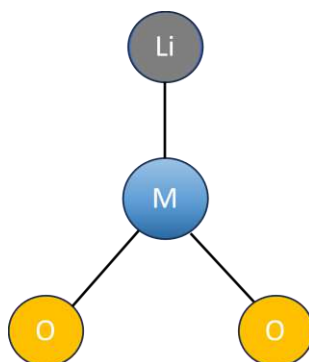
CL	Cathodoluminescence
CB	Conduction Band
CCD	Charge-Coupled Device
CTB	Charge Transfer Band
DAC	Diamond Anvil Cell
DSC	Differential Scanning Calorimetry
EL	Electroluminescence
EXAFS	Extended X-Ray Absorption Fine Structure
EDS	Energy Dispersive Spectroscopy
EPR	Electron Paramagnetic Resonance
FE-SEM	Field Emission Scanning Electron Microscopy
FWHM	Full Width at Half Maximum
HP	High Pressure
IR	Infrared
LMO	Lithium Metal Oxides
LVP	Large Volume Press
LT	Low Temperature
ML	Mechanoluminescence
NIR	Near-Infrared
OPO	Optical Parametric Oscillator
PL	Photoluminescence
PTM	Pressure Transmitting Medium
PMT	Photomultiplier Tube
QE	Quantum Efficiency
QS	Quadrupole Splitting
RE	Rare Earth
SEM	Scanning Electron Microscope
SIMS	Secondary-Ion Mass Spectrometry

TSL	Thermo-Stimulated Luminescence
TL	Thermoluminescence
TM	Transition Metal
TS	Tanabe-Sugano
TPa	Tera Pascal
TCSPC	Time-Correlated Single-Photon Counting
UV	Ultraviolet
VB	Valence Band
VUV	Vacuum Ultraviolet
XRD	X-Ray Diffraction
XAS	X-Ray Absorption Spectroscopy
ZPL	Zero Phonon Line

KEY SCIENTIFIC OBJECTIVES ACHIEVED

- Detailed luminescence analysis of Fe^{3+} -doped $\beta\text{-LiGaO}_2$ (lithium gallate) phosphor under ambient and high-pressure conditions.
- First experimental demonstration of pressure-induced quenching of Fe^{3+} luminescence in $\beta\text{-LiGaO}_2$ above 14 GPa.
- Observation of near-infrared (NIR) mechanoluminescence in $\beta\text{-LiGaO}_2\text{:Fe}^{3+}$ phosphor for the first time.
- Clearing of the long-standing ambiguities in the interpretation of Fe^{3+} related luminescence in LiGaO_2 phosphor.
- First time experimental observation of Mn^{2+} luminescence in GaN at extreme pressures (>15 GPa).
- First time experimental identification of a novel high-pressure phase of LiYO_2 using combined high-pressure luminescence and synchrotron X-ray diffraction techniques.

1. Introduction to Lithium Metal Oxides



1.1. Introduction

Lithium metal oxides (LMO) doped with rare-earth (RE) and transition-metal (TM) elements have attracted considerable scientific attention due to their excellent applications in optoelectronics, energy storage, and catalysis [1–4]. Understanding their structural, optical, and electronic properties under different external conditions, such as low-temperature and high-pressure, is essential for their real-world applications. High-pressure spectroscopy is a versatile tool for examining material properties under extreme conditions, providing unique insights into phase transition behaviour, electronic band structure, and bonding characteristics of the material under pressure. Investigating ternary metal oxides with lithium is highly relevant, as they are among the crucial materials to consider for next-generation portable energy sources. They are very essential components of lithium-ion batteries found in many modern-day electronic gadgets and the automotive industry. The general properties of LMOs, such as stability, conductivity, and capacity retention, can be significantly controlled and enhanced by incorporating RE and TM ions into their crystal lattice [5–8]. However, doped and undoped LMO's under extremely harsh conditions like high pressure and low-temperature conditions are still very much unexplored. The present dissertation primarily focuses on the high-pressure spectroscopy of LMO materials doped with TM and RE elements. The primary objective of this work is to elucidate the impact of high

pressure on the structural and optical characteristics of these materials, utilising both experimental methods and theoretical support. The studies were primarily conducted using powder X-ray diffraction (XRD), ambient and high-pressure luminescence, Raman spectroscopy, and various other spectroscopic techniques.

1.2. Lithium metal

Lithium (Li) is the lightest metal and the least dense solid at ambient conditions. Its atomic number is three ($Z = 3$). Due to its single valence electron, it is highly reactive. Lithium is mainly extracted from rare minerals like Spodumene ($\text{LiAl}(\text{SiO}_3)_2$) [9], Lepidolite ($\text{K}(\text{Li},\text{Al})_3(\text{Al},\text{Si},\text{Rb})_4\text{O}_{10}(\text{F},\text{OH})_2$) [10], Zinnwaldite ($\text{KLiFeAl}(\text{AlSi}_3)\text{O}_{10}(\text{OH},\text{F})_2$) and Petalite ($\text{LiAlSi}_4\text{O}_{10}$) [11], and it does not occur naturally in nature. It is also highly reactive with other metal oxides and readily forms ternary lithium metal oxides. Due to its wide application in energy storage devices, lithium attracted significant global interest.

This is due to its low atomic mass and high charge density (resulting from its small ionic radius and single +1 charge state), making it a suitable material for contemporary energy solutions, such as lithium-ion batteries. Additionally, lithium compounds are widely used in other areas, including the nuclear industry. Lithium and its compounds are integral parts of both nuclear fission and fusion technologies, and are also used as scintillating materials to detect ionising radiation. Additionally, they have found applications in underground neutrino detectors [12]. Also, they found applications in the ceramics, glass, medical, and aerospace industries, etc. [12–15]. Lithium's growing significance in both scientific and industrial applications underscores the need for a better understanding of its physical properties, chemical reactivity, and interactions with other materials, especially under extreme conditions, such as high pressure and varying temperatures.

As seen in the phase transition diagram in Figure 1.1, lithium exhibits superconducting properties above 20 GPa and at low temperatures. Although extrapolation suggests a transition temperature of 0.4 mK at ambient pressure, superconductivity has not been experimentally observed [16,17]. As a result, little is known about how lithium behaves at pressures below 20 GPa. Hence, studying lithium and its oxide compounds under extreme conditions can provide valuable insights into their physical properties, thereby extending potential applications.

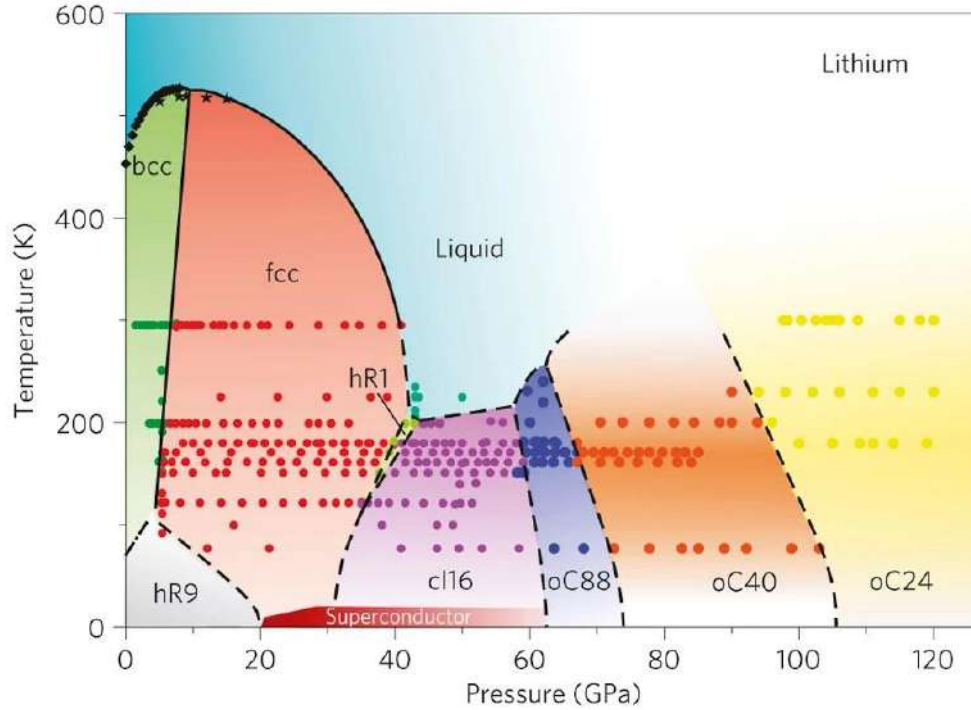


Figure 1.1. Proposed phase transition diagram of the element lithium (Li) over a wide pressure (GPa) and temperature (K) range. Reprinted with permission from “*Cold melting and solid structures of dense lithium*”, Nature Physics 7, 211-214, DOI:10.1038/nphys1864. © Springer Nature 2011 [17].

1.3. Previous high-pressure studies on lithium metal oxides (LMO)

Previously, high-pressure studies were conducted on a few LMO materials; some of them are listed in Table 1.1. However, many key LMO materials were not included in the list, despite their potential applications in various devices. The high pressure of LMO is particularly intriguing because it provides information on structural transformations, phase transitions, electronic, optical, and thermodynamic properties, among others. The previous studies listed here are focused on Raman, luminescence, XRD, EXAFS, and conductivity studies under the influence of high pressure. The list below illustrates how nearly every LMO material exhibits distinct behaviour under pressure when the secondary metal ion (M) is changed. Some materials exhibit phase transitions at comparatively low pressures; however, others do not show any phase transition even at elevated pressures.

Table 1.1. Compilation of previously reported high-pressure data of lithium metal oxide samples using various experimental techniques.

Lithium metal oxides (LMO)	Initial phase (Space group)	New phase (Space group)	Main Study	P-T* pressure (GPa)	Max. pressure reached (GPa)	Ref.
Lithium vanadate (LiV ₂ O ₄)	Cubic (<i>Fd</i> $\bar{3}$ <i>m</i>)	Rhombohedral (<i>R</i> -3 <i>m</i>)	EXAFS	~ 6–12	21.7	[18]
Lithium metavanadate (LiVO ₃)	Monoclinic pyroxene-type (<i>C2/c</i>)	Triclinic (<i>P1</i>)	Raman /XRD	5	21.2	[19]
Lithium tantalate (LiTaO ₃)	Trigonal (<i>R3c</i>)	Orthorhombic (<i>Pnma</i>)	XRD	33	56.1	[20]
Lithium chromate (LiCrO ₂)	Layered rhombohedral (<i>R</i> -3 <i>m</i>)	**	Raman /XRD	**	41.2	[21]
lithium cobaltite (LiCoO ₂)	Layered rhombohedral (<i>R</i> -3 <i>m</i>)	**	Raman /AD-XRD	**	26	[22]
Lithium gallate (LiGaO ₂)	Orthorhombic (<i>Pna</i> 2 ₁)	Trigonal, (<i>R</i> -3 <i>m</i>)	XRD	3	14	[23]
Lithium aluminate (LiAlO ₂)	Tetragonal γ -phase (<i>P4</i> ₁ 2 ₁ 2)	Tetragonal high-pressure phase (<i>I4</i> ₁ / <i>amd</i>)	Shock compression/XRD	9	48	[24]
Lithium titanate (Li ₂ TiO ₃)	Monoclinic (<i>C2/c</i>)	NaCl-type high-symmetry phase (<i>Fm</i> -3 <i>m</i>)	Raman/DFT	43	45	[25]
Lithium–manganese oxide (LiMn ₂ O ₄)	Cubic spinel (<i>Fd</i> -3 <i>m</i>)	Tetragonal (<i>I4</i> ₁ / <i>amd</i>)	XRD	1.9	8.5	[26]
Lithium tungstate (Li ₂ WO ₄)	Phenacite-type (trigonal)	Monoclinic high-pressure phase	Calorimetry	1.6	4	[27]
Lithium ferrite (LiFeO ₄)	Rocksalt cubic (<i>Fm</i> -3 <i>m</i>)	**	HP -XRD	** (Spin crossover ~50)	82	[28]
Lithium copper oxide (LiCuO ₂)	Orthorhombic (<i>Cmcm</i>)	Monoclinic (<i>C2/m</i>)	HP -XRD	~3–4	6.3	[29]

Lithium niobate (LiNbO_3)	Trigonal ferroelectric (R3c)	NaIO3-type high-pressure phase	HP -XRD	42-54 (stoichiometry dependent)	54	[30]
Lithium yttriate (LiYO_2)	Tetragonal ($I4_1/amd$)	Unknown	HP-XRD	5.1	18.5	Present work
*Phase-transition ** Not observed						

1.4. Lithium metal oxides presented in this work

The high-pressure spectroscopy work covered in this thesis mainly focused on two materials: LiGaO_2 and LiYO_2 . Additionally, one chapter discusses the formation of the unintentional LiGa_5O_8 impurity phase in LiGaO_2 material through thermal annealing. LiGa_5O_8 is another LMO material that has gained significant interest recently due to its unique properties.

1.4.1. Lithium gallium oxide: lithium gallate (LiGaO_2)

Lithium gallium oxide (LiGaO_2), also known as lithium gallate or lithium metagallate, is a ternary metal oxide of both lithium and gallium. It exists in at least four different types of polymorphs: α , β , γ , and δ . The phase occurring at ambient conditions, β - LiGaO_2 , has an orthorhombic crystal structure with the $Pna2_1$ space group. The material shows excellent thermal and chemical stability with a comparatively very high bandgap of ~ 5.6 eV [31–33]. Undoped LiGaO_2 exhibits photoluminescence emission in the UV region, which is desirable for the fabrication of UV emitters and detectors. The material exhibits piezoelectric properties, which are essential for the fabrication of sensors and actuators. Additionally, LiGaO_2 is utilised as a lattice-matching substrate for the commercial production of GaN crystals.

1.4.2. Lithium gallium oxide: lithium pentagallium octaoxide (LiGa_5O_8)

Lithium gallium oxide (LiGa_5O_8), known as lithium pentagallate, is classified as a spinel-type material. LiGa_5O_8 mainly crystallises in two forms: a low-temperature ordered cubic primitive phase with space group $P4_332$ and a high-temperature disordered phase with $Fd\bar{3}m$ space group [34]. It exhibits potential luminescence properties when doped with TM or RE elements. Recently, the material has been of interest to the materials science community due to its p-type conductivity [35]. It is considered one of the highest bandgap materials that exhibit p-type conductivity. The material is also highly stable at elevated temperatures.

1.4.3. Lithium yttrium oxide (LiYO_2)

Lithium yttrium oxide (LiYO_2) crystallises mainly in tetragonal and monoclinic phases depending on its synthesis conditions; at high temperatures, the material is in tetragonal form and at low temperatures, the material is monoclinic. As a result, the material exhibits excellent thermochromic properties. The band gap of LiYO_2 is also comparatively high, at approximately 5.23 eV [36]. The material is also promising due to its carbon capture capabilities and, when doped with RE elements, it can also be utilised as a phosphor material. It has also found applications in the nuclear industry and is considered a promising material in lithium-ion batteries due to its thermal stability and ionic conductivity.

1.5. General characteristics of LiGaO_2 , LiGa_5O_8 , and LiYO_2

The general characteristics of LMO samples presented in the thesis are summarised in Table 1.2.

Table 1.2. General characteristics of Lithium Metal Oxide (LMO) samples presented in the thesis

Material	Structure	Space Group	Bandgap	Unique features
LiGaO_2	Orthorhombic	$Pna2_1$	~ 5.6 eV [31]	Piezoelectric, scintillation, and dosimetric properties
LiGa_5O_8	Cubic	$P4_332$	~ 5.36 eV [35]	p-type-conductivity, persistent luminescence
LiYO_2	Monoclinic Tetragonal	$P2_1/c$ $I4_1/amd$	~ 5.23 eV [36]	Thermochromic, negative thermal expansion behaviour

2. Luminescent Materials & Activators



2.1. Introduction to luminescent materials

A luminescent material is a material that re-emits part of its absorbed energy as light in the UV, visible, or IR part of the electromagnetic spectrum. German physicist E. Wiedemann introduced the term “luminescence” in 1888 from the Latin name for light, “lumen”. Depending on various excitation energies provided to the luminescent material, the luminescence property is classified into many types and is usually identified by a prefix along with the word luminescence [37]. If excitation energy is given in the form of sound or light then it is sono- or photoluminescence (PL), if it is excited with moderate heating then its thermoluminescence (TL), by an electric field then it is electro luminescence (EL) or with electrons then cathodoluminescence (CL) and by applying mechanical stress then its tribo- or mechanoluminescence (ML), by chemical reaction its chemiluminescence, and if with some biological activity then it is called bioluminescence [38–41].

Another main classification for luminescent materials is based on the time elapsed between excitation and emission of light. In other words, the phosphorescence (also known as afterglow) occurs when the emission continues for a considerable amount of time after the excitation. In

contrast, fluorescence occurs when the emission ceases as the excitation stops. Based on this time classification, materials are classified into fluorescent materials and phosphorescent materials [42]. The cover image of **Chapter 2** depicts a LiGaO₂ crystal doped with Fe³⁺ ions that exhibit NIR emission (744 nm) when exposed to a 261 nm UV laser line in our laboratory, the phenomenon attributed to the TM ions present in the crystal. However, the colour (wavelength) of the emitted light by a luminescent material is influenced by several intrinsic and extrinsic factors.

- **Intrinsic properties:** The electronic band structure of the luminescent material and its optical transitions determine the fundamental emission wavelengths
- **Impurities and defects:** Doping and structural defects can introduce new electronic states, modifying emission characteristics (e.g. defect-related luminescence)
- **External fields:**
 - **Stress/Pressure:** Alters the bandgap (e.g. blue or redshifts due to strain).
 - **Magnetic fields:** They influence the spin states and lead to magneto-optical effects.
 - **Electric fields:** Modify carrier recombination pathways (e.g. Stark effect)
- **Temperature:** Higher temperatures can broaden emission spectra due to increased electron-phonon interactions and non-radiative recombination.
- **Particle size:** In nanoscale materials, quantum confinement shifts emission energy, leading to tunable photoluminescence.

2.1.1. Luminescence mechanisms

The luminescence phenomenon of luminescent materials can occur in various ways, most notably by electronic transitions. This electronic process that leads to luminescence is also classified into many categories based on its unique characteristics [38,43,44].

Band-to-band emission: it occurs when an electron excited into the conduction band (CB) recombines with a free hole in the valence band (VB), emitting a photon.

Excitonic emission: An exciton is an electron-hole pair bound by Coulomb interaction. It emits light at a below bandgap energy and can also be excited at an energy below the bandgap; the difference between the emission (absorption) and the bandgap energies is equal to the binding energy. Materials with high exciton binding energies are used in optoelectronics.

Impurity luminescence: Most materials contain trace amounts of other elements (impurities) either intentionally introduced by doping or contained in the precursors used for synthesis, which introduce localised energy levels into the forbidden gap. The absorption and emission energies of such impurities are not related to the material's bandgap. The same applies to energy levels associated with lattice defects.

Energy transfer between the energy donor (D) and energy acceptor (A): The intentional or unintentional distribution of impurities within the sample plays a significant role. An impurity D (the energy donor or sensitizer) transfers a part of the excitation energy (non-radiatively or radiatively) to a neighbouring impurity A (energy acceptor or activator), which undergoes radiative decay. The energy transfer process involving resonant D and A excited states is shown in Figure 2.1.

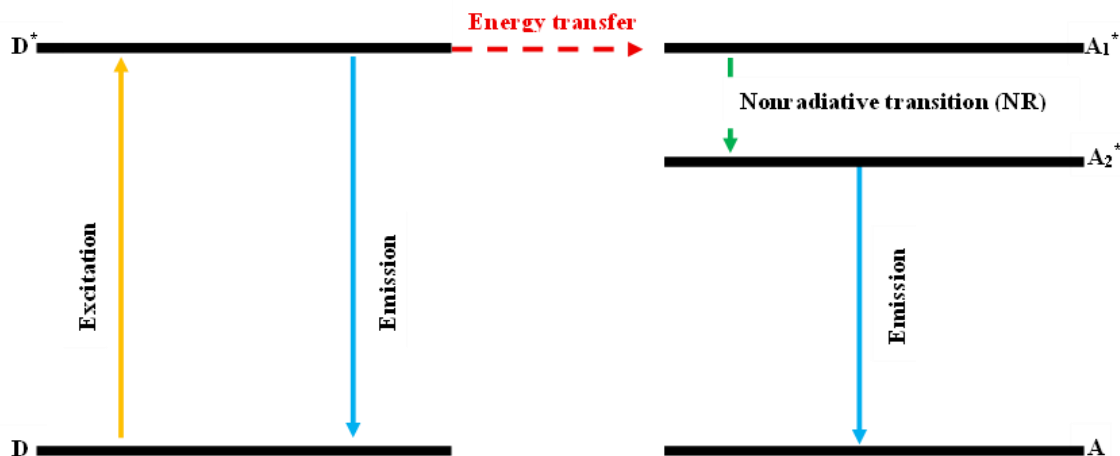


Figure 2.1. An illustration of the energy transfer between the energy donor and the acceptor, also called the sensitizer and the activator.

2.1.2. Luminescence centres

In condensed matter, when a luminescence centre substitutes a host ion, the interaction between the electronic states and lattice vibrations (phonons), known as electron-phonon coupling (or electron-lattice coupling), can affect the shapes of the absorption and emission bands. For strong coupling, the emission often occurs at a lower energy (a longer wavelength) than the excitation energy, which is known as the Stokes shift. The Frank-Condon principle explains this energy shift as due to different equilibrium positions of the luminescent centre's ground and excited states in the lattice, which are represented with the use of a configurational coordinate diagram.

Figure 2.2 shows the simplest representation of a configuration coordinate diagram, with total energy on the Y-axis and the configuration coordinate Q on the X-axis. Q is a one-dimensional parameter depending on the ion-ligand distance. The displacement ΔQ of the equilibrium positions of the nuclei is induced during photoexcitation and critically depends on the sizes and the charges of the host and the luminescence ions.

According to the Frank-Condon principle, optical transitions happen so rapidly that the nuclei cannot move. As a result, the transitions are effectively vertical on a configurational coordinate diagram. Harmonic-oscillator eigenstates precisely describe the vibrational energies and wavefunctions linked to these transitions.

$$E = \left(n + \frac{1}{2}\right) \hbar\omega \quad (n = 0, 1, 2, \dots), \quad (1)$$

where $\hbar\omega$ is the energy quantum of the vibrational mode. As the vibrational quantum number increases, the corresponding wavefunctions extend farther from the equilibrium position and exhibit increased spatial amplitude near the turning points of the potential.

The electron-phonon coupling strength in such systems is described by the Huang-Rhys parameter S , which depends on the displacement between the equilibrium positions of the ground and excited electronic states. Experimentally, the Huang-Rhys parameter S is calculated from the Stokes shift between the absorption and emission spectra. Within the displaced-harmonic-oscillator approximation, the Stokes shift is related to the vibrational mode energy through.

$$E_{\text{Stokes}} = (2S - 1)\hbar\omega \quad (2)$$

or, in a simplified form, $E_{\text{Stokes}} \approx 2S\hbar\omega$. These expressions provide a valid approximation for estimating the electron-phonon coupling strength; however, a more precise determination of the S parameter often requires analysing the full Franck-Condon progression or calculating the spectral barycentres, as the exact relationship can depend on temperature, mode anharmonicity, and whether spectral maxima or integrated intensities of the spectrum are used [45].

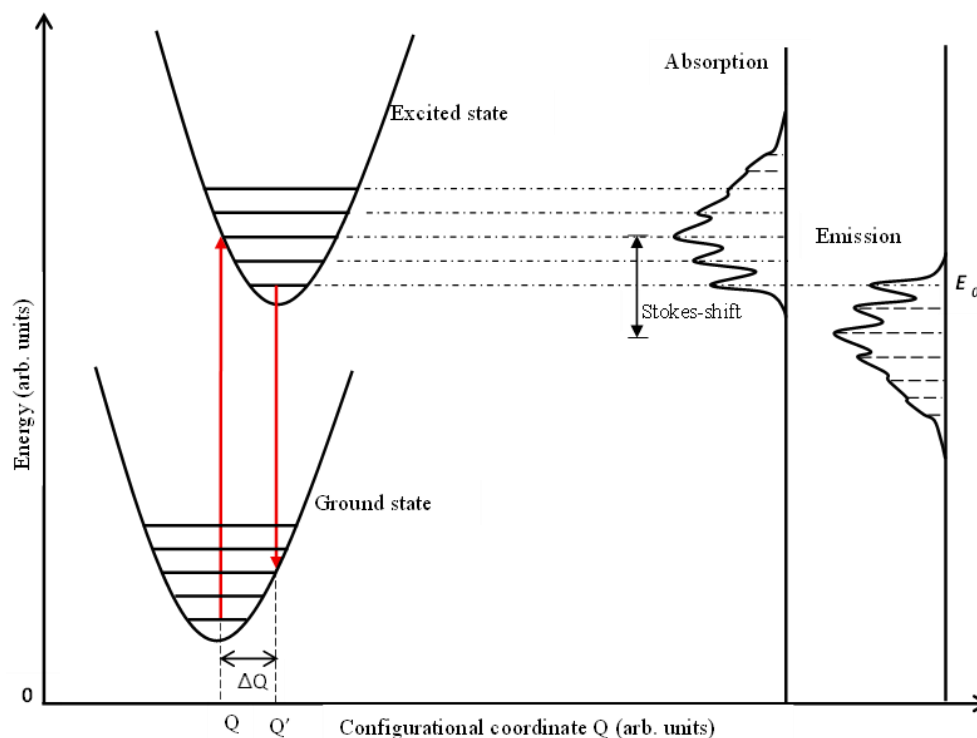


Figure 2.2. Schematic representation of a configuration coordinate diagram showing the energy shift between absorption and emission [46].

2.2. Transition metal activators

The elements in the d-block of the periodic table (groups 3 to 12) are known as transition metals or simply transition elements; however, groups 3 (Sc, Y, La) and 12 (Zn, Cd, Hg) elements are excluded from this classification because they do not exhibit the typical behaviours of d-block elements. The lanthanide and actinide f-block elements are sometimes referred to as inner transition metals, although they are distinct from the d-block elements because of the filled d shell. When transition elements are doped into crystalline solids, these elements exhibit varying oxidation states, typically ranging from +1 to +6. Due to their partially filled d orbitals, transition elements exhibit specific characteristics in common that are not found in other elements. The small energy differences between the ground states of different oxidation states allow them to form compounds in various oxidation states, which often result in different emission energies of d-d electronic transitions. The existence of unpaired d electrons is also responsible for the occurrence of paramagnetism in TM compounds. It is possible to synthesise a wide range of transition metal

complexes, as the majority of transition metals can form complexes by attaching to different ligands, which results in interesting chemical and physical properties. The electronic configurations of some optically active TM ions are listed in Table 2.1.

Table 2.1. Electronic configurations of some optically active TM ions.

Electronic configuration	Transition metal ions				
3d¹	Ti ³⁺	V ⁴⁺	Cr ⁵⁺	Mn ⁶⁺	
3d²	Ti ²⁺	V ³⁺	Cr ⁴⁺	Mn ⁵⁺	
3d³		V ²⁺	Cr ³⁺	Mn ⁴⁺	
3d⁴			Cr ²⁺	Mn ³⁺	
3d⁵			Cr ⁺	Mn ²⁺	Fe ³⁺
3d⁶				Mn ⁺	Fe ²⁺ Co ³⁺
3d⁷					Co ²⁺ Ni ³⁺
3d⁸					Co ⁺ Ni ²⁺
3d⁹					Ni ⁺ Cu ²⁺

2.2.1. Transition metals as luminescence activators

The luminescence properties of TM ions in solids are well described in a rich literature; they are considered suitable activator ions for creating luminescent materials in different spectral ranges, from visible to near-infrared [6,47]. The d orbitals of TM ions are extended in space and thus interact strongly with the surrounding ligands. The crystal field splits the degenerate terms of the free ion into a set of different energy levels, which affects their optical properties. Allowed transitions between these levels lead to broad absorption and emission bands with different wavelengths. The strong electron-phonon interaction significantly affects the shift between the equilibrium positions of the ground and excited states in the configuration coordinate diagram [48].

2.2.2. Tanabe-Sugano diagrams

In a system with multiple d-electrons, electron-electron repulsion is described by semi-empirical Racah parameters A, B, and C. The inter-electronic repulsion within the d-electrons is

primarily defined by the Racah parameters B and C, while the Racah parameter A produces only a uniform shift of all energy levels and therefore does not affect the energy separation. For most transition metal ions, the B/C ratio is approximately 4.5 and remains nearly constant. The separation between different electronic levels of a given ion is determined mainly by two factors: the crystal-field strength Dq and the Racah parameter B. The relative magnitudes of these quantities govern the positions and spacings of energy levels. In the Tanabe-Sugano (TS) diagrams, the x-axis represents the ligand-field strength expressed as Dq/B , which reflects the crystal-field splitting relative to electron repulsion. The y-axis represents the energy of crystal field split states relative to electron repulsion (E/B). Different curves correspond to different levels, and their energies vary as Dq increases. The TS diagram is typically divided into two regions corresponding to high-spin and low-spin configurations. For small Dq/B values (weak ligand field), the metal ion remains in a high-spin configuration determined by Hund's rule. For large Dq/B values (strong ligand field), the system adopts a low-spin configuration. TS diagrams are extremely useful in identifying optical d-d transitions [49].

The splitting of electronic terms of a TM ion in a cubic crystal field depends on its coordination number. The sequence of crystal field split levels of a d^n ion in octahedral coordination corresponds to that of a d^{10-n} ion in tetrahedral or 8-fold coordination. The splitting of the free ion energy terms for the d^5 configuration in a cubic symmetry crystal field is presented in the Tanabe-Sugano diagram shown in Figure 2.3. The ground state for the high-spin case is ${}^6A_1$, whereas a strong ligand field results in a low-spin ${}^2T_2$ ground state.

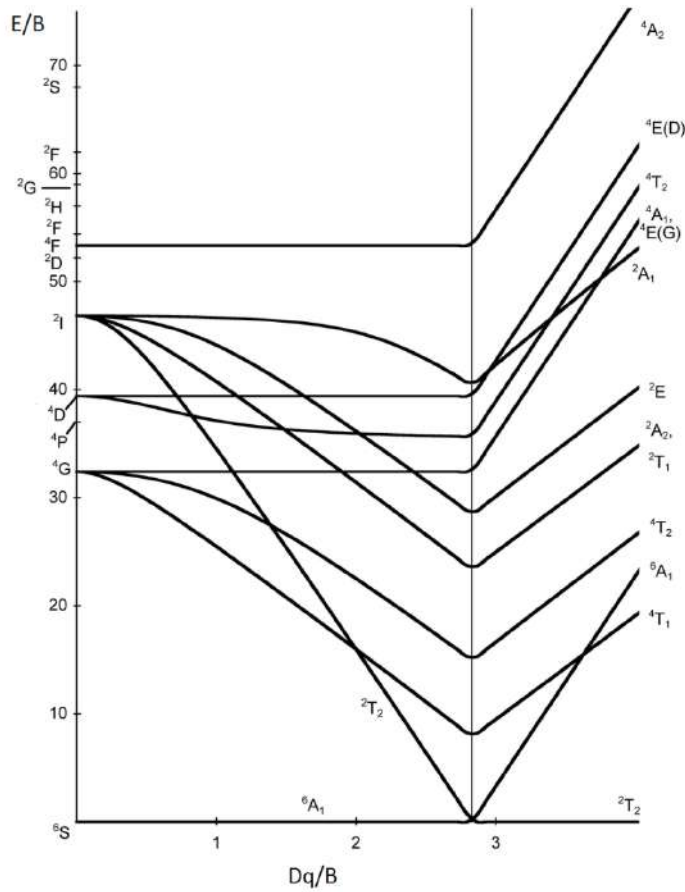


Figure 2.3. Tanabe-Sugano (TS) diagram for the d^5 configuration in octahedral/tetrahedral crystal field.

2.3. Rare-earth activators

The RE elements are in the top row in the periodic table's f block, which includes 15 elements with atomic numbers 57 to 71 (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu). They are considered RE elements according to the International Union of Pure and Applied Chemistry (IUPAC) terminology. The rare term in its name means they are relatively less abundant in the earth's crust, and it is difficult to extract them into pure form [50]. Despite their low abundance, these elements have significant strategic and commercial applications. Today, they are essential components in the manufacturing of solid-state lasers, display devices, lighting, and scintillating devices [51]. Some of them also show significant magnetic properties due to the presence of unpaired 4f electrons. At room temperature, they mostly exhibit paramagnetic

behaviour; however, at low temperatures, they may show some collective magnetic order. The electronic configurations of trivalent RE ions are listed in Table 2.2.

In contrast to transition metal ions having an outer d shell, the inner 4f shell is screened by filled 5s² and 5p⁶ outer shells, which suppresses electron-phonon interactions. Moreover, optical transitions between 4f energy levels are parity forbidden. All this leads to sharp absorption and emission lines. An example of the excitation spectrum of Eu³⁺ in a polymer nano composite is shown in Figure 2.4 (unpublished data).

Table 2.2. Electronic configuration of trivalent RE ions.

RE ion	Atomic number (Z)	Electrons in 4f shell	Ground state (2s+1) L_J
La³⁺	57	0	¹ S ₀
Ce³⁺	58	1	² F _{5/2}
Pr³⁺	59	2	³ H ₄
Nd³⁺	60	3	⁴ I _{9/2}
Pm³⁺	61	4	⁵ I ₄
Sm³⁺	62	5	⁶ H _{5/2}
Eu³⁺	63	6	⁷ F ₀
Gd³⁺	64	7	⁸ S _{7/2}
Tb³⁺	65	8	⁷ F ₆
Dy³⁺	66	9	⁶ H _{15/2}
Ho³⁺	67	10	⁵ I ₈
Er³⁺	68	11	⁴ I _{15/2}
Tm³⁺	69	12	³ H ₆
Yb³⁺	70	13	² F _{7/2}
Lu³⁺	71	14	¹ S ₀

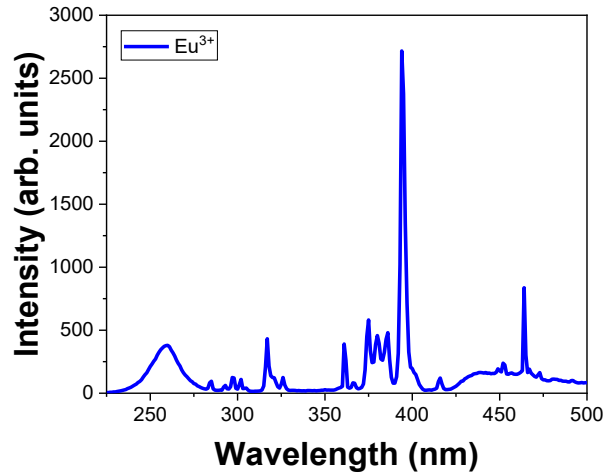


Figure 2.4. Sharp excitation lines of europium (Eu^{3+}) ions in a polymer nano composite.

2.4. 4f-4f and 4f-5d transitions of rare-earth ions

The Coulomb interaction within the 4f shell electrons splits the 4f energy level into spectroscopic terms. In the Russell-Saunders coupling the terms are described as ^{2S+1}L , where L and S are the total orbital and the total spin momenta, respectively, and $2S+1$ is the spin multiplicity. Due to spin-orbit coupling, each term is further split into manifolds designated as $^{2S+1}L_J$, where $\mathbf{J}=\mathbf{L}+\mathbf{S}$ is the total angular momentum with quantum numbers $J = |L-S|, \dots, |L+S|$. Typically, the energy separation caused by the spin-orbit interaction is of the order of 10^3 cm^{-1} . Under the influence of the local crystal field, these $^{2S+1}L_J$ levels are further split into Stark components when placed in a crystalline host [37]. Because of the screening of the electric field exerted by the ligands, this splitting is only of the order of 10 to 100 cm^{-1} .

In a free ion, only magnetic dipole transitions between some J multiplets are allowed, according to the selection rules: $\Delta S=0$, $\Delta L=0, \pm 1$, $\Delta J=0, \pm 1$. Transitions between multiplets with $J=0$ are strictly forbidden. However, according to Judd-Ofelt theory [52,53], a low symmetry crystal field can admix 5d into 4f wavefunctions, which relaxes the Laporte selection rules and allows the so-called forced electric dipole transitions with $\Delta J \leq 6$ (except restrictions related to transitions from and to $J=0$ multiplets). All these transitions have low oscillator strengths, which, together with negligible electron-phonon coupling, make intra-4f absorption and luminescence lines extremely narrow [54–56].

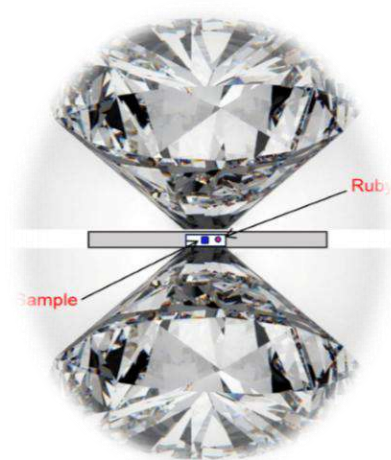
In wide band-gap materials, higher energy $4f^n - 4f^{n-1}5d^1$ transitions can occur in addition to intra-4f transitions [52,55,56]. These transitions have much more intense absorption and emission probabilities than f-f transitions because they are parity-allowed. Moreover, due to the lack of screening of the 5d-shell electrons, they are subject to strong electron-phonon interaction, making the absorption and emission bands very broad.

2.5. Dopants studied in the thesis

The present thesis primarily discusses lithium metal oxide (LiGaO_2 , LiGa_5O_8 & LiYO_2) host materials doped with iron (Fe^{3+}) and manganese (Mn^{2+}), as well as europium (Eu^{3+}) and gadolinium (Gd^{3+}). Iron was generally not regarded as an efficient activator ion; however, a few percent of iron ions in the $3+$ state in LMO can produce excellent near-infrared luminescence properties. Using Fe^{3+} as an activator reduces the need for hazardous elements such as Cr to generate NIR light. Additionally, the thesis explores the properties of manganese-doped LiGaO_2 , investigating the origin of dual-band luminescence in this material and comparing its luminescence under high pressure with that of other Mn-doped materials, such as ZnS, GaN, and AlN. It provides a detailed analysis of various optical, mechanical, and thermoluminescence properties of isoelectronic Fe^{3+} and Mn^{2+} ions within the same host. The luminescence features of Fe^{3+} and Mn^{2+} in LiGaO_2 are explained using the d^5 state Tanabe-Sugano diagram. It also discusses the formation and influence of the LiGa_5O_8 impurity phase on the main phase.

The RE dopants, Eu and Gd, are highly reactive metals with atomic numbers $Z = 63$ ($[\text{Xe}] 4f^7 6s^2$) and 64 ($[\text{Xe}] 4f^7 5d^1 6s^2$), respectively, and relatively similar ionic radii. Europium is typically trivalent (Eu^{3+}); however, in some materials it can also occur in a divalent (Eu^{2+}) valence state due to the increased stability provided by the half-filled $4f^7$ shell. Eu^{3+} exhibits excellent luminescence properties when doped into a matrix, with a relatively long decay time of the order of one millisecond. Gadolinium has strong magnetic as well as optical properties. In the present case, Gd acts as a sensitiser, absorbing energy and then transferring it to the europium (activator) ion present in the matrix, which enhances the light-emitting property of the material by fine-tuning the concentration of Gd [57,58].

3. High-Pressure Methods with Diamond Anvil Cell



3.1. High-Pressure techniques

Pressure-related experimental and theoretical studies have been ongoing for many years. The early studies were conducted by Robert Boyle, resulting in Boyle's Law, which describes the inverse relationship between pressure and volume of a gas. However, traction in pressure-related research started with Prof. Percy W. Bridgeman's systematic study of solid-state materials under high pressure in 1905. He developed a piston-cylinder device capable of generating pressures up to 10 GPa. He conducted extensive research on the effects of pressure on the electrical, thermal, and mechanical properties of materials, and he received the Nobel Prize in physics (1946) for his contributions to material science [59–62], particularly for his invention of an apparatus for obtaining extremely high pressures. The concept of using a diamond anvil cell (DAC) for high-pressure measurement was first introduced by Alvin Van Valkenburg; however, the first DAC was developed by Charles E. Weir, Ellis R. Lippincott, and Elmer N. Bunting at the National Bureau of Standards (NBS), which allowed researchers to achieve pressures in the gigapascal (GPa) regime. Later, the development of the shock-wave compression technique expanded the research field into the terapascal (TPa) regime [60,61,63]. In recent years, these techniques have been

applied to various fields, including the discovery of new phases of matter, the synthesis of superhard materials, planetary science, and studies in superconductivity, etc. High-pressure measurements employ various techniques, depending on the type of experiment, the pressure range, and the material being studied. The following are the most common techniques used in high-pressure studies for generating extremely high pressures [59,60].

- **Diamond anvil cell:** The DAC consists of two opposing diamonds used to squeeze the samples and a gasket with a hole made of metal alloys to confine them, as well as a pressure-transmitting medium used to achieve hydrostatic pressure. It can achieve pressure ranges up to 400 GPa. Transparent diamonds enable their use in optical spectroscopy techniques.
- **Large volume press (LVP):** use multiple anvils (cubic or octahedral) to compress samples in a large volume scale, particularly useful in synthesising novel materials with new phases. Larger volume of sample in use compared to DAC
- **Shock compression:** A high-velocity impact using gas guns, explosives or lasers to generate intense pressure waves, which produce enormous pressure in a short time scale. The method is, however, destructive, and a short time scale limits detailed measurement of the sample at a particular pressure.
- **Gas and liquid pressure cell:** This device utilises gases such as argon or helium, or liquids such as water or alcohol as pressure-transmitting media, and generates pressure using a pump. However, it can achieve very low pressures compared to other methods. Primarily used for electrical superconductivity measurements, and also used for magnetic and optical studies.

3.2. Introduction to diamond anvil cell

A diamond anvil cell consists of two diamonds with a flat or bevelled culet of a specific diameter (typically 100-700 μm) pressing against each other with externally applied pressure. The diamond should have minimal defects to prevent breakage.

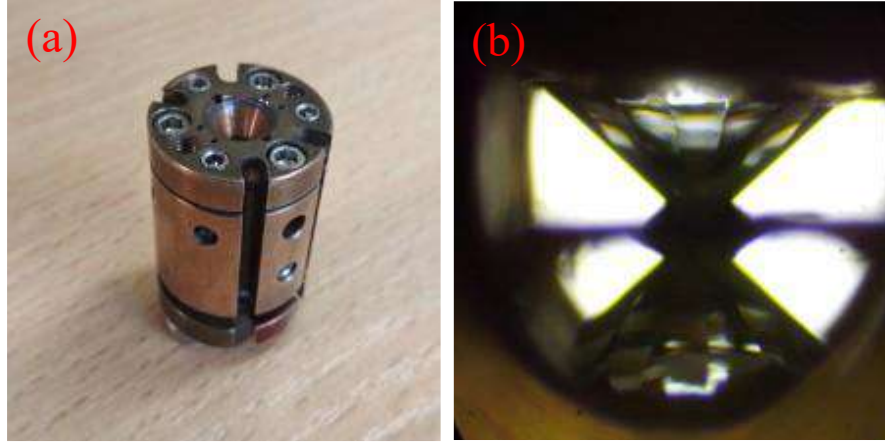


Figure 3.1. Photograph of (a) DAC used for measurements, (b) inside DAC culets of the diamonds pressing each other with an Inconel gasket in the middle.

The highest safe pressure that a culet of diameter d can produce in a DAC is [63]

$$P_{max} (GPa) = 12.5/(d(mm))^2 \quad (3)$$

However, the maximum pressure used in experiments should be somewhat lower, such as $0.8 P_{max}$. This is valid for diamonds with a mass of 60 mg (0.3 carats) and a table ~ 3 mm in diameter - the most commonly used size. Both diamonds are always placed on these tables and inserted into a rigid, tube-like metal body with attached screws for aligning the diamonds parallel and axially, as shown in Figure 3.1(a). In some diamonds, there are ports for optical and electrical measurements. During sample preparation, a gasket made of stainless steel, rhenium, beryllium, or Inconel is used, as shown in Figure 3.1(b). It acts as a sample holder, preventing the lateral escape of the sample during pressure buildup, and supports uniform pressure distribution. The small sample chamber hole is always drilled with drills of various diameters, which is an essential parameter in reaching the maximum pressure value. There is a conical hole for optical access on the top and bottom of the anvil cell, through which the optical experiments are carried out. Additionally, it enables the simultaneous measurement of high-temperature, high-pressure conditions using the laser-heating method.

3.3. Gasket preparation

In 1965, Van Valkenburg was the first to demonstrate the use of a gasket to contain a hydrostatic medium. The gaskets in DAC serve two functions: they are punctured to create the high-pressure chamber required for loading samples into the experiment, and to provide lateral

support for the conical faces. Gaskets are typically made from steel, Inconel, beryllium, and copper. Tungsten and molybdenum gaskets are also sometimes used [63,64]. Rhenium is also a suitable material for manufacturing gaskets for extreme pressure and temperature conditions. Usually, gaskets are made from the metal sheets mentioned earlier, initially with a thickness of 100 to 450 μm , then cut into a specific shape and pre-indented to a typical value of 30-50 μm to ensure proper pressure build-up. Subsequently, the gaskets are pierced with microdrills of various diameters; the hole diameter is related to the pressure and must be precisely centred within the gasket. Figure 3.2 shows a gasket prepared in our laboratory for measurement using Inconel 750 alloy. The larger holes on either side of the gasket in Figure 3.2(a) are used to secure it with pins internally, preventing movement.

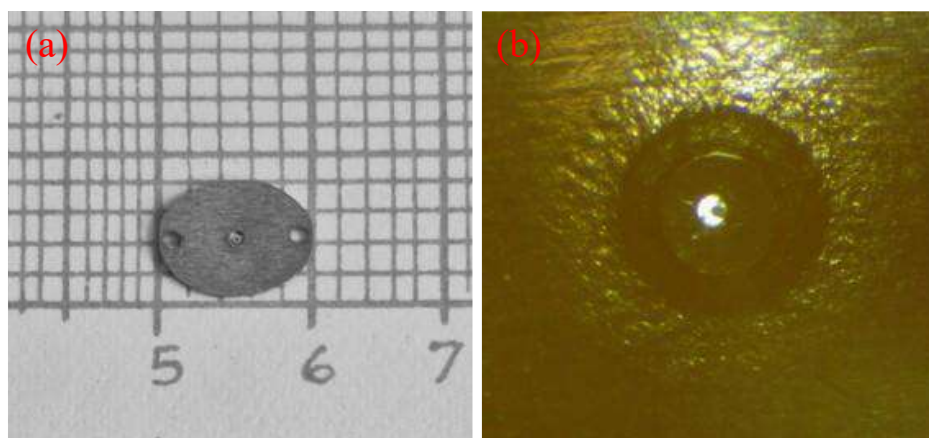


Figure 3.2. Photograph of (a) an Inconel 750 gasket for DAC, (b) enhanced image under microscope showing an indentation, a 0.2 mm hole with a sample and a ruby pressure gauge.

A suitable pressure-transmitting medium (gas or liquid) is introduced into the central hole (sample chamber) to fill the chamber around the sample and the pressure gauge. The selection of the pressure-transmitting medium depends on the sample's reaction with it, maximum pressure, and ease of access. The gasket deforms plastically and loses thickness when squeezed between the two diamonds. This reduces the volume of the cylindrical hole, resulting in a pressure buildup within the sample.

3.4. Pressure calibration methods

A calibrated standard is necessary to determine the pressure inside the DAC. Ruby fluorescence is one of the most commonly used methods for calibrating pressure in DAC

investigations. A tiny chip (~ 5 to $10\ \mu\text{m}$) of ruby ($\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ (0.05%)) is placed in the pressure chamber for calibrating ruby fluorescence, and an appropriate laser (Ar-ion, He-Cd, or He-Ne) is used to stimulate the fluorescence [59]. An optical spectrometer is used to detect the fluorescence. Two distinct peaks (R1 and R2) in the ruby fluorescence spectrum move to higher wavelengths as pressure increases. Typically, pressure is calibrated using the shift rate of the lower energy R1 line. Figure 3.3 shows a typical ruby fluorescence spectrum recorded from our DAC during the experiment at IPPAS.

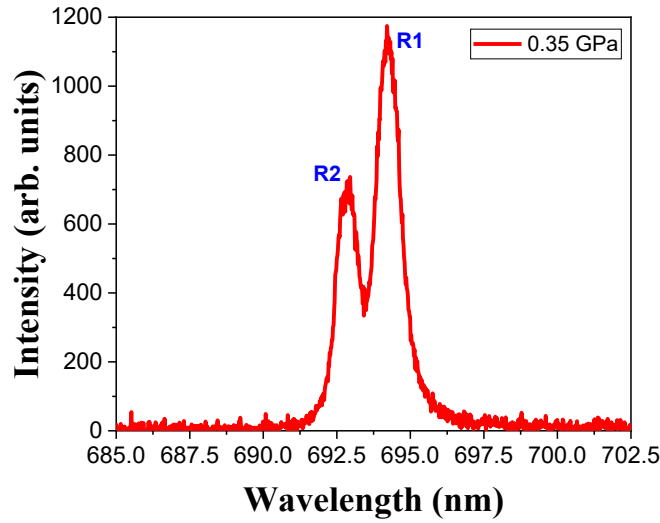


Figure 3.3. Typical ruby fluorescence spectra observed from DAC when excited with 532 nm green laser at room temperature (observed pressure value 0.35 GPa).

The pressure scale has been created by calibrating the shift of the ruby fluorescence lines against a standard substance, using the equation:

$$P(\text{GPa}) = \frac{A}{B} \left[\left(\frac{\lambda}{\lambda_0} \right)^B - 1 \right] \quad (4)$$

A and B are constant values based on the calibration, λ_0 is the peak wavelength at ambient pressure, and λ is the peak wavelength at the measured pressure. Ruby's pressure shift has also been measured at both high and low temperatures [65]. In addition to ruby, several other materials are employed as optical pressure sensors, including $\text{SrB}_4\text{O}_7:\text{Sm}^{2+}$, $\text{BaFCl}:\text{Sm}^{2+}$, $\text{SrFCl}:\text{Sm}^{2+}$, and $\text{YAG}:\text{Eu}^{3+}$ [66–68]. Figure 3.4 (a) and (b) illustrate the sample and rubies placed into the gasket hole before conducting high-pressure measurement with DAC.

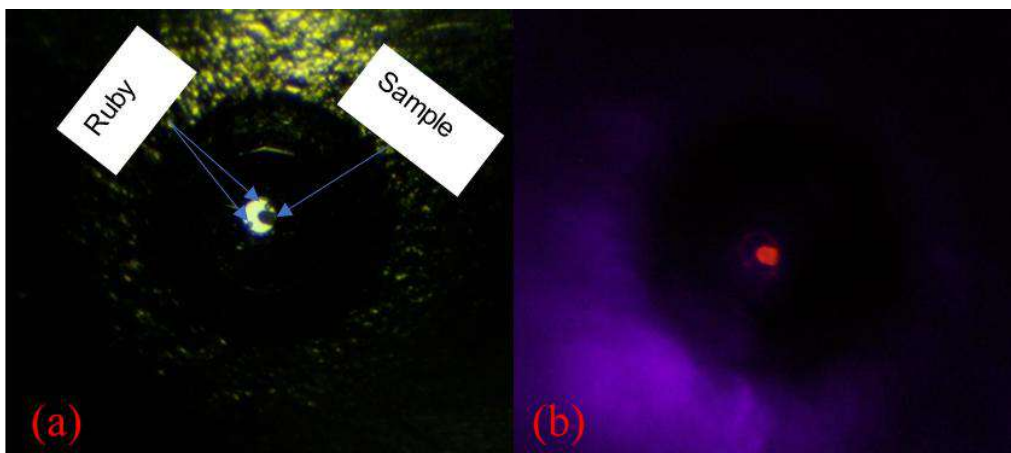


Figure 3.4. Photograph of (a) sample and ruby inside the sample chamber under normal white light, (b) sample (Mn^{2+}) luminescence from gasket hole under 325 nm UV excitation.

3.5. Pressure transmitting medium

The samples are rarely placed directly between anvils; they are usually encapsulated in a medium while being inserted into the gasket. This medium is referred to as the pressure transmitting medium (PTM). Without a pressure transmitting medium, the applied pressure will result in a higher shear strain due to the loss of hydrostatic equilibrium. This is not required in most scientific experiments. In most scientific contexts, this is typically undesirable. Any material will harden and become susceptible to anisotropic stresses above a certain pressure, but the material surrounding the sample helps make the stress isotropic (hydrostatic), which is possible when the pressure medium is a gas or liquid. However, some inert gases used as PTMs exhibit non-hydrostatic behaviour at elevated pressures. Solids such as NaCl, KCl, and MgO are also used as pressure-transmitting media [60,61,69]. These materials are typically selected due to their transparency and low thermal conductivity. Liquids like silicone oil, alcohol, and selected alcohol mixtures are also used. One of the most popular liquid pressure-transmitting media is a 4:1 volume mixture of methanol and ethanol, which offers hydrostatic conditions at ambient temperature until its glass transition at 104 kbar [70]. Up to around 200 kbar, it is only slightly non-hydrostatic above the glass transition; at higher pressures, it becomes significantly non-hydrostatic. It has been reported that the hydrostatic limit can be extended to approximately 140 kbar by adding a small amount of water to the mixture (16:3:1 methanol: ethanol: water) [65]. Inert gases, such as argon (Ar), neon (Ne), nitrogen (N_2), helium (He), or xenon (Xe), are also used. A gas-loading system

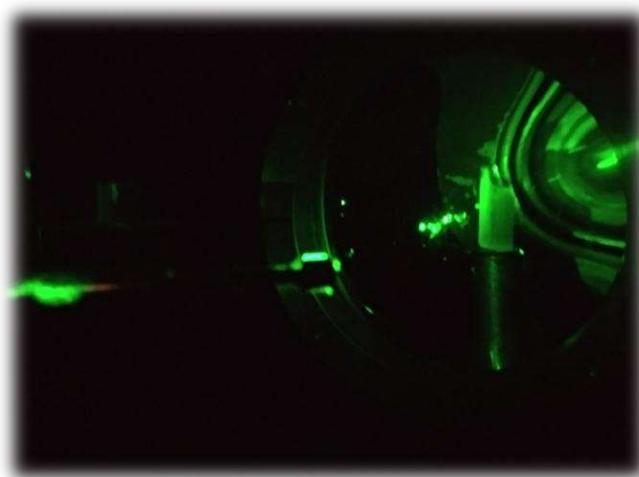
is also required to pump the gaseous pressure-transmitting media to the DACs. This technique involves pumping and pressurising the desired gas around the sample inside the DAC gasket. A piston is used to externally close the DAC, and screws are used to hold it in place. Also, external cooling with liquid nitrogen condenses the gas.

3.6. Drive mechanism and operation

In a reasonably well-made DAC (as shown in Figure 3.1(a)), the piston-cylinder clearance is typically 10-20 μm . The cell is fitted with two clamp bolts, primarily for ease of loading. The cell's driver mechanism transmits pressure via a lightweight Bowden-cable principle-based system, where a continuously supported wire carries tensile forces and the enclosing tube is mechanically stabilised to prevent instability [71]. The tube-wire assembly is driven externally by a hydraulic drive. The pressure is applied to the cell mechanically by the clockwise rotation of the drive and released by the anticlockwise rotation. Saddles are provided at the bottom of the cell to avoid sharp bends in the wire; these may be semicircular or relatively flat, depending on the available space.

The compact size of the DAC makes aligning and loading the cell delicate tasks; before loading the cell with the gasket and sample, careful alignment of the diamond culets is required in both the tilt and radial directions. In the present thesis, the following method is used for the high-pressure measurement. Once the cell is correctly aligned, an Inconel 718 or 750 gasket is indented to a thickness of $\sim 40\text{-}70\text{ }\mu\text{m}$, and a sample hole, 150-250 μm in diameter, is drilled at the centre of the indentation. The polished crystal sample of $\sim 20\text{-}30\text{ }\mu\text{m}$ or the powder sample, together with the calibration ruby, is placed in the hole made in the gasket that is already mounted on the bottom diamond anvil. A drop of the alcohol mixture is placed over the indentation using a needle or syringe, and the piston and cylinder are closed. The 4:1 methanol-ethanol mixture serves as a pressure-transmitting medium in our experiments. The absence of bubbles in the sample chamber is also visually checked. The clamp bolts are then tightened, and some yielding is felt. At this stage, the pressure is in the range of 5-25 kbar. The drive mechanism can now be assembled around the cell, and, if desired, the clamp bolts can be slackened or withdrawn completely. The cell is now ready for insertion into the cryostat. The measurements were carried out (with or without a cryostat) using the two-lens arrangement described in Chapter 4 and shown in Figure 4.5 (a) and (b).

4. Experimental Techniques Used in the Study



4.1. Introduction to experimental techniques

This chapter is devoted to the experimental methods and techniques used in this thesis, excluding the high-pressure technique. The author himself conducted most of the experiments mentioned, with some assistance from colleagues and collaborators from other research groups. High-pressure X-ray diffraction and X-ray absorption spectroscopy (XAS) measurements were done at different synchrotrons in remote mode.

4.2. Powder X-ray diffraction studies at ambient and high pressure

When a solid substance is exposed to an X-ray beam, some of the X-ray waves are scattered in different directions by the atoms. However, destructive interference prevents all diffracted waves from being visible. According to Bragg's law, when X-rays with a specific wavelength, λ , interact with a crystal having parallel planes spaced d_{hkl} apart, constructive interference occurs

only when the angle θ between the incident X-ray and the crystal plane satisfies the following relation:

$$2d_{hkl}\sin\theta = n\lambda \quad (5)$$

where n is a positive integer, h , k , and l are integers known as Miller indices that indicate the planes' orientation, and θ is the angle formed by the incident beam and the diffracting planes.

For this thesis, the powder samples were analysed at ambient pressure using a BRUKER D2 PHASER with Cu K α radiation for the XRD experiment, which was run at 30 kV and 10 mA. The measurements were taken with a scan step of 0.02° and acquisition duration of 1 s per step was used to capture the XRD pattern. The BRUKER and ICDD PDF-4 databases and DIFFRAC. EVA V4.1 evaluation software was used to conduct the crystal phase analysis (2023).

Synchrotron radiation sources are among the most potent instruments for X-ray diffraction and crystallography, and they are among the brightest light sources on the planet. Electrons and other electrically charged particles are accelerated to almost the speed of light in synchrotrons, which use magnetic fields to confine them in a (about) circular loop to produce X-ray beams.

High-pressure X-ray diffraction (HP XRD) experiments were conducted in a Mao-Bell-type DAC at the synchrotron facility BL-11, Indus-2, RRCAT, Indore, India. The powdered sample Debye-Scherrer patterns were collected on a MAR-345 image plate detector shown in Figure 4.1. The 2D patterns were converted to intensity vs. 2θ patterns using Fit2D [72]. Analysis of the XRD patterns and Le-Bail refinement were carried out using the FullProf suite [73].

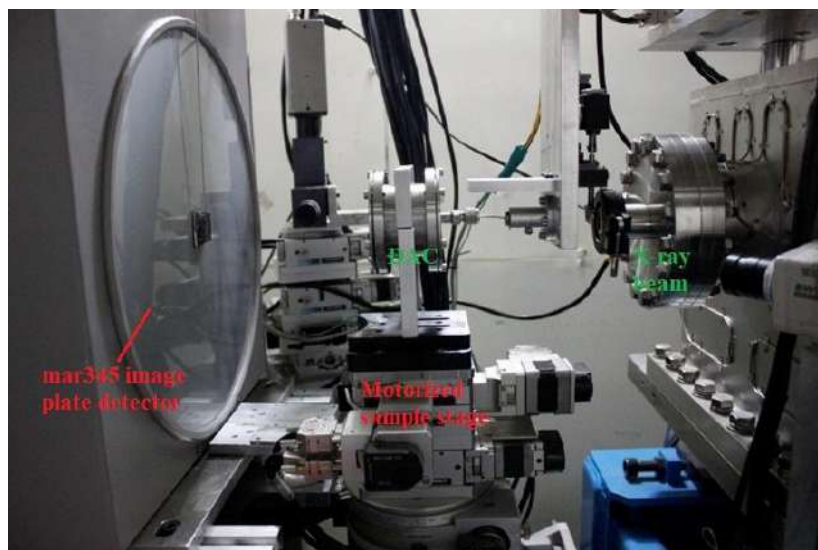


Figure 4.1. Detector and DAC of BL-11 beamline at RRCAT, India, used for High-Pressure XRD.

4.3. Morphological studies with scanning electron microscope (SEM)

The surface morphology of the synthesised powder samples was examined using a Hitachi SU-70 scanning electron microscope (SEM), shown in Figure 4.2. Energy Dispersive Spectroscopy (EDS) and Field Emission Scanning Electron Microscopy (FE-SEM) were performed on a TESCAN MAIA3 XMH system, which featured a Schottky FE gun source and provided ultra-high-resolution imaging via a secondary electron detector.



Figure 4.2. Hitachi SU70 scanning electron microscope equipped with an additional Gatan MonoCL cathodoluminescence attachment, the Institute of Physics, IPPAS.

4.4. Raman spectroscopy

The Raman spectroscopy technique is based on the phenomenon known as Raman scattering, also referred to as inelastic photon scattering. The monochromatic light source is often a laser in the visible, near-infrared, or near-ultraviolet spectrum; however, X-rays can also be employed to excite the samples. When photons from laser light interact with phonons, molecular vibrations, or other excitations in the system, the photons' energy can increase or decrease. This energy shift in photons indicates the vibrational modes of the system. The system typically features a laser source (often operating at 532 nm or 785 nm) that illuminates the sample. Most of these photons generated by illumination scatter elastically (which is called Rayleigh scattering), while a small fraction undergoes inelastic scattering, referred to as Raman scattering. A spectrometer is used to gather and analyse this inelastically scattered light to produce a Raman spectrum. The spectrum provides information about the sample's molecular vibrations by plotting intensity against Raman shift (cm^{-1}).

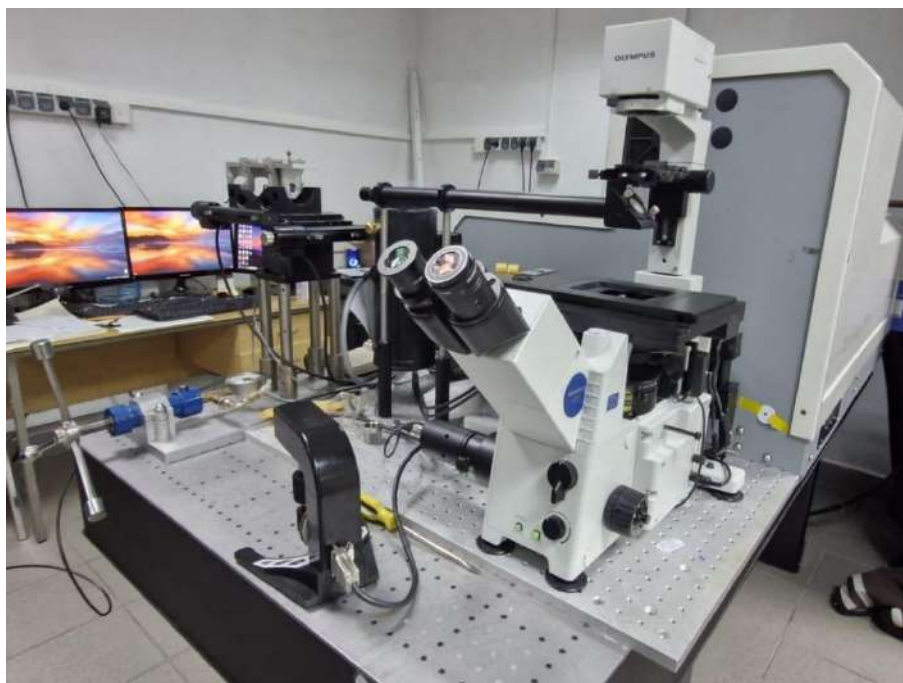


Figure 4.3. S&I GmbH Monovista Raman spectrometer used for the Raman analysis, the Institute of Physics, IPPAS.

In this thesis, the powder samples are analysed using the S&I GmbH Monovista CRS+ Raman spectrometer, equipped with an Acton Princeton monochromator, shown in Figure 4.3. This instrument features a liquid nitrogen-cooled CCD detector and a holographic grating with 2400 grooves/mm, used to record Raman spectra at ambient temperature. The excitation source used for the measurement was a 532 nm solid-state laser. Also, the spectrometer was equipped with edge filters to suppress Rayleigh-scattered light and transmit Raman-shifted photons.

4.5. Photoluminescence studies

4.5.1. Photoluminescence at ambient pressure

A Horiba/Jobin-Yvon Fluorolog-3 spectrofluorometer, shown in Figure 4.4, was used to analyse the photoluminescence emission and excitation spectra, as well as the luminescence decay kinetics. A 450 W continuous xenon lamp was used as the excitation source. The xenon lamp's excitation light is directed through a single-grating monochromator in the spectrofluorometer.



Figure 4.4. A Horiba Fluorolog-3 spectrofluorometer coupled to a cryostat is used for both room temperature and low-temperature photoluminescence measurements at ambient pressure; the Institute of Physics, IPPAS.

The FluorEssence software was used to operate a fully automated computer system that collected the sample's emission and linked it to a single-grating monochromator. To acquire spectra, a Hamamatsu R928P photomultiplier tube (PMT) was utilised for the visible range, while a thermoelectrically cooled NIR PMT was used for the near-infrared range. Low-temperature measurements were conducted without altering the geometry, using a Janis continuous-flow liquid-helium cryostat that operates over the temperature range 4.5 to 310 K. A Lake Shore 331 temperature controller was used to perform the low-temperature luminescence measurements.

4.5.2. Photoluminescence at high-pressure

The high-pressure luminescence at ambient and low temperatures was measured using multiple setups with a similar two-lens arrangement, as shown in Figure 4.5 (a) & (b). The measurements were performed using a Horiba Jobin-Yvon FHR 1000 monochromator, an Acton Spectra Pro SP-2500 monochromator from Princeton Instruments for visible-UV measurements, or a Horiba Jobin-Yvon HR 460 monochromator with an InGaAs detector (Figure 4.5(a)) for NIR measurements.

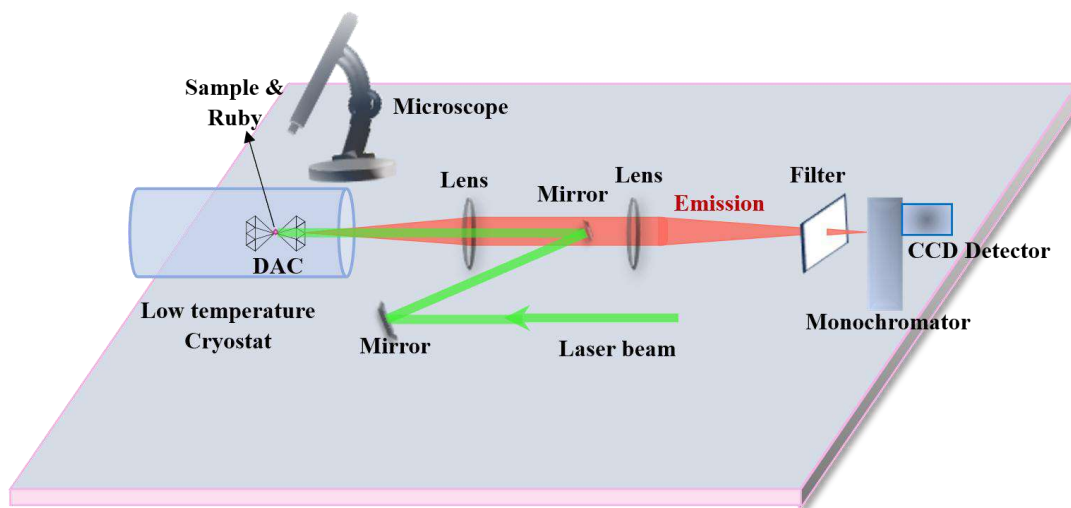
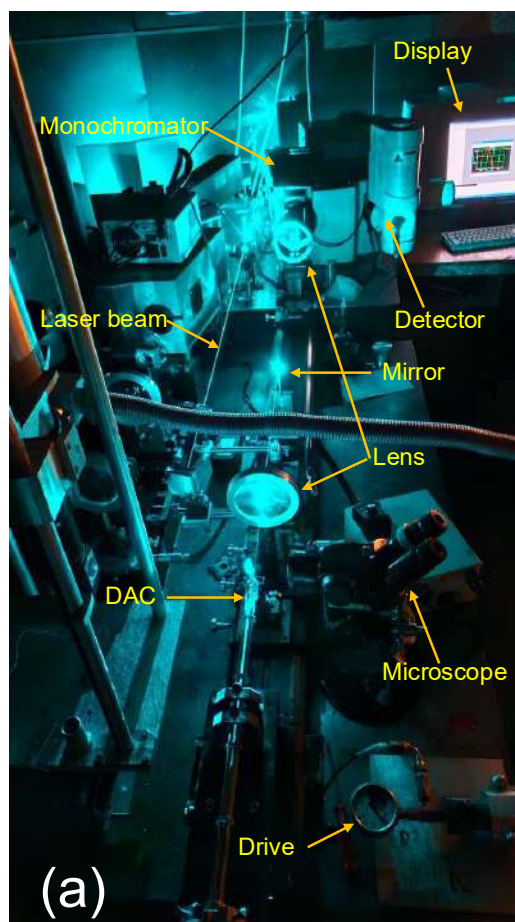


Figure 4.5. High-pressure photoluminescence setup used for room-temperature and low-temperature measurements (with an additional cryostat). (a) photograph, the Institute of Physics, IPPAS and (b) schematic representation of the experimental setup.

Additionally, a variety of lasers as the excitation source were used, including the Coherent Inova 200/400 Ar-ion laser, which has a wavelength range from 275.4 to 514.5 nm, and the He-Cd laser, with a wavelength of 325 nm in the UV region and pulsed laser excitation source from NT342/3 series tunable optical parametric oscillator (OPO) equipment with an Nd: YAG laser from EKSPLA. All components are aligned in a parallel way to the optical axis of the system. The DAC is also placed in the optical axis, and luminescence is collected in reflective mode and ruby is used as a pressure gauge. For low-temperature experiments, the DAC was installed in an Oxford Optistat CF cryostat, which was coupled to a temperature controller.

4.6. Photoluminescence decay and quantum yield measurements

4.6.1. Luminescence decay

Luminescence decay refers to the time-dependent decrease in emission intensity of a material after it has been excited with a light source, such as a pulsed laser or an intermittent illumination with a xenon lamp. In other words, the lifetime (τ) is the average time an electron stays in the excited state before returning to the ground state by emitting a photon. The decay is typically monitored after pulsed excitation, and the emission intensity is plotted as a function of time. It provides insights into electronic transitions, excited-state lifetimes, defect states, and energy transfer mechanisms in materials. The decay curves are fitted with either a single-exponential or a multi-exponential equation.

For single exponential decay

$$I_t = I_0 \exp\left(-\frac{t}{\tau_1}\right) + C \quad (6)$$

For multi-exponential decay

$$I_t = \sum_i I_i \exp\left(-\frac{t}{\tau_i}\right) + C \quad (7)$$

where I_t is the time-dependent intensity, I_i is the amplitude of the i -th component, τ_i is the corresponding lifetime, and C is the background constant.

The present thesis utilises the same Horiba/Jobin-Yvon Fluorolog-3 spectrofluorometer shown in Figures 4.4 and 4.6(a), equipped with a xenon lamp, for both ambient and low-temperature decay measurements of the sample. In addition to the standard photoluminescence setup, a chopper is added in front of the lamp source along with time-correlated single-photon

counting (TCSPC). The TCSPC module primarily consists of a FluoroHub photon counting controller and a DataStation Hub for data acquisition. The system is capable of measuring decay times from nanoseconds to milliseconds in various modes. For the high-pressure luminescence decay experiments shown in Figure 4.6(b), a pulsed Nd:YAG OPO laser excitation source from EKSPLA is used. The emitted photons were counted using a micro photon device (MPD), with a PDM series photon-counting module attached to a Princeton Instruments Acton Spectra Pro SP-2500 monochromator. The high-pressure luminescence for the decay measurements was collected using the same two-lens arrangement as shown in Figure 4.5(b).



Figure 4.6. Luminescence decay measurements at (a) room temperature or low temperature, and (b) high pressure, the Institute of Physics, IPPAS.

4.6.2. *Quantum yield*

In optical spectroscopy, the PL quantum yield (PLQY [Φ]) is a handy tool for determining the quenching rate constant, lasing ability, energy transfer, and other parameters. It is used to determine the efficiency of the PL process and to calculate the absolute rates for both radiative and non-radiative transitions. The absolute and the relative quantum yield methods are the two main techniques used to estimate the quantum yield of a material based on its PL emission. The relative method compares the fluorescence intensity of an unknown sample with that of standard samples, such as quinine sulphate dehydrate and 9,10-diphenylanthracene, and calculates the quantum yield. An integrating sphere attachment with sphere correction software is utilised in the absolute method to calculate the quantum yield directly from sample fluorescence. The present work determined

the quantum yield of the powder sample using a Horiba "Quanta-φ" integrating sphere attachment on the same Horiba/Jobin-Yvon Fluorolog-3 spectrofluorometer, with a xenon lamp for excitation. The inner surface of the integrating sphere sample holder is made up of a high-reflectivity material called Spectralon, the standard reference material used for the powder sample, also made up of the same fluoropolymer and in-built software with sphere correction formula used for the accurate measurement without errors.

4.7. Other luminescence studies

4.7.1. Thermoluminescence

Thermoluminescence is the process by which a material that has previously been exposed to radiation emits light when heated. This phenomenon results from exposure to UV light or ionising radiation, which releases trapped charge carriers (electrons or holes) held in defect sites. The thermoluminescence results were measured using the same Horiba/Jobin-Yvon Fluorolog-3 spectrofluorometer used for photoluminescence studies, equipped with an additional Linkam LNP96 heating/freezing stage and T96 Controller, which enables high-temperature thermoluminescence measurements. This stage allows us to provide measurements in the 80 K to 600 K temperature range. The thermoluminescence was also analysed using the same cathodoluminescence equipment described below (see Figure 4.8) from 4 K to 300 K to further investigate its low-temperature characteristics.

4.7.2. Vacuum ultraviolet (VUV) luminescence

The vacuum ultraviolet luminescence (VUV) of the powder samples was measured using the instrument shown in Figure 4.7. A 150-W deuterium discharge lamp (Hamamatsu L11798), and a McPherson 234/302 vacuum monochromator were utilised for excitation in the VUV region. To detect PL, grating monochromators Andor SR 303i-B or ARC SpectraPro 300i with H8259– and H6240-01 photon counting heads, respectively, were employed.

A JANIS VPF-800 or an ARS closed-cycle helium cryostat was used to mount thin pellets on a sample holder for measurements in the UV–Vis and vacuum UV (VUV) spectral regions, respectively. The detectors' spectral sensitivity and the monochromator's spectral efficiency were taken into account when adjusting all emission spectra.



Figure 4.7. The VUV luminescence setup used for studies at the Institute of Physics, University of Tartu (IPUT), Estonia.

4.7.3. Cathodoluminescence

Cathodoluminescence (CL) is an optical and electromagnetic phenomenon in which photons with UV-visible-IR-spectrum wavelengths are emitted when electrons strike a luminescent substance, such as a phosphor. The CL measurements were carried out on a system shown in Figure 4.8 with a Kimball Physics EGPS 3101E electron gun ≤ 10 keV, $\leq 30 \mu\text{A}/\text{mm}^2$, steady state or pulsed (10 ns, 5 kHz) with a vacuum system $\sim 10^{-7}$ mbar and a monochromator for VUV-UV-Vis-NIR spectral range (110 – 1700 nm).

The temperature dependence was measured using an ARS Closed Cycle Vacuum Cryostat (temperature range of 5-400 K, controlled by a Lake Shore 331) and a manipulator that allowed for the mounting of multiple samples. Cathodoluminescence, thermally stimulated luminescence (also spectrally detectable in the UV-C range), and decay kinetics measurements are also possible with this setup.



Figure 4.8. Cathodoluminescence setup used for studies at the Institute of Physics, University of Tartu (IPUT), Estonia.

4.7.4. *Mechanoluminescence*

When a material responds directly to mechanical stimuli, such as compression, tension, bending, friction, or fracture, by emitting light, it is known as mechanoluminescence (ML). ML can be triggered by applying the mechanical stimulation mentioned above. Depending on the type of mechanical stimulus and the process of light emission, ML can be broadly categorised.

In the present thesis, the friction-induced ML was measured using a custom-designed setup operated within a LabVIEW environment. A schematic diagram of the ML setup is shown in Figure 4.9. The sample was affixed to a PMMA (poly(methyl methacrylate)) plate, using carefully selected adhesive tape to ensure secure attachment. ML was generated by a glass rod mounted on a linear rail, which applied a controlled force to the sample. The rod executed a predefined number of strokes at a fixed speed and force. The emitted ML signal was collected using a Shamrock 500i spectrometer equipped with a thermoelectrically cooled IDus 420 camera from Andor Technology.

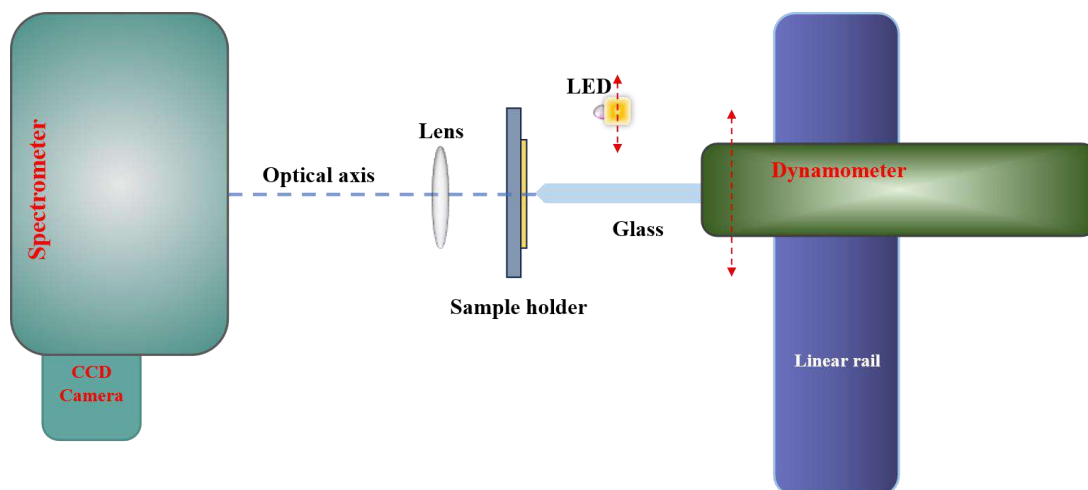


Figure 4.9. Schematics of the equipment used in the friction-induced mechanoluminescence studies. The experimental setup is located at the Institute of Experimental Physics, University of Gdansk (UG), Poland.

4.8. Other spectroscopic techniques

4.8.1. X-ray absorption spectroscopy (XAS)

XAS is a general term for a group of techniques that measure how a material absorbs X-rays as a function of energy, typically near and above the absorption edge of specific elements. It offers element-specific details regarding the absorber's local atomic environment and electronic structure. The XAS spectrum is broadly divided into two regions. The X-ray absorption near-edge structure (XANES), measured in the spectral region typically extending ~ 50 eV around the absorption edge, is characterized by distinct resonance peaks. It is sensitive to local electronic structure, including oxidation states and coordination symmetry, making it a powerful tool for probing the chemical state and environment of the absorbing atom.

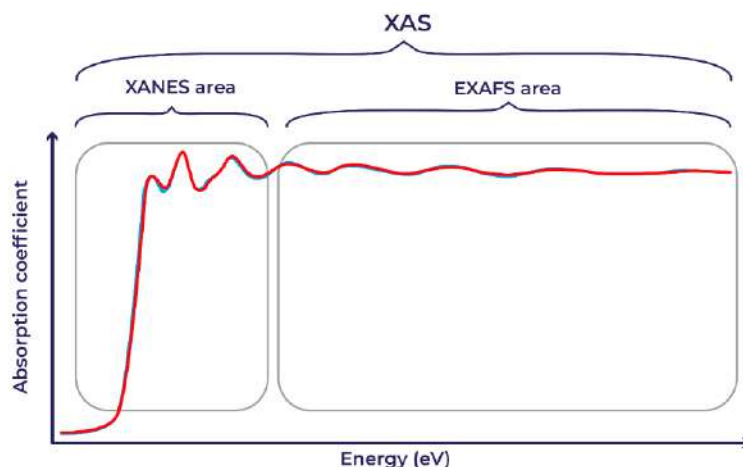


Figure 4.10. XANES and EXAFS areas are marked in the XAS spectrum. Reproduced from Kartashov et. al. (2021), *Materials*, 14(24):7884, CC-BY 4.0. [74].

The extended X-ray absorption fine structure (EXAFS) region, located beyond the XANES region and extending from about 50 eV to as much as ~ 1000 eV or more above the absorption edge, is characterised by subtle oscillations in the absorption spectrum. The interference between the outgoing photoelectron wave and those scattered by nearby atoms causes these oscillations. EXAFS is a valuable tool for structural analysis at the atomic scale because it provides comprehensive information about the local atomic environment, including bond lengths, coordination numbers, and types of surrounding atoms. Figure 4.10 shows a typical XAS spectrum, with the XANES and EXAFS regions marked.

XAS measurements at the Fe K-edge were carried out in fluorescence mode at the beamline I20-scanning of the Diamond Light Source, United Kingdom. The beamline features a high-resolution four-bounce Si (111) monochromator and a multi-element solid-state Ge detector. The incident beam was focused to a spot size of $400 \times 300 \mu\text{m}^2$ at the sample position. Measurements were taken at room temperature on a powder sample that had been pressed into a pellet for analysis.

4.8.2. Mössbauer spectroscopy

The first experimental observation of resonant absorption and recoil-free emission of nuclear γ -rays in materials was made by Rudolf Mössbauer in 1957, and it's called the Mössbauer effect. The principle behind Mössbauer spectroscopy is the effect, where gamma rays are emitted and absorbed without recoil by nuclei in a solid lattice. The energy required to absorb or emit a γ -ray

from a nucleus can be used to explain the Mössbauer effect very simply. A free nucleus must recoil to preserve momentum when it absorbs or emits a γ -ray, hence in terms of energy:

$$E_{\gamma\text{-ray}} = E_{\text{nuclear transition}} - E_{\text{recoil}} \quad (8)$$

Since the nucleus's effective mass is so great and momentum can be preserved with tiny nucleus movement, the recoil energy in a solid matrix is zero. Thus, for solid matrix nuclei:

$$E_{\gamma\text{-ray}} = E_{\text{nuclear transition}} \quad (9)$$

This is the Mössbauer effect, which causes γ -rays to be resonantly absorbed or emitted, providing a way to examine the extremely delicate interactions between an atom's nucleus and its environment.

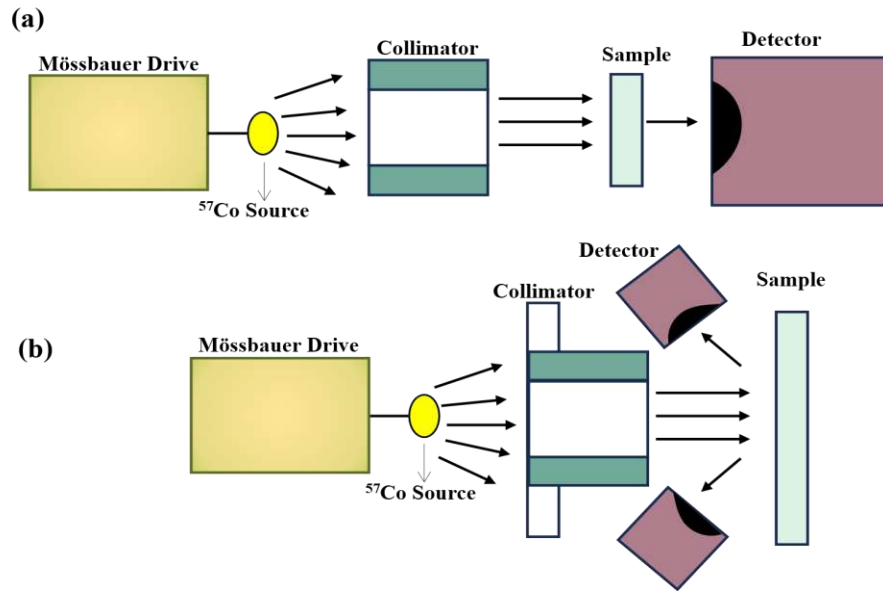


Figure 4.11. Mössbauer spectrometer scheme in the (a) transmission and the (b) backscatter mode of measurement using a ^{57}Co source.

Figure 4.11 shows the schematic diagram of a Mössbauer spectrometer operation. The components of a Mössbauer spectrometer system include a detector, a collimator to filter the γ -rays, the sample, and a γ -ray source that is oscillated toward and away from the sample by a "Mössbauer drive." Room temperature Mössbauer spectroscopy of Fe ions was performed using a ^{57}Fe -in-Rh source in transmission geometry. The isomer shift values are reported relative to an

α -Fe standard. The Mössbauer spectroscopy measurements were carried out at Łukasiewicz Research Network Institute of Microelectronics and Photonics (IMiF), Poland.

4.8.3. *Electron paramagnetic resonance (EPR)*

Electron paramagnetic resonance (EPR) is a powerful spectroscopic method for identifying and characterising paramagnetic species, which contain unpaired electrons. For the simplest case of a paramagnetic two-level system with spin $S = \frac{1}{2}$ in the absence of an external magnetic field ($B = 0$) the spin states are degenerate, with spin-up and spin-down electrons having equal energy. When an external field $B \neq 0$ is applied, this degeneracy is lifted due to the Zeeman effect. The electron spin aligns either parallel, $M = +\frac{1}{2}$, or antiparallel, $M = -\frac{1}{2}$, to the field direction, where M is the quantum number of the S_z spin operator. The resulting energies for each spin state are given by:

$$E = g\mu_B MB, \quad (10)$$

where μ_B is the Bohr magneton and g is the spectroscopic splitting factor.

In the presence of an oscillatory magnetic field of frequency ν applied perpendicular to the direction of $\mathbf{B}$, a transition between the Zeeman split levels will occur when the following resonance condition is satisfied:

$$h\nu = g \mu_B B_0. \quad (11)$$

Here h is the Planck constant, and B_0 is the resonant field.

This resonance condition permits a wide range of combinations of microwave frequencies and magnetic field strengths. However, most experimental EPR measurements are performed using microwaves in the 9-10 GHz range, which corresponds to resonance magnetic fields of approximately 3500 gauss (0.35 T). In practice, EPR spectra are most commonly obtained by fixing the microwave frequency and sweeping the magnetic field until the resonance condition is satisfied. As the external magnetic field is increased, the energy gap between the spin up and spin down states also increases. When the gap matches the energy of the incident microwaves, resonance occurs, and unpaired electrons are promoted between spin states. According to the Maxwell-Boltzmann distribution, electrons tend to occupy the lower energy states more frequently. This results in a population imbalance, leading to a net absorption of microwave radiation at resonance, which is detected and plotted as the EPR spectrum.

A Bruker EMX plus spectrometer (shown in Figure 4.12 (a)) operating at 9.5 GHz (X band) was used to record the room-temperature EPR spectra of the Fe-doped LiGaO_2 crystal and powder samples. The spectrometer's magnetic field was applied horizontally, while the microwave RF field was oriented vertically to the applied field. The powder samples were stored inside a quartz tube and placed within the microwave cavity for measurement. For the crystal sample, a small piece was carefully cut and affixed to a quartz tube as shown in Figure 4.12 (b), which is then inserted into the cavity.



Figure 4.12. (a) Bruker EMX EPR spectrometer used for the study, (b) an iron (Fe^{3+}) doped LiGaO_2 single crystal sample attached to a quartz tube for EPR measurement, the Institute of Physics, IP PAS.

4.8.4. *X-ray photoelectron spectroscopy (XPS)*

XPS is another type of photoemission spectroscopy technique used to study materials, in which the spectra are obtained by exposing a material to an X-ray beam. XPS relies on the photoelectric effect to identify the elements within a material (elemental composition) or on its surface, along with their chemical states, electronic structure, and density of electronic states. It is an effective technique because it provides information about both the elements present and their bonds. XPS typically probes 5-10 nm of the top of the sample surface due to the limited escape depth of the photoelectron. The instrument generally consists of an X-ray source, an ultra-high-vacuum chamber that maintains a pressure below 10^{-9} mbar, and a sample stage for precise positioning. The electron energy analyser measures the kinetic energy (KE) of the emitted

photoelectrons, and the detector records the photoelectron intensity as a function of binding energy (BE), which is calculated using the following formula.

$$BE = h\nu - KE - \phi \quad (12)$$

Where $h\nu$ represents the energy of a photon from the X-ray source and ϕ the work function of the spectrometer.

In this thesis, the X-ray photoelectron spectra were recorded at the Institute of Physics, IP PAS, using a Scienta R4000 hemispherical analyser (pass energy 200 eV) with monochromatic Al K α (1486.7 eV) excitation (Scienta MX-650) operating at 150 W. The powdered samples were pressed onto conductive tape to create a flat surface and then mounted on a sample holder. The XPS data were treated with Shirley-type background subtraction and fitted with a Gaussian–Lorentzian function, and the analysis was performed using CasaXPS software.

4.8.5. Secondary ion mass spectroscopy (SIMS)

SIMS is one of the most sensitive methods for elemental surface analysis, capable of detecting elements at levels from parts per million to parts per billion. It is used to analyse the composition of solid samples or thin films by using a focused primary ion beam to collect and analyse the secondary ions ejected. A mass spectrometer measures the charge-to-mass ratios of secondary ions to identify the elemental, isotopic, or molecular composition of the surface, with a depth resolution of 1 to 2 nm. The spectrometer comprises a primary ion gun that produces the ion beam, a primary ion column that accelerates and focuses the beam onto the sample surface, a high-vacuum sample chamber that holds the sample and houses the secondary-ion extraction lens, a mass analyser that sorts the secondary ions by their mass-to-charge ratios, and a detector.

In the present thesis, depth profiles of the crystal samples were measured using SIMS with a CAMECA IMS6F micro-analyser, shown in Figure 4.13. The detector has two primary ion beams, O²⁺ and Cs⁺. The crystals were sputtered with 100 nm-thick gold before the measurements due to their semi-insulating nature. The measurements of Mg, Fe, Cr, and Mn ions in the crystal were performed using an oxygen (O²⁺) beam at 8 keV and 600 nA. The SIMS signals were detected by the electron multiplier. The size of the ion beam raster is about 150×150 mm², and the secondary ions are collected from a central region of approximately 60 μ m diameter. The concentration of

atmospheric elements, primarily H, C, and O, along with silicon, was measured using the SIMS setting outlined in the Ref. [75].



Figure 4.13. The CAMECA IMS6F spectrometer used for the SIMS study, the Institute of Physics, IPPAS.

4.9. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is a thermos-analytical technique in which the difference between the heat required to raise the temperature of a sample and that of a reference is measured as a function of temperature. Throughout the experiment, the sample and reference are kept at nearly identical temperatures. The reference sample should exhibit a well-defined heat capacity across the temperature range to be scanned. It must also be stable, of high purity, and undergo minimal changes during the temperature scan. Typically, reference standards include metals such as indium, bismuth, aluminium and tin. The fundamental principle of DSC is that during a physical change, such as a phase transition, the sample requires a different amount of heat than the reference to maintain the same temperature. The amount of heat required varies depending on whether the process is endothermic or exothermic. By measuring the heat flow difference between the sample and the reference, DSC can determine the amount of heat absorbed or released during transitions. Generally, a DSC measurement produces a heat flow curve as a function of

temperature or time. Based on the device and measurement standards, exothermic processes might show as positive or negative peaks. The transition enthalpy is determined by integrating the area beneath the relevant peak. The enthalpy of transition can be represented by the following equation.

$$\Delta H = KA \quad (13)$$

where ΔH represents the enthalpy of transition, K stands for the calorimetric constant, and A denotes the area under the curve. DSC experiments are typically conducted in an inert atmosphere, with gases such as nitrogen (N_2) and argon (Ar) continuously purged into the instrument. This avoids further oxidation and unwanted chemical reactions of the sample. In the present thesis, standard DSC measurements were performed using a DSC 3 instrument from Mettler Toledo located at the Laboratory for Soft Matter Research, Institute of Physical Chemistry, PAS, in a temperature range of -80 to 550 °C in a nitrogen atmosphere, using an aluminium pan as the sample holder.

5. LiGaO₂: Fe³⁺ Phosphor Under High Pressure

5.1. Description of the published articles

Lithium gallate (LiGaO₂) is a ternary oxide semiconductor in the Li-Ga-O system, widely recognised for its wide band gap, structural stability, and versatile physicochemical properties. Under ambient conditions, it crystallises predominantly in an orthorhombic β -phase derived from a distorted wurtzite framework, with lithium and gallium cations tetrahedrally coordinated by oxygen. This ordered tetrahedral network provides a stable host lattice suitable for ionic substitution without major structural distortion. Due to its large band gap and chemical robustness, LiGaO₂ has attracted attention in both electronic and optical material research.

Chapter 5 comprises two articles published by the PhD candidate during his PhD studies at IPPAS. The first one was published in the ACS '*Inorganic Chemistry*' journal, and the second one in the MDPI '*Molecules*' journal. The results presented in both papers were obtained on the same nanocrystalline β -LiGaO₂ phosphor doped with 0.25% Fe³⁺, synthesised by solid state reaction, and thus can be treated as a whole.

The first article reports the results of a comprehensive study of the near-infrared (NIR) luminescence of Fe³⁺, investigated under ambient, low-temperature, and high-pressure conditions. At ambient conditions, the synthesised phosphor displays a photoluminescence band at about 746 nm, associated with the $^4T_1 \rightarrow ^6A_1$ transition, with a quantum efficiency of 28% under 275.4 nm excitation. The photoluminescence excitation spectra of Fe³⁺ allowed the determination of the Racah and crystal-field parameters. At low temperatures, the sample shows a zero-phonon line (ZPL) at 709 nm, together with phonon replicas superimposed on the main band. An additional, weak ZPL line at 695 nm is also detected, the origin of which is explored in the next paper.

The high-pressure experiment was carried out at 7 K in a diamond anvil cell up to a maximum pressure of 15 GPa. As pressure increase, a redshift of the 746 nm Fe³⁺ emission band is observed

up to 14 GPa, above which the luminescence is quenched. This quenching is attributed to pressure-induced amorphisation of the host lattice. However, the rich phonon structure disappears already around ~3 GPa, which indicates a pressure-induced phase transition from its initial structure. While the material recrystallizes with the release of pressure, the orthorhombic to trigonal phase transition is irreversible.

The study also explored the mechanoluminescence behaviour of the synthesised sample. Notably, mechanoluminescence in the NIR region was observed for the first time in this system, emphasising its potential for stress sensing and various optoelectronic applications.

The second article examines the possible presence of multiple Fe^{3+} luminescent centres in the synthesised $\text{LiGaO}_2\text{:Fe}^{3+}$ phosphor. The idea for this research evolved from a previously unknown low-temperature luminescence peak reported at 695 nm in the first article. It was initially believed that this peak was related to Fe^{3+} on octahedrally coordinated Ga sites in the 0.8% LiGa_5O_8 impurity phase detected in XRD. Complementary characterisation techniques reported in the second paper, including Raman, EXAFS, Mössbauer, and EPR spectroscopy, as well as luminescence decay measurements, support the multisite occupancy of Fe^{3+} .

Mössbauer spectroscopy measurements revealed the presence of three different types of Fe centres in the sample, two of which are tetrahedrally coordinated in the LiGaO_2 phase and one related to octahedral coordination. EXAFS investigations have demonstrated that the majority of Fe^{3+} ions are incorporated into tetrahedrally coordinated Ga sites in the lattice. The results of the EPR study also identified three distinct Fe centres with orthorhombic symmetry. However, detailed investigations of the 695 nm line show that it has the same intra-centre excitation spectrum and the same pressure dependence as the ZPL at 709 nm stemming from Fe^{3+} ions occupying tetrahedral Ga sites in LiGaO_2 . Thus, we attribute this line to Fe^{3+} ions in LiGaO_2 having some defects in their vicinity.

As part of the study, I annealed the same sample to increase the LiGa_5O_8 impurity phase. Powder diffraction revealed a substantial increase of the LiGa_5O_8 impurity phase after annealing. However, no change of the emission spectrum was observed, which confirms that the luminescence of Fe ions in octahedral Ga sites in the LiGa_5O_8 impurity phase is too weak to be detected. Additionally, mechanoluminescence, thermo-stimulated luminescence (TSL), cathodoluminescence, and antibacterial properties of the phosphor were examined.

5.2. Published Article No.1

Ajeesh Kumar Somakumar, Lev-Ivan Bulyk, Volodymyr Tsiumra, Justyna Barzowska, Puxian Xiong, Anastasiia Lysak, Yaroslav Zhydachevskyy, and Andrzej Suchocki. "High-Pressure Near-Infrared Luminescence Studies of Fe³⁺-Activated LiGaO₂." *Inorganic Chemistry* 62, no. 31 (2023): 12434-12444. <https://doi.org/10.1021/acs.inorgchem.3c01627>.

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The description of the doctoral candidate's contribution can be found on page 158.

5.3. Published Article No. 2

Ajeesh Kumar Somakumar, Ivo Romet, Agnieszka Grabias, Marcin Kruk, Shusaku Hayama, Damian Włodarczyk, Justyna Barzowska, Yadhu Krishnan Edathumkandy, Eduard Feldbach, Puxian Xiong, Yaroslav Zhydachevskyy, Monika Trzaskowska, Hanka Przybylińska, Andrzej Suchocki. “Multisite Fe³⁺ luminescent centers in the LiGaO₂: Fe nanocrystalline phosphor.” *Molecules* 30, no. 11 (2025): 2331. <https://doi.org/10.3390/molecules30112331>.

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The description of the doctoral candidate’s contribution can be found on page 165.

Supplementary Information

Multisite Fe³⁺ luminescent centers in the LiGaO₂:Fe nanocrystalline phosphor

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Text S1: Antimicrobial properties

The near-infrared emitting $\text{LiGaO}_2\text{:Fe}^{3+}$ phosphor has been recently shown to exhibit excellent persistent luminescence properties which, together with the reported cytotoxicity tests on biological tissues, indicate its potential for bio-imaging applications [1]. This inspired us to check, whether the material shows also antibacterial properties. We found that in the as grown form it does not exhibit any significant antibacterial action against the following gram-positive and gram-negative bacteria investigated: *Salmonella enterica* ATCC 29631, *Salmonella enterica* ATCC 14028, *Escherichia coli* ATCC 15922, *Escherichia coli* ATCC 11775, *Listeria monocytogenes* ATCC 15131, *Listeria monocytogenes* ATCC 7644. This may change if a suitable capping is introduced. The experimental method used for the antimicrobial studies is described below.

The agar-based well diffusion method was used to analyse the antimicrobial properties of nanoparticles. Initially, *Salmonella enterica* ATCC 29631, *Salmonella enterica* ATCC 14028, *Escherichia coli* ATCC 15922, *Escherichia coli* ATCC 11775, *Listeria monocytogenes* ATCC 15131, *Listeria monocytogenes* ATCC 7644 were activated at 80°C. Bacterial strains were activated on a Mueller Hinton Agar plate (Oxoid, UK) and incubated aerobically for 24 h at 37°C. Then one colony was transferred to 10 mL of Mueller-Hinton broth (Oxoid, UK) and incubated overnight at 37 °C. Then the cultures were serially diluted in phosphate-buffered saline (Sigma-Aldrich, Poznań, Poland) to obtain bacteria concentration between 4-5 log CFU/mL. On each 90 mm diameter Petri dish, 25 mL of the Muller Hinton Agar was poured and solidified before culturing. Bacterial supersites were cultured in the volume of 100 µL and spread on the surface of agar plates. Wells were cut in the agar using a 6 mm diameter knife. A solution of nanoparticles in water was poured into each well in a volume of 100 µL. Two concentrations of nanoparticles were tested: 1 g/100 mL (1%) and 0.1 g/100 mL (0.1%). The plates were incubated for 24 hours at 37°C under aerobic conditions. The experiment was carried out in three biologically independent repetitions.

[1] Z. Zhou, X. Yi, P. Xiong, X. Xu, Z. Ma, M. Peng, Cr^{3+} -Free near-infrared persistent luminescence material $\text{LiGaO}_2\text{:Fe}^{3+}$: Optical properties, afterglow mechanism and potential bioimaging, J Mater Chem C Mater 8 (2020) 14100–14108. <https://doi.org/10.1039/d0tc03212c>.

S1: FE-SEM and EDS elemental mapping

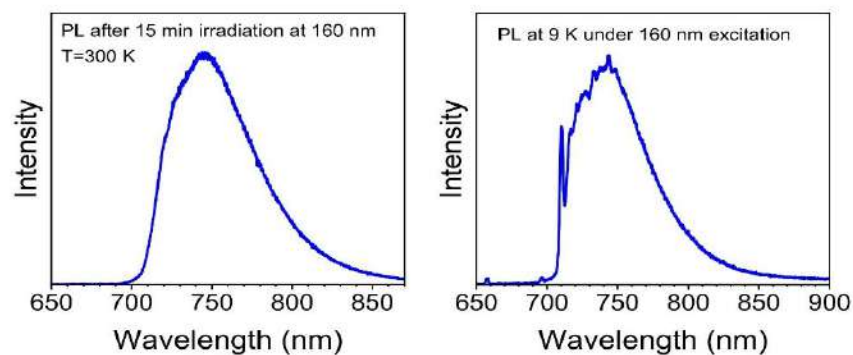


Figure S2. Afterglow after exposure to 15 min irradiation at 160 nm detected at room temperature (left) and luminescence under the same excitation at 9 K (right).

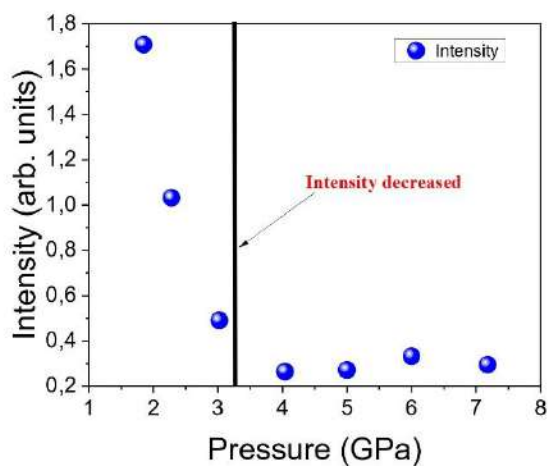


Figure S3. Pressure dependence of the 695 nm emission line intensity.

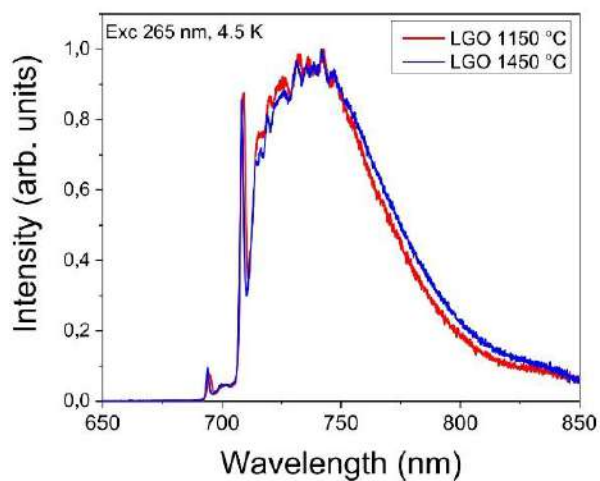


Figure S4. Low temperature luminescence spectra of the sample annealed at 1150 °C, containing mainly LiGaO₂ phase, and the sample annealed at 1450 °C, with a large amount of the additional LiGa₅O₈ phase.

6. Mn^{2+} Luminescence Under High Pressure



6.1. Introduction

As discussed in previous chapters, LiGaO_2 is a wide-bandgap material with an orthorhombic structure that is structurally derived from a wurtzite lattice and retains a tetrahedrally coordinated cation sublattice, meaning it has a distorted wurtzite structure compared to that of wurtzite. Moreover, it is an ideal host for manganese (Mn^{2+}) ions, which typically substitute for the cation sites of tetrahedral coordination, similar to Fe^{3+} in LiGaO_2 , as discussed in previous chapters. The $3d^5$ electronic configuration of Mn^{2+} ions is susceptible to changes in the crystal field strength and local site symmetry of the materials; fine-tuning of these factors can achieve strong, controllable luminescence in the visible to near infrared spectral region. The distorted wurtzite-like structure of LiGaO_2 provides a perfect host material for studying the structural property relations of Mn^{2+} activated luminescence, including the effects of site occupancy, crystal field interaction, and lattice distortion. The spectrum locations and intensities related to the spin-forbidden ${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$ electronic transitions of Mn^{2+} are highly influenced by the tetrahedral crystal field environment in the LiGaO_2 host. This makes Mn-doped LiGaO_2 especially well-suited for solid-state lighting, optoelectronic devices, and NIR phosphors.

Mn^{2+} emission in LiGaO_2 host crystal is made more efficient and tunable by its low phonon energy and structural stability, which makes it a key system of interest for comprehending the basic principles of TM luminescence in tetrahedral coordination. Moreover, structurally similar elements are taken into consideration to put LiGaO_2 in a larger context. Comparative investigations of crystal field effects in oxide hosts are made possible by a similar luminescence behaviour to that of Mn^{2+} in LiAlO_2 . Other related spinel-type materials, such as LiGa_5O_2 and LiAl_5O_2 , which have both tetrahedral and octahedral sites, shed light on site-selective Mn^{2+} occupation and its effect on emission characteristics. To assess the impact of lattice symmetry and bonding on Mn^{2+} luminescence, classical wurtzite semiconductors such as ZnS , GaN , and AlN provide optimal tetrahedral environments with varying degrees of covalency and crystal field splitting.

Secondary hosts give context for the main observations in LiGaO_2 and allow a thorough knowledge of how changes in structure and covalency impact Mn^{2+} electronic transitions. As has been mentioned in Chapter 5, an undoped LiGaO_2 crystal is used as a lattice-matched substrate for the crystal growth of many of these materials. Furthermore, it can also act as a gallium source for GaN crystal growth. Therefore, understanding Mn^{2+} luminescence in LiGaO_2 and comparing it to that of related hosts under pressure is important from both scientific and technological perspectives. Mn^{2+} -activated LiGaO_2 phosphors offer controllable emission for NIR LEDs, persistent luminescence, photonic devices, and pressure-sensing applications. Together with LiGaO_2 's excellent mechanical and thermal stability, the wurtzite-derived structure facilitates strong crystal field interactions and anisotropic bonding, making it the perfect model system for investigating pressure-dependent luminescence and electron-lattice interactions.

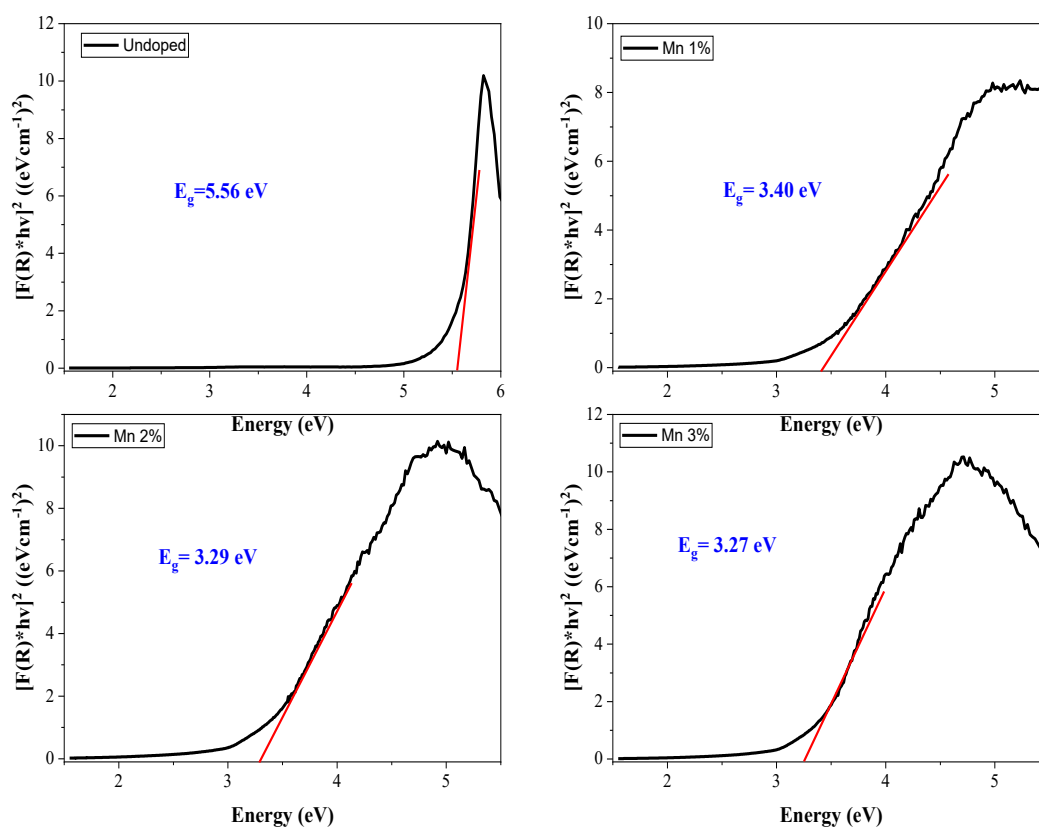
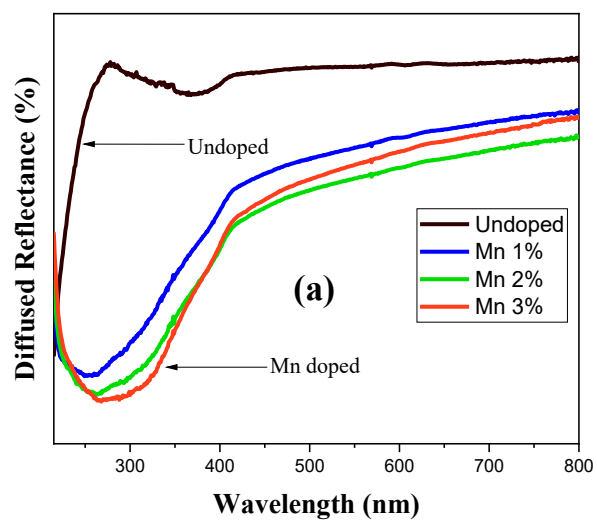
The host-dependent tuning of Mn^{2+} emission is better understood through comparative research with LiGaO_2 , ZnS , GaN , and literature data for AlN . These studies also contribute to the rational design of high-performance phosphors for advanced photonic and optoelectronic applications. To clarify structure–property correlations, crystal-field effects, and the influence of lattice symmetry and covalency on Mn^{2+} electronic transitions, this chapter focuses primarily on the luminescence behaviour of Mn^{2+} in LiGaO_2 , while systematically examining and comparing other hosts. Spectroscopic analyses, including crystal field calculations, measurements of the Racah parameter, and pressure-dependent investigations, provide a comprehensive understanding of Mn^{2+} activated luminescence in wurtzite and wurtzite-derived materials. This chapter begins

with the spectroscopic data of in-house synthesised LiGaO₂:Mn phosphor, followed by the ambient and high-pressure characteristics of other phosphors with wurtzite structure, such as ZnS:Mn and GaN:Mn (own studies performed as part of this doctoral thesis) and AlN: Mn (based on literature data).

6.2. Vacuum-assisted synthesis of LiGaO₂:Mn²⁺ phosphor

The LiGaO₂:xMn²⁺ (x = 0.05%, 0.1%, 0.5%, 1.0%, 2.0%, and 3%) samples were synthesised by high-temperature solid-state reaction in a vacuum furnace. The chemicals Li₂CO₃, Ga₂O₃, and MnCO₃ were weighed and mixed according to specific stoichiometric ratios, then thoroughly ground in a mortar. The resulting mixtures were sintered at temperatures ranging from 1000 °C to 1300 °C for 2 hours in ceramic crucibles under vacuum conditions. Finally, the prepared samples were cooled to room temperature, ground into powder, and used for subsequent optical analysis. An undoped sample was also prepared following the same procedure to serve as a reference for comparison with the Mn-doped samples.

Figure 6.1 (a) presents the diffused reflectance spectra (DRS) of the undoped and doped LiGaO₂ samples with different manganese percentages, which shows that the undoped LiGaO₂ has an absorption peak below 350 nm. However, the samples with increasing manganese concentrations show a gradual increase in absorption below 500 nm. Moreover, the peak width increases with the increase of Mn content. The optical gap of the materials is calculated using the Kubelka-Munk function. Figure 6.1(b) presents the graphs of the Kubelka-Munk functions versus energy of the samples, which show that the undoped sample has a bandgap of 5.56 eV at ambient conditions, and the optical gap decreases with the increase of Mn concentration. For 1%, 2%, and 3% of Mn, it shows an optical gaps of 3.40 eV, 3.29 eV, and 3.27 eV, respectively, which are comparable with previously reported values for Mn-doped and undoped LiGaO₂.



(b)

Figure 6.1 (a) Diffused reflectance spectra and (b) Kubelka-Munk function versus energy plots of undoped and manganese-doped (1,2,3 % of Mn) LiGaO₂.

6.3. Mn^{2+} luminescence in LiGaO_2

6.3.1. Photoluminescence at ambient pressure

Figure 6.2 shows the room temperature luminescence spectra of the undoped and Mn-doped samples. The undoped sample in Figure 6.2 (a) exhibits a broad emission band in the UV-blue region when excited with 260 nm light; however, this is not as strong as the emission spectra of the doped samples shown in Figure 6.2(b). The undoped LiGaO_2 sample has recently gained interest as a scintillating material due to its emission properties in this region, with fast decay time components [76].

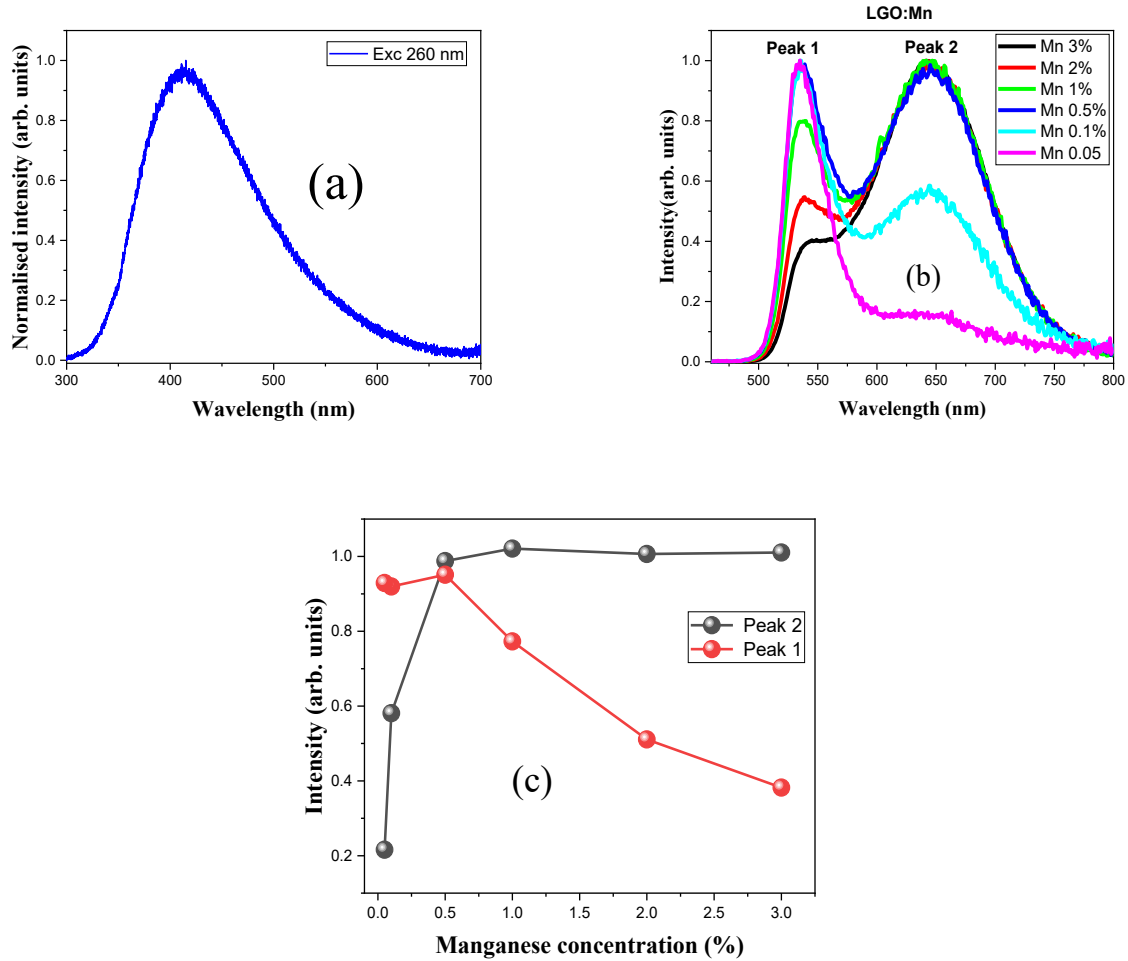
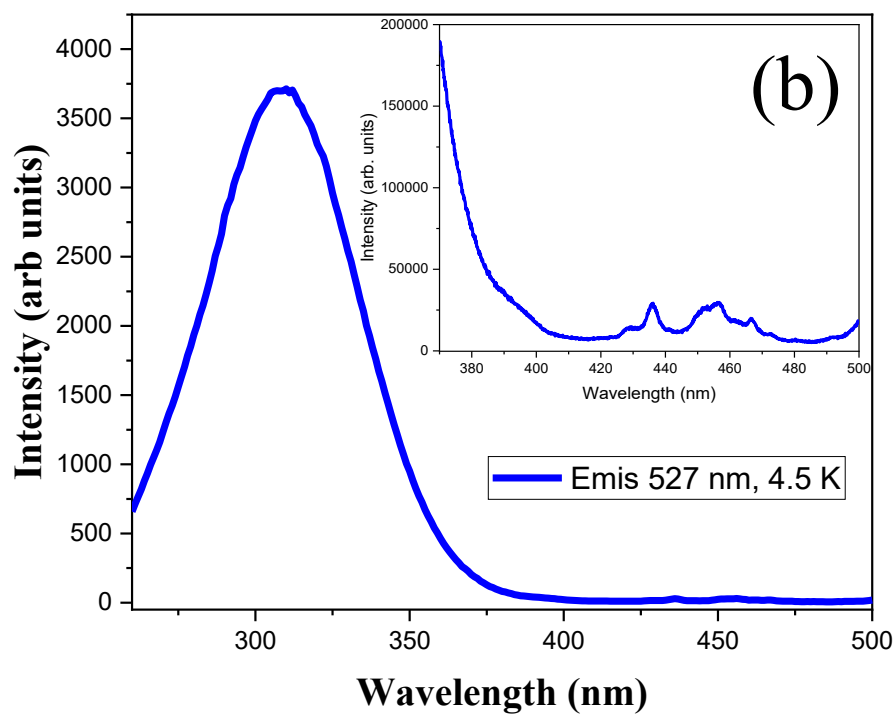
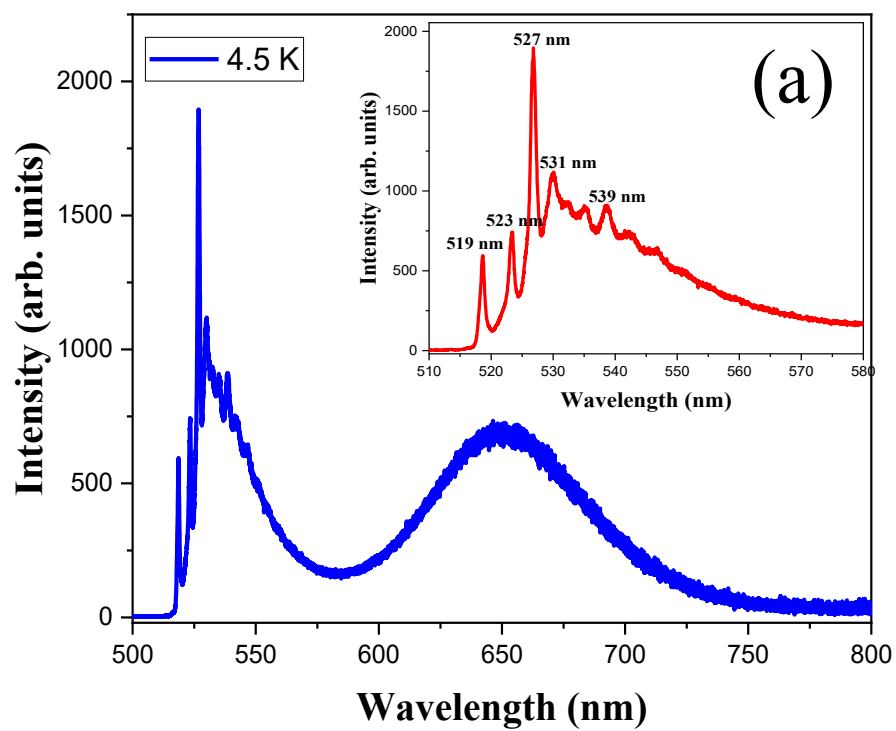


Figure 6.2 (a) Room temperature photoluminescence spectra of undoped LiGaO_2 with 260 nm excitation and (b) manganese-doped samples with 300 nm excitation; (c) intensity of peak 1 and peak 2 versus manganese concentration in percentage.

Figure 6.2 (b) shows the luminescence spectra of doped LiGaO_2 : x Mn phosphor samples with various percentages of manganese ions ($x = 0.05\%$, 0.1% , 0.5% , 1% , 2% , and 3%) excited with 300 nm light. Unlike in the case of its isostructural compound LiAlO_2 :Mn where only one Mn peak is observed [77], here, the luminescence spectrum is composed of twin peaks. Moreover, the Mn^{2+} emission peak maximum in LiAlO_2 varies from 500 nm to 600 nm depending on the synthesis procedures and conditions [77–79]. However, in this case the twin luminescence peak one (peak 1) is observed at 540 nm and the other peak two (peak 2) at 650 nm. The latter one has a much broader shape, and its intensity increases with the increase of Mn concentration; vice versa, the peak one's intensity decreases with the increase of Mn concentration. Moreover, both peaks are not observed in the undoped sample prepared under the same conditions, which means that both peaks are evolved from the effect of manganese doping. The graph in Figure 6.2(c) shows the normalised intensity of peak 1 and peak 2 versus manganese concentration in percentage. It shows that, from Mn concentration 0.5% onwards, the peak 1 intensity decreases with increasing Mn concentration.

For a more precise analysis, we select the LiGaO_2 sample doped with a 1 % Mn concentration, as its peak 2 luminescence intensity is slightly higher than that of peak 1. Moreover, we initially assume that peak 2 at room temperature is more similar to the Mn^{2+} luminescence in other Mn-doped wurtzite-like and wurtzite materials than peak 1 [80]. Figure 6.3 shows the low-temperature emission and excitation spectra of a 1% Mn-doped LiGaO_2 sample. From Figure 6.3(a), it is evident that peak 1 exhibits a significant difference compared to peak 2 at low temperatures. At 4.5 K, peak 1 consists of zero-phonon lines and phonon sidebands, unlike peak 2, which retains its room-temperature shape, indicating that both peaks are probably related to the Mn ions; however, they occupy different sites [81]. The low temperature excitation spectra from both emission maxima (527 nm and 650 nm) shown in Figure 6.3(b & c) depict that both consist of very large, intense, and broad charge transfer bands (CTB) near 300 nm, compared to the weak d-d transition bands at longer wavelengths. The inset images show enlarged views of the d-d transition bands in the respective excitation spectra. This supports our conclusion that both peaks belong to Mn^{2+} ions; however, they are located in different sites.



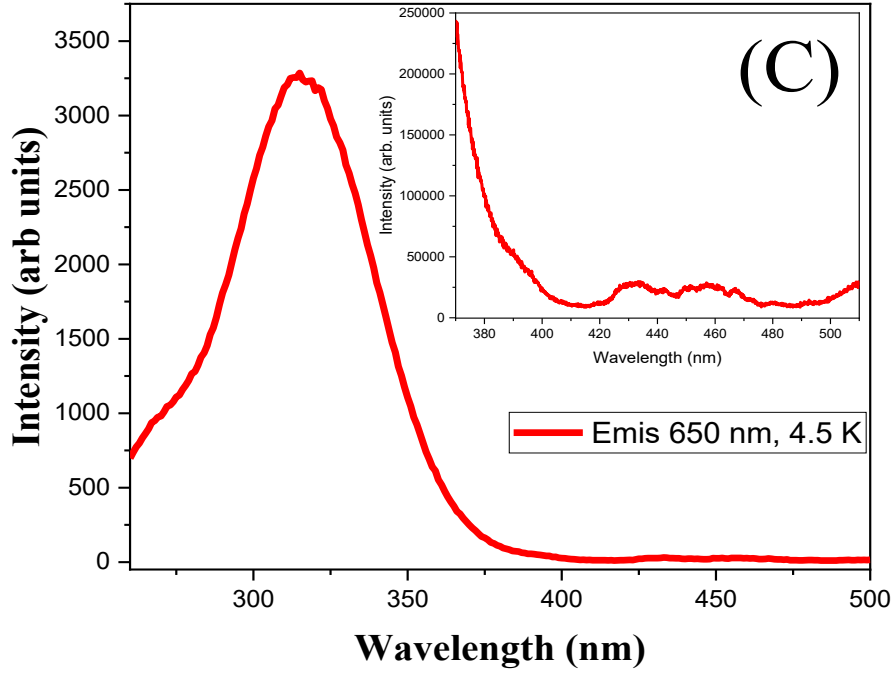


Figure 6.3 (a) Low temperature photoluminescence spectra of LiGaO₂:Mn (1%) sample with 300 nm UV excitation. The inset graph shows the enlarged view of zero phonon lines and phonon replicas. (b) & (c) Excitation spectra recorded from 527 nm and 650 nm emission peaks, respectively. The inset shows the enlarged view of the d-d transition bands in the excitation spectra.

The multi-site occupation-tendency of dopants in the LiGaO₂ host was well studied previously; however, it was with another prominent d⁵ ion, Fe³⁺ [82]. Figure 6.4 depicts the temperature dependence of the luminescence spectrum of the LiGaO₂: Mn 1% sample from 4.5 K to 300 K with 300 nm excitation. It shows that as the temperature increases from 4.5 K to 300 K, the intensity of both peak one and peak two decreases; moreover, the zero-phonon line related to peak 1 started appearing below 100 K, which indicates that peak 1 has a weak electron-phonon coupling compared to the Mn²⁺ ion related to the peak 2 luminescence.

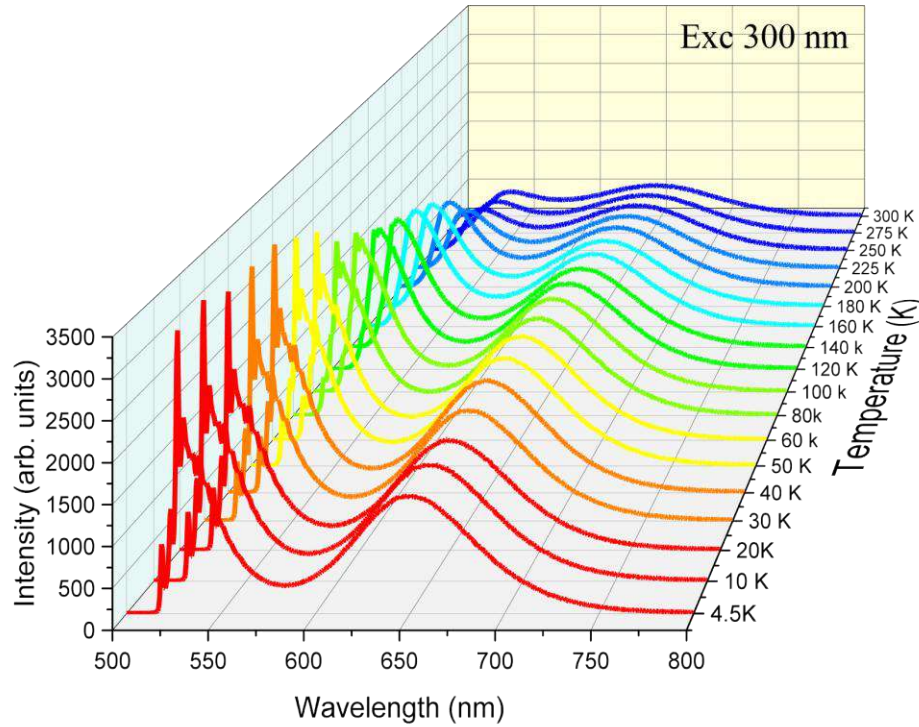


Figure 6.4 Temperature-dependent photoluminescence spectra of LiGaO₂:Mn (1%) sample from 4.5 K to 300 K with 300 nm UV excitation.

To further confirm that both luminescence peaks originate from Mn²⁺, we performed temperature-dependent EPR analysis on the sample. In principle, when manganese ions are incorporated in the LiGaO₂ host, they can exist in at least three paramagnetic oxidation states: Mn²⁺ (3d⁵, $S = 5/2$), Mn³⁺ (3d⁴, $S = 2$), and Mn⁴⁺ (3d³, $S = 3/2$), which probably exhibit luminescence in the visible region [83]. However, it is challenging to observe Mn³⁺ in EPR spectra due to its high spin ($S=2$) with large zero-field splitting. Figure 6.5(a) depicts the temperature-dependent EPR spectra of the LiGaO₂ sample with 1% Mn.

The sample exhibits highly intense, symmetric, and narrow hyperfine structure between 3000 and 4000 G at 200 K, attributed to the significant Mn²⁺ ion content in the host material. As the temperature decreases, the broadness of this hyperfine structure increases. Moreover, a minor peak began to appear between 0 and 1000 G (below 12 K), which is likely related to the very low concentration of Mn⁴⁺ ions in the sample; however, it was observed only at extremely low temperatures. For improved clarity, an XPS measurement of the same sample was performed, as

displayed in Figure 6.5 (b). It appears that the peaks for binding energy around 640.7 eV are associated with Mn^{2+} ions, and a shake-up satellite is also observed at a higher binding energy of 645.2 eV, related to Mn^{2+} . Additionally, the binding energy peak at around 642.1 eV is primarily associated with Mn^{3+} . However, this excludes the possibility of no Mn^{3+} presence in the phosphor sample, but the Mn^{2+} concentration is still higher than the Mn^{3+} concentration. Moreover, no Mn^{4+} related binding energy peaks were observed in this sample, which confirms the EPR observation of only a very minute percentage of Mn^{4+} charge state ions present in the sample.

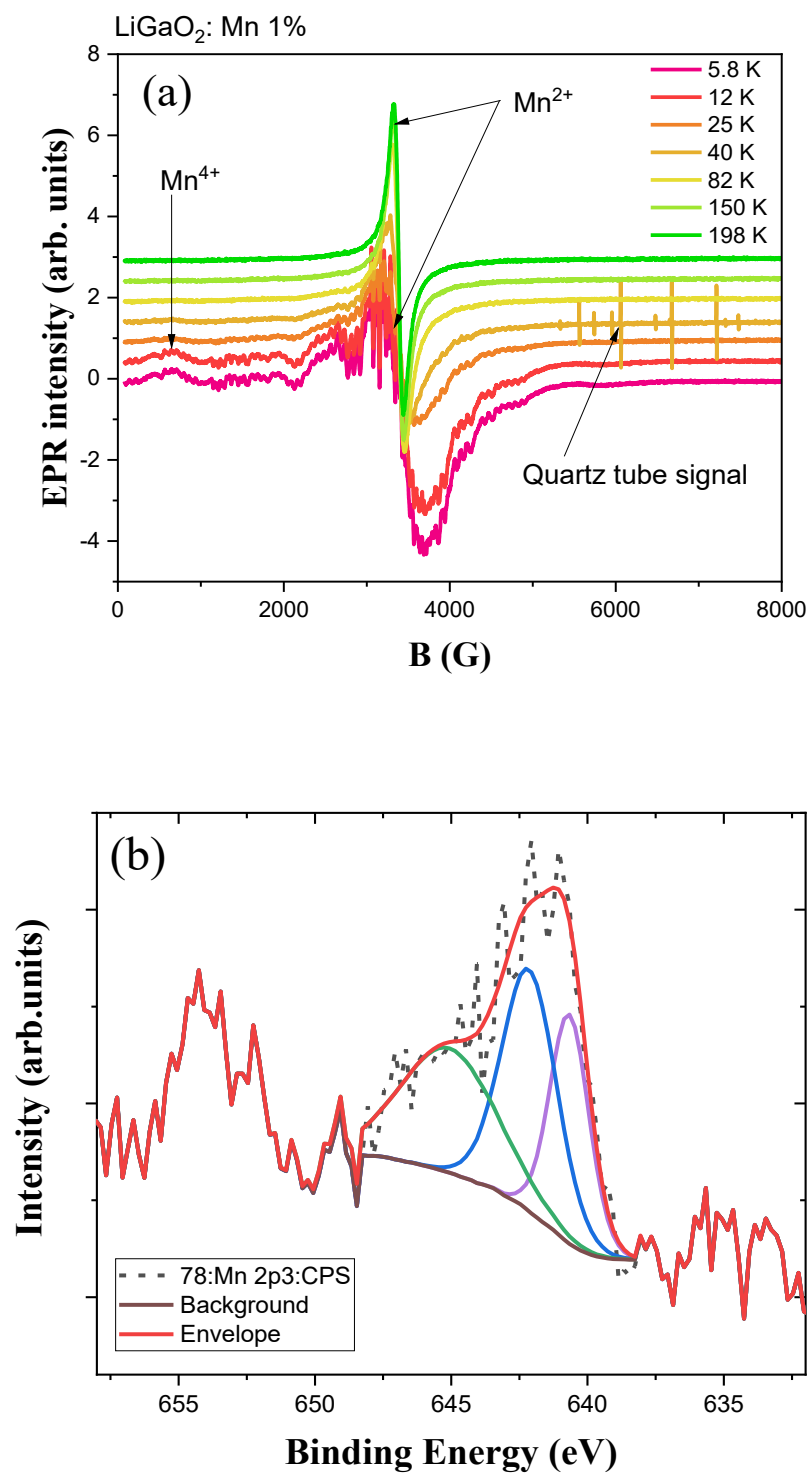
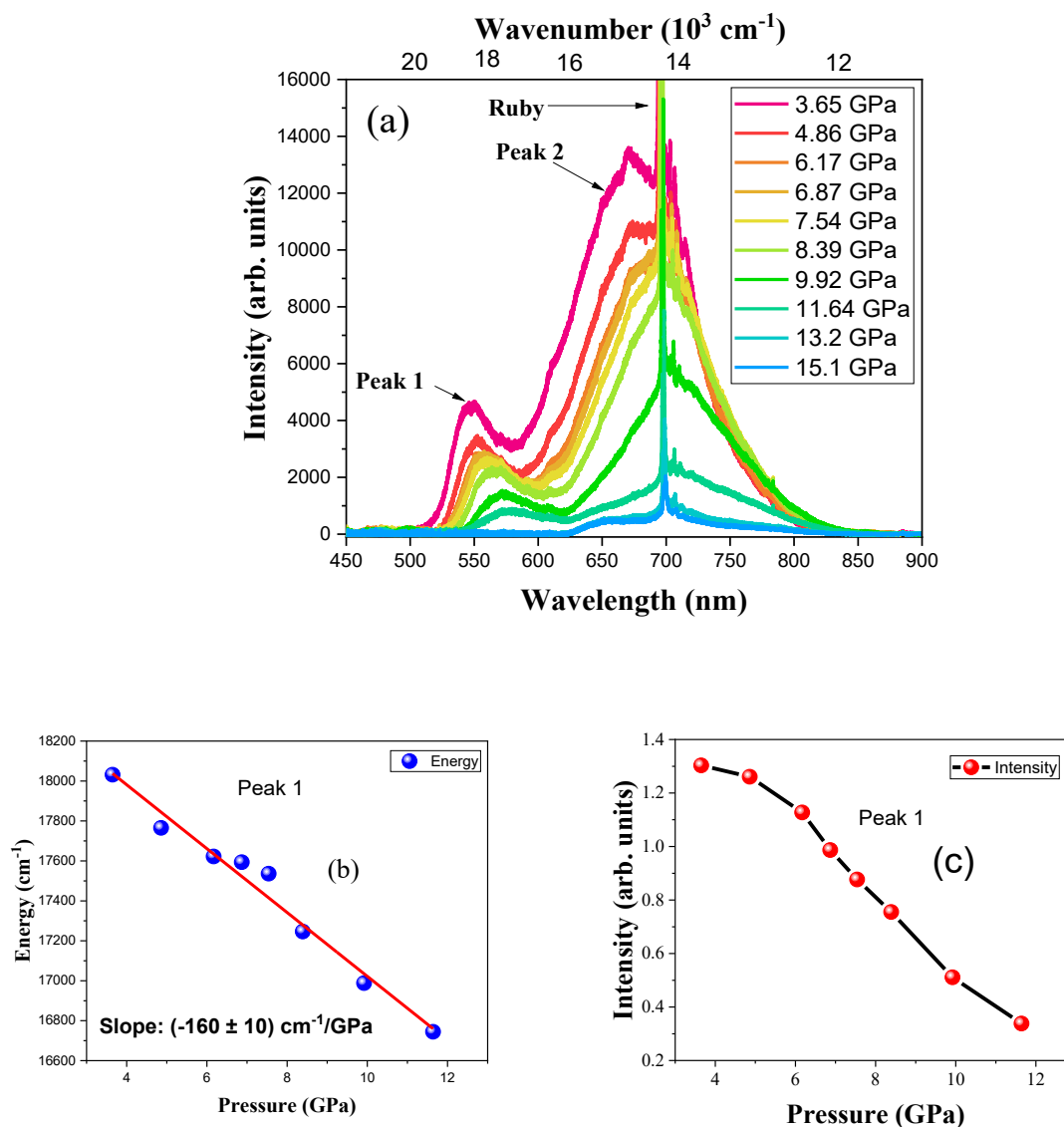


Figure 6.5 (a) Temperature-dependent EPR spectra and (b) XPS spectra of LiGaO₂: Mn 1%.

6.3.2. Pressure dependence of photoluminescence

Pressure-dependent luminescence spectra of the LiGaO₂: Mn 1% sample measured at room temperature are shown in Figure 6.6 (a). The sample was excited with a 261 nm line of continuous laser; in this experiment, a methanol-ethanol mixture was used as the pressure-transmitting medium, and ruby was used as the pressure gauge. The peak 2 luminescence overlapped with the ruby luminescence, because a 261 nm laser excitation falls into the ruby absorption band corresponding to the $^4A_2 \rightarrow ^4T_1$ transition.



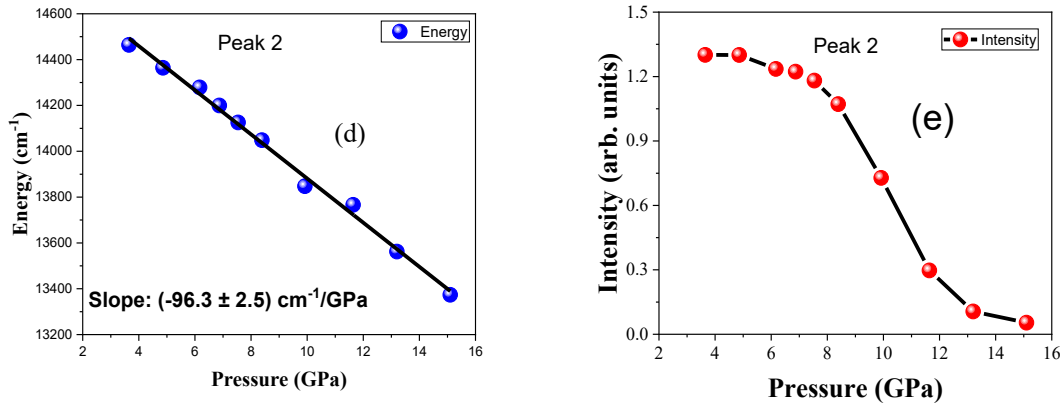


Figure 6.6 (a) Pressure-dependent luminescence spectra of LiGaO₂: Mn 1% sample, (b & d) energy and (c & e) intensity versus pressure of peak 1 and peak 2, respectively.

So, this ruby emission slightly affected the shape of peak 2 of the emission spectra. The figure also shows that as pressure increases from 3.7 GPa to 15.1 GPa, both luminescence peaks, peak 1 and peak 2, consistently redshift to higher wavelengths. Moreover, the intensities of both peaks decrease gradually with increasing pressure, and peak 1 completely disappears above 12 GPa. In comparison, peak 2 is close to disappearing at 15.1 GPa, which is comparable to previously reported high-pressure data for LiGaO₂ materials. The luminescence vanished due to the pressure-induced amorphization of the host material. Figure 6.6 (b & d) shows the PL peak energy versus pressure dependence for peak 1 and peak 2, respectively. Both graphs show a linear decrease in energy with an increase in pressure, indicating that both peaks are related to Mn²⁺ rather than Mn³⁺. This is consistent with the TS diagram of d⁵ ions, such as Mn²⁺, which exhibit a decrease in energy of the first excited state with increasing pressure [84]. However, in the case of Mn³⁺ (TS diagram for d⁴ system in tetrahedral coordination), an increase in energy with respect to the rise in pressure is expected [85,86]. The TS diagram for the d³ system, like that of Mn⁴⁺ in tetrahedral coordination, also indicates an increase in energy with pressure however such systems are very rare. Additionally, the analytical experiments didn't show any significant trace of Mn⁴⁺ ions in the sample that can contribute to any visible luminescence. This concludes that both peaks are associated with the Mn²⁺ ions. Another important observation from figures 6.6 (b & d) concerns the pressure coefficients for both peak 1 and peak 2: the pressure coefficients for peak 1, $\frac{dE_1}{dp} = (-160 \pm 10) \text{ cm}^{-1}/\text{GPa}$ and peak 2, $\frac{dE_2}{dp} = (-96.3 \pm 2.5) \text{ cm}^{-1}/\text{GPa}$. The significant difference

in the pressure coefficient of peak 1 compared to peak 2 indicates that the local environment of peak 1 is highly sensitive to pressure, compared to peak 2, and a strong crystal field variation is observed along Mn^{2+} ions related to peak 1 with pressure. Figures 6(c & e) present luminescence intensity versus pressure for peak 1 and peak 2, respectively. Both intensities decrease with increasing pressure. Above 6 GPa, the intensity drops rapidly due to the onset of the amorphization process. However, the intensity of Peak 1 quenches at a lower pressure than that of Peak 2 due to the collapse of the weakly coupled local environment. Moreover, no intermediate phase transition-related changes are observed at room temperature.

6.4. Mn^{2+} luminescence in ZnS

Zinc blende (cubic) and wurtzite (hexagonal) are the two primary crystalline forms of ZnS phosphor materials under ambient pressure, with the former being the most widely obtainable. At room temperature, ZnS in its cubic zinc blende form has a band gap of 3.54 eV, while the wurtzite structure exhibits a slightly larger band gap of 3.91 eV [87]. We selected ZnS:Mn^{2+} samples with a zinc blende structure and extremely small particle sizes for the current study to examine the luminescence decay behaviour as a function of pressure. Also, we did a detailed analysis of previous high-pressure measurements of the ZnS:Mn samples with zinc blende structure reported in our paper [84]. The phase transition to the rock-salt phase was not covered in many of these publications on high-pressure photoluminescence investigations of ZnS:Mn quantum dots with zinc blende and wurtzite structure [88–90]. The same chemical precipitation technique previously described in the literature was used to prepare the manganese-doped zincblende ZnS nanophosphor [91,92], and a conventional solid-phase synthesis procedure was used to prepare the wurtzite ZnS:Mn (1%) sample for comparison. **Chapter 6** cover image shows the Mn^{2+} luminescence in zinc blende and wurtzite ZnS samples used for the study under UV light excitation.

Part of the results shown in this chapter are published in the following paper: Ajeesh Kumar Somakumar, Yaroslav Zhydashkevskyy, Damian Wlodarczyk, Justyna Barzowska, Kodavamparambil Rajagopalan Bindu, Yadhu Krishnan Edathumkandy, Tatiana Zayarniuk, Andrzej Szewczyk, Saranya Narayanan, Anastasiia Lysak, Hanka Przybylinska, Edathottiyil Issac Anila, Andrzej Suchocki. "Temperature and pressure dependent luminescence mechanism of a zinc blende structured ZnS: Mn nanophosphor under UV excitation." *Journal of Materials Chemistry C* 12, no. 19 (2024): 7041-7052. <https://doi.org/10.1039/D4TC00960F>.

The doctoral candidate's contribution to this article consisted of investigation, writing the original draft, review & editing, and data curation.

6.4.1. *Ambient and high-pressure luminescence studies*

Initially, the luminescence analysis of the 2% Mn-doped cubic ZnS sample was conducted at room temperature and pressure. Bhargava et al. claim that when ZnS nanocrystals get smaller, the quantum confinement effect causes their bandgap energy to rise from 3.66 eV to higher energies [92,93]. At room temperature, the sample exhibits strong photoluminescence related to Mn^{2+} ions, which replace Zn^{2+} ions in ZnS host lattice. The sample's normalised photoluminescence excitation and emission spectra are displayed in Figure 6.7 (a).

The excitation spectrum seen in Figure 6.7 is made up of numerous minor peaks associated with various transitions and a reasonably intense broad CT band centred around 335 nm. The d-d transitions between the energy levels of the Mn^{2+} ion are responsible for these smaller peaks. The magnified view of these d-d transition bands is shown in Figure 6.7 (b). Table 6.1 lists the transitions observed experimentally at ambient conditions.

There are two distinct bands in the emission spectrum: an orange luminescence band at 605 nm and a broad blue luminescence band centred at 435 nm. The orange band is caused by the Mn^{2+} dopant's ${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$ transition, whereas the blue band is most likely connected to defects in the host material. According to some earlier research, the ${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$ emission-related band shifts toward lower energies when the Mn dopant fraction in the matrices increases. Additionally, this band's intensity increases as the concentration of Mn dopant rises [94]. Furthermore, this primary luminescence band's location somewhat changes as the size of the nanoparticle changes [95]. Figure 6.7 (a) shows a much weaker blue luminescent band (435 nm) in contrast to the highly intense orange emission at 605 nm. It verifies that the Mn^{2+} ions within the ZnS host lattice are perfectly doped. The Tanabe Sugano diagram for d^5 state explains the optical characteristics of the Mn^{2+} ions in ZnS (cf. Fig.2.3).

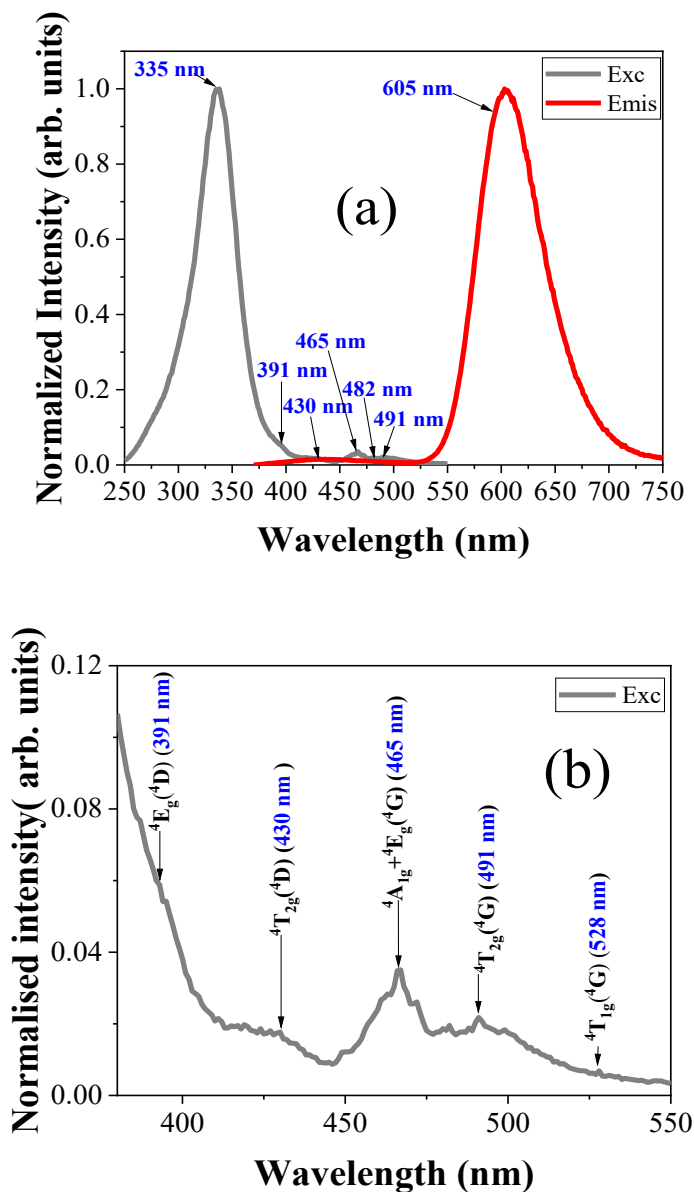


Figure 6.7. (a) Excitation spectrum recorded for the 605 nm emission peak and photoluminescence emission spectrum with 335 nm UV excitation (b) A closer look at the excitation spectrum in the range of d-d transition bands. Adapted from *Temperature and pressure dependent luminescence mechanism of a zinc blende structured ZnS: Mn nanophosphor under UV excitation*. Journal of Materials Chemistry C, 2024, 12(19), pp.7041-7052. DOI:10.1039/D4TC00960F [84].

Table 6.1: The locations of Mn^{2+} ions' lowest quartet excited states in ZnS in relation to the ${}^6\text{A}_{1g}$ ground state measured at 605 nm emission

Terminating state	Wavelength and energy of the PLE peak
${}^4\text{T}_{1g}({}^4\text{G})$	528 nm (18939 cm^{-1})
${}^4\text{T}_{2g}({}^4\text{G})$	491 nm (20367 cm^{-1})
${}^4\text{A}_{1g} + {}^4\text{E}_g({}^4\text{G})$	465 nm (21505 cm^{-1})
${}^4\text{T}_{2g}({}^4\text{D})$	430 nm (23256 cm^{-1})
${}^4\text{E}_g({}^4\text{D})$	391 nm (25575 cm^{-1})
C.T	335nm (29851 cm^{-1})

ZnS:Mn's pressure-dependent photoluminescence spectra at room temperature are displayed in Figures 6.8 (a) and (b). The shift in emission spectra during compression is illustrated in Figure 6.8 (a), while the emission spectra at decreasing pressure are shown in Figure 6.8 (b). Figure 6.8 (a) demonstrates that initially, the spectra were highly similar to those observed under ambient conditions; however, at the starting pressure, they were slightly shifted from their original position at 605 nm to around 610 nm. Additionally, it demonstrates how the Mn^{2+} fluorescence gradually shifts to the near-infrared (NIR) region, approximately 800 nm, at high pressure and is completely quenched at a pressure of 16.4 GPa. This indicates that a phase transition takes place at this pressure. The Mn-doped ZnS nanoparticle most likely changes into the rock salt ($\text{Fm}\bar{3}\text{m}$) phase at this pressure, losing its zincblende structure ($\text{F}\bar{4}3\text{m}$). Previous DFT investigations have suggested that the zinc blende structure is more compressible than the rock salt one and that the phase transition from zinc blende to rock salt occurs between 14.7 and 17.6 GPa [96,97]. Additionally, upon compression, the primary luminescence band redshifted to approximately 775 nm (1.6 eV), which falls within the NIR bio-window region. The sample luminescence returns to its initial position and regains its original luminescence intensity after decompression. Figure 6.8 (b) demonstrates the reversibility of the zinc blende to rock salt phase transition. In contrast to ZnS nanoparticles with a wurtzite phase, earlier synchrotron investigations of ZnS nanoparticles with a zinc blende structure showed a reversible phase transition [98]. It is also clear that the phase transition pressure of ZnS nanoparticles is significantly influenced by their grain size [99].

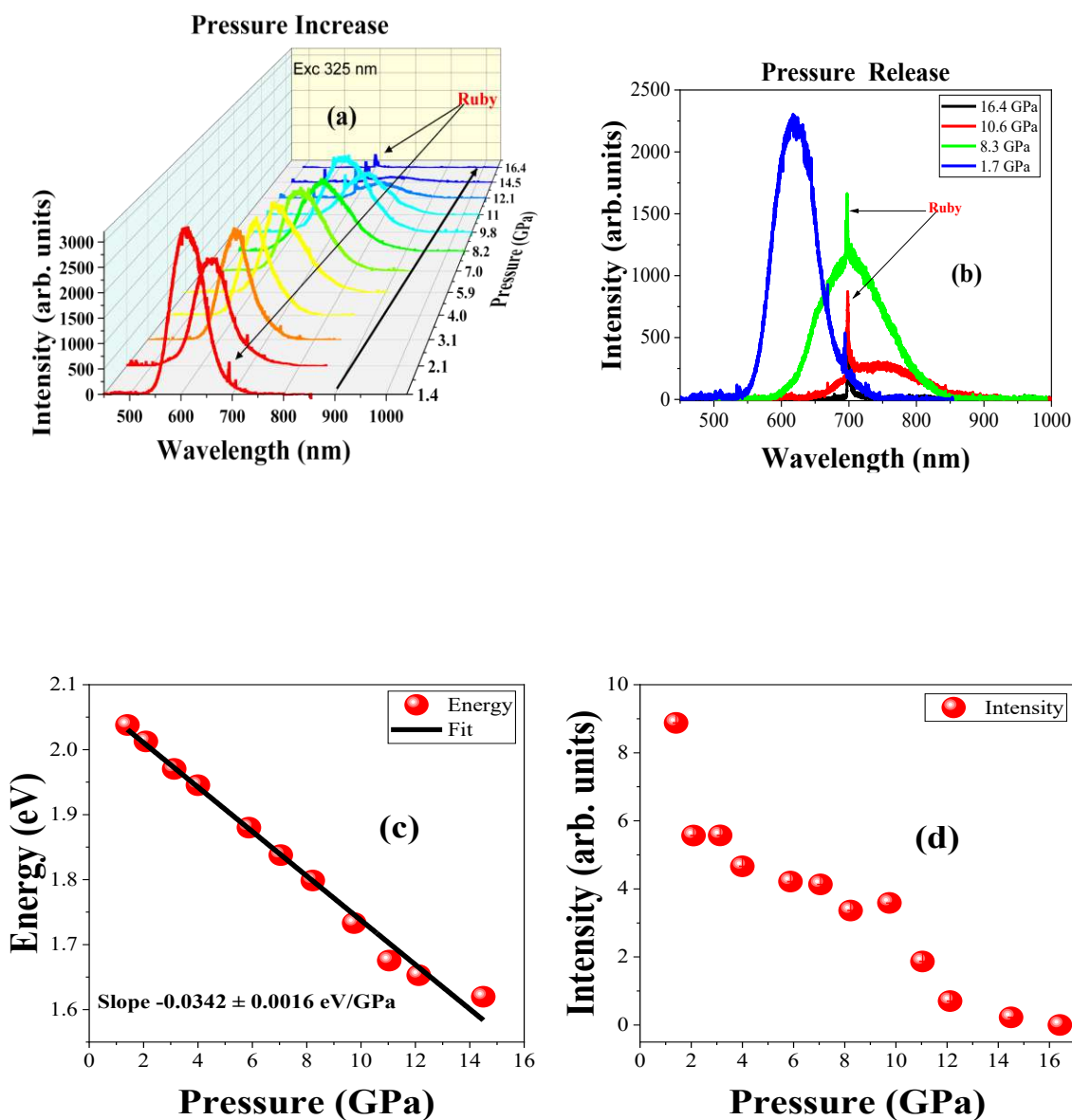


Figure 6.8 (a) The luminescence of ZnS:Mn²⁺ as a function of pressure and (b) pressure release measured at room temperature. (c) A graph showing PL peak energy versus pressure, and (d) a graph showing integrated emission intensity versus pressure. Adapted from *Temperature and pressure dependent luminescence mechanism of a zinc blende structured ZnS: Mn nanophosphor under UV excitation*. Journal of Materials Chemistry C, 2024, 12(19), pp.7041-7052. DOI:10.1039/D4TC00960F [84].

The linear drop in PL peak energy with the rise in pressure is depicted in Figure 6.8 (c). The linear fit of the data yielded a pressure coefficient of approximately -35.8 meV/GPa. It is similar to the values found in other high-pressure investigations of ZnS nanoparticles with comparable size and structure [84]. However, because of the larger surface-to-volume ratio, the ZnS:Mn²⁺ nanoparticle exhibits a slightly higher-pressure coefficient than the bulk crystal [89,90]. The integrated emission intensity, dependent on pressure, is shown in the graph in Figure 6.8 (d). It illustrates how the emission intensity gradually decreases as pressure rises. Moreover, the emission intensity was totally quenched at 16.4 GPa. The luminescence gradually shifted from the bright visible orange (2.037 eV) to the weak near-infrared (1.619 eV) region, as both graphs in Figure 6.8 (c) and (d) clearly demonstrate. The phase change caused the light emission to disappear with the subsequent increase in pressure.

6.4.2. Pressure dependence of luminescence decay

The sample's photoluminescence decay analysis was done as a function of pressure to gain a better understanding of how pressure affects the Mn²⁺ luminescence band. A 335 nm pulsed laser excitation from OPO was used to stimulate the sample, and the emission was detected at 610 nm, corresponding to the primary luminous band associated with the ⁴T₁→⁶A₁ transition. The flawless incorporation of a bigger percentage of Mn²⁺ ions inside the ZnS nanoparticles rather than over their surface is confirmed by the millisecond decay time of the longer τ_3 component. The other decay time component indicates the occupation of a few per cent of ions near the surface. The pressure-dependent decay kinetics of the ZnS:Mn sample were also examined to learn more about the high-pressure phase transition. The pressure-dependent decay kinetics of Mn²⁺ luminescence are displayed in Figure 6.9 (a). These decays have been fitted with a triple-exponential decay described by the Eq. (8). Figure 6.9 (b) shows the decay time versus pressure graph, indicating that during compression, all three PL decay components τ_1 , τ_2 , and τ_3 decrease. The flawless incorporation of a bigger percentage of Mn²⁺ ions inside the ZnS nanoparticles rather than over their surface is confirmed by the millisecond decay time of the longer τ_3 component. The other decay time components indicate the occupation of a few per cent of ions near the surface. At a pressure increase from 1atm to 15.24 GPa, the τ_3 component dropped from 2.98 ms to about 1.97 ms, the τ_2 component from 0.99 ms to 0.44 ms, and the τ_1 component from 0.28 ms to 0.067 ms. Compared to the other two components, the τ_3 component exhibits a greater decrease in decay time

with compression. Due to the previously mentioned pressure-induced zinc blende to rock salt phase transition, the Mn^{2+} fluorescence was completely quenched at the subsequent pressure step, reducing the signal to background noise. However, despite a remarkable decrease in luminescence intensity with high pressure, previous pressure-dependent decay analysis of the ZnS:Mn sample up to 12 GPa did not indicate a significant change in the primary decay component and did not reach the phase transition point [100].

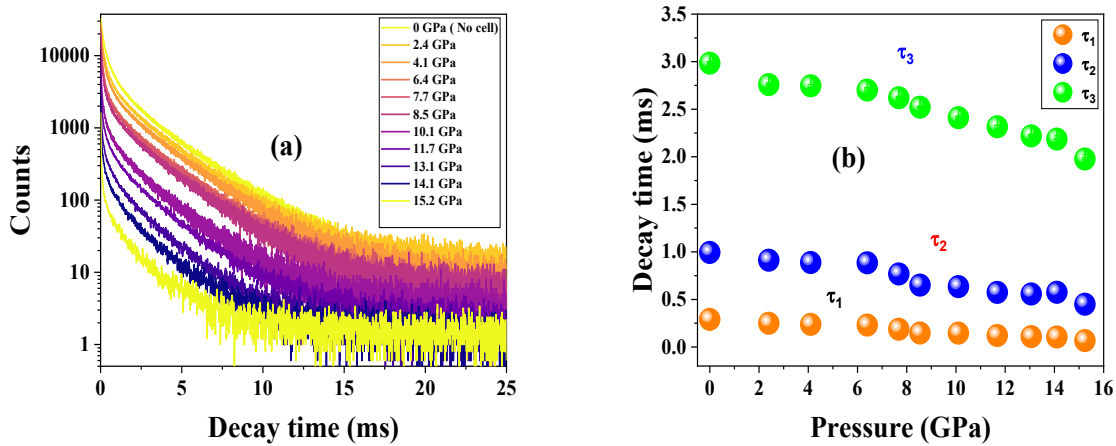


Figure 6.9. (a) The pressure-dependent photoluminescence decay kinetics of the Mn^{2+} emission in ZnS and (b) graphs showing the decay times against pressure. Adapted from *Temperature and pressure dependent luminescence mechanism of a zinc blende structured ZnS: Mn nanophosphor under UV excitation*. Journal of Materials Chemistry C, 2024, 12(19), pp.7041-7052. DOI:10.1039/D4TC00960F [84].

The presence of Mn^{2+} ions at various locations within the ZnS nanocrystal is indicated by the measurement of pressure-dependent multi-exponential luminescence decay times in millisecond time ranges. The Mn^{2+} ions occupying the non-perturbed cation sites are marked by the long decay component of approximately 3 ms in the trials. In contrast, the Mn^{2+} ions occupying the lattice sites closer to the nanocrystals' surface are likely responsible for the shorter decay component of approximately 1 ms. Nevertheless, either the Mn^{2+} ions occupying the lattice sites of the nanocrystal's surface or the blue emission that overlapped with the orange band associated with the ${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$ transition of Mn^{2+} are responsible for the additional low-intensity decay component that changed from milliseconds to microseconds during the high-pressure study using the pulsed

laser [101]. Furthermore, ZnS phosphor doped with 5% Mn^{2+} synthesised via the reverse micelle technique also showed a similar three-exponential decay behaviour [102]. A slight size variation in ZnS: Mn^{2+} nanoparticles also significantly affects the decay time values [103].

Tanabe Sugano diagrams and crystal field theory are also used to analyse the Mn^{2+} ion luminescence in ZnS, as shown in Figure 6.7 (a), which explains the observed electronic absorption energy levels in relation to crystal field strength affecting the Mn^{2+} dopant in the material. The size of the nanoparticle also affects the strength of the crystal field. The TS diagram for d^5 configuration, created with Racah parameters B, C, and crystal-field strength Dq , is utilised for the calculations due to the half-filled $3d^5$ electronic configuration of the Mn^{2+} ion. The crystal-field theory fit and $10Dq = \Delta = 4526 \text{ cm}^{-1}$, $B = 580 \text{ cm}^{-1}$, $C = 3140 \text{ cm}^{-1}$, $\Delta/B = 7.8$, and $C/B = 5.41$ yield the most likely values for this. Furthermore, the experimentally observed values in Table 6.1 are similar to the theoretically calculated levels for this crystal field: ${}^4T_1({}^4G)$ at 528 nm, ${}^4T_2({}^4G)$ at 482 nm, ${}^4A_1$, and ${}^4E({}^4G)$ at 465 nm. To determine the Racah parameters B and C, formulas (16) and (17) from Chapter 5 were used. Based on the excitation spectra, the experimentally determined values for ${}^4E_g({}^4D)$ and ${}^4A_{1g} + {}^4E_g({}^4G)$ are 391 nm (25063 cm^{-1}) and 465 nm (21505 cm^{-1}), respectively. The Racah parameters are $B = 581.5 \text{ cm}^{-1}$, $C = 3138 \text{ cm}^{-1}$, and $C/B = 5.4$. The primary Mn^{2+} luminescence band associated with the ${}^4T_1 \rightarrow {}^6A_1$ transition shifts towards the upper crystal field in the TS diagram as pressure rises. In other words, when the strength of the crystal field increases, the energy of this quartet ${}^4T_{1g}$ level gradually decreases. The energy of the main luminescence band decreases linearly with increasing pressure, as shown in Figure 6.8 (c). However, the zinc blende to rock salt phase transition near 16.5 GPa completely quenches the Mn^{2+} luminescence band before the TS diagram's crossing point between the quartet ${}^4T_{1g}$ level and the doublet ${}^2T_2$ level. Nevertheless, the excitation spectra do not show the strongly spin-forbidden transitions to the ${}^2T_2$ level. The crossing between the radiative ${}^4T_{1g}$ level and the non-radiative ${}^2T_2$ level was indicative of earlier pressure-induced quenching of Mn^{2+} luminescence belonging to the same d^5 system [104]. Another pressure-induced analysis of a Fe^{3+} doped oxide sample from the same d^5 class of system reveals a phase transition-induced luminescence quenching at about 14 GPa [105]. The overall decay times of the Mn^{2+} ions in ZnS are weakly affected by the increase in the strength of the crystal field, even though the ${}^4T_1 \rightarrow {}^6A_1$ luminescence

band is quenched (due to the previously mentioned phase transition and a decrease in the distance between the $^4T_{1g}$ level and the non-radiative $^2T_2$ level with the increase of pressure).

In summary, ZnS nanophosphor doped with 2% Mn^{2+} underwent a detailed pressure-dependent luminescence investigation. The bright Mn^{2+} luminescence observed at ambient pressure shifted from the visible orange to the near-infrared spectral region with increasing pressure, as determined by high-pressure luminescence analysis using a DAC. Furthermore, a reversible phase transition from zinc blende to rock salt structure near 16.4 GPa caused the Mn^{2+} luminescence become fully quenched. In contrast to the irreversible phase transition of ZnS: Mn^{2+} phosphor with a wurtzite structure, the sample maintained its original intense orange light upon the full release of pressure [98,106]. The millisecond decay times further confirm the perfect integration of Mn^{2+} ions inside the host lattice, and demonstrate that the pressure affects the multi-exponential Mn^{2+} decays.

6.5. Mn^{2+} luminescence in GaN

Gallium nitride (GaN) is a popular group III/V direct-bandgap semiconductor with a wide band gap ($E_g = 3.4$ eV at room temperature [107]) and remarkable electronic and optical properties. It has attracted considerable interest for its existing and potential applications in photonics, optoelectronics, electronics, and possibly quantum technologies [108,109]. GaN is a very stable, hard material with a wurtzite crystal structure. Doping GaN with TM ions - like Mn, Fe, Co, Ni, Cu, etc., allows for obtaining a semi-insulating bulk GaN [110]. The electrical and optical properties of some of these TM metals in GaN at ambient conditions are well studied and reported earlier [111–113]. TM elements like manganese doped to GaN substitute gallium in the crystal lattice, and show a stable nature under high-pressure [114]. The pressure studies of blue and yellow luminescence bands of undoped GaN have been reported in several papers [115–117]. The pressure-dependent luminescence studies at gigapascal (GPa) pressure range are ideal for investigating the pressure-dependent optical properties of the manganese ion. Therefore, the current work focused on the Mn^{2+} luminescence of intentionally added Mn dopants present in the sample. For that, we chose an ammono thermally grown GaN crystal doped with Mn ions, and examined the Mn^{2+} luminescence properties in GaN under high-pressure and low-temperature conditions.

As has been mentioned in the Chapter 4.8.5 SIMS is one of the tools used to determine the level of various impurity doping in GaN crystals. The measurements with SIMS shown in Figure 6.10 (a) highlight the presence of a very high Mn dopant concentration of more than 10^{19} at/cm³ in ammonothermal GaN compared to the other important elements. This demonstrates the relevant quality of the GaN:Mn film using ammonothermal method selected for luminescence studies. Ammonothermally grown crystal shows an overall much lower impurity level (limited to a negligible level), particularly as concerns unintentional Fe and Cr impurities. In ammonothermal GaN, Mn ions usually make complexes with Mn during the time of crystal growth [118,119]. The room-temperature absorption spectrum of ammonothermal GaN: Mn is shown in Figure 6.10 (b). A small shoulder band at 1.5 eV, and additional absorption between 2 and 3.5 eV is present along with the fundamental absorption edge of the GaN substrate. Most probably, this small shoulder peak at 1.5 eV is related to the $^5(D) \rightarrow ^5T_2(D)$ intraband transition of Mn^{3+} [120–122]. When Mn ions are incorporated into GaN, they induce some extra charge states in between the valence band and conduction band, and this intraband transition, related to d-d transition, absorbs the Vis-NIR light; the carrier lifetime of this shoulder band was reported earlier at around 1.7 ns [123]. Additionally, a broad absorption band is observed around 3.0 eV, which is not present in the absorption spectra of undoped GaN. According to previous publications, the broadband at 3.0 eV is likely due to the transition from the valence bands to the first excited state of the Mn^{2+} acceptor [121].

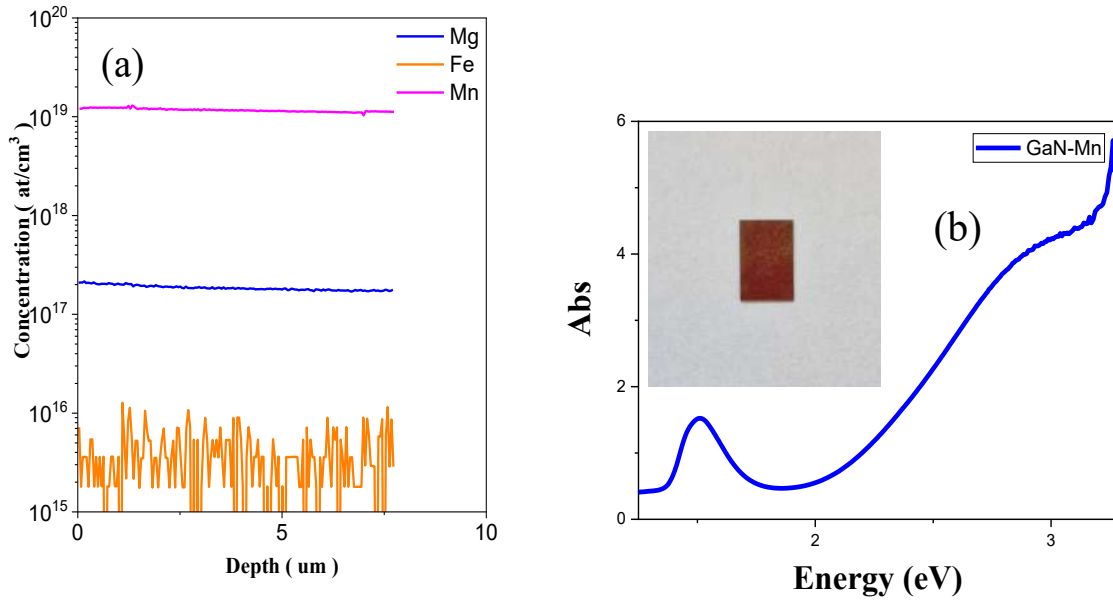


Figure 6.10 (a) SIMS profiles and (b) room temperature absorption spectra of ammonothermal GaN:Mn sample (inset: image of the crystal used for this study).

The low-temperature luminescence spectrum of ammonothermal GaN:Mn is shown in Figure 6.11(a). It exhibits the blue emission of GaN in the visible region and other defect-related emissions in the near-UV region. The excitation spectrum from the main blue emission band is shown in Figure 6.11(b). However, the origin of the sharp peaks in the violet-near-UV region is unclear, whether they are due to defects or to the UV memory effect observed in GaN crystals under non-laser (Xenon lamp) excitation. A weakly intense, slight broadening is also observed around the yellow region (near 600 nm), and no other luminescence peak is observed up to 800 nm. Moreover, it is important to note that we didn't find any impurity-related luminescence peaks in the ammonothermal GaN, which is particularly important in the case of iron (Fe^{3+}) related impurity emission usually associated with Mn ions.

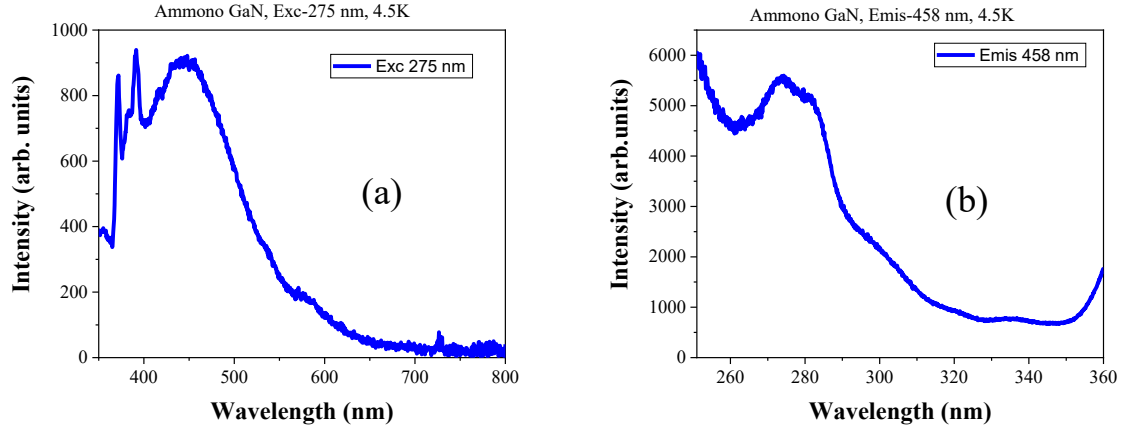


Figure 6.11. (a) Low-temperature (a) emission and (b) excitation spectra of ammonothermal GaN:Mn at ambient pressure.

At ambient conditions, the observation of the majority of the Mn-doped GaN shows Mn^{3+} luminescence rather than Mn^{2+} luminescence compared to the aluminium nitride AlN [124]. This is because GaN has a narrower bandgap than AlN. Due to the wider bandgap of AlN around 6.03 eV at room temperature [125], Mn^{2+} energy levels are well within the range of the bandgap; however, in the case of GaN (with the bandgap around 3.42 eV at room temperature [107]), this is not the case. So, the most practical thing to observe Mn^{2+} luminescence in GaN is to alter the bandgap of the material with the high-pressure method. It is known that applying pressure to GaN causes an increase in its energy gap with the pressure coefficient equal to about 40 meV/GPa [126,127]. Therefore, the selected ammonothermal GaN crystal, with almost negligible iron impurity, was polished to 20 μm for the high-pressure measurement, and an alcohol (methanol-ethanol) mixture was used as the pressure-transmitting medium. Figure 6.12. (a) shows the high-pressure luminescence spectra of GaN:Mn sample grown via the ammonothermal method, excited with 300 nm line of a continuous laser. However, at ambient and low pressure, the sample only shows the typical band-to-band and defect-related UV-blue emission from the host material.

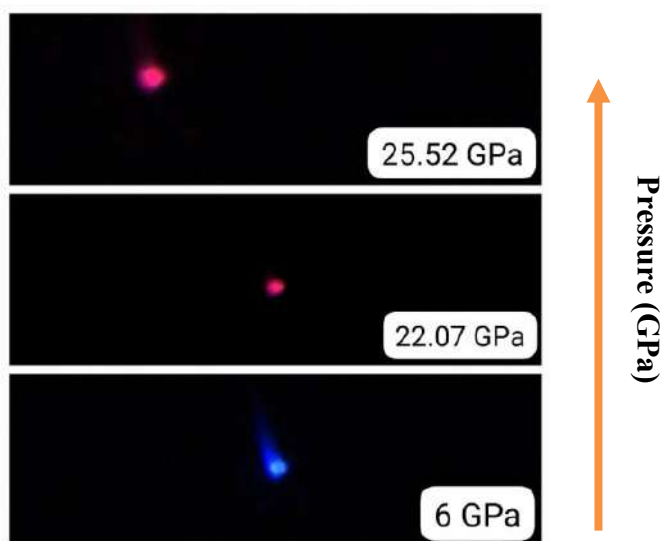
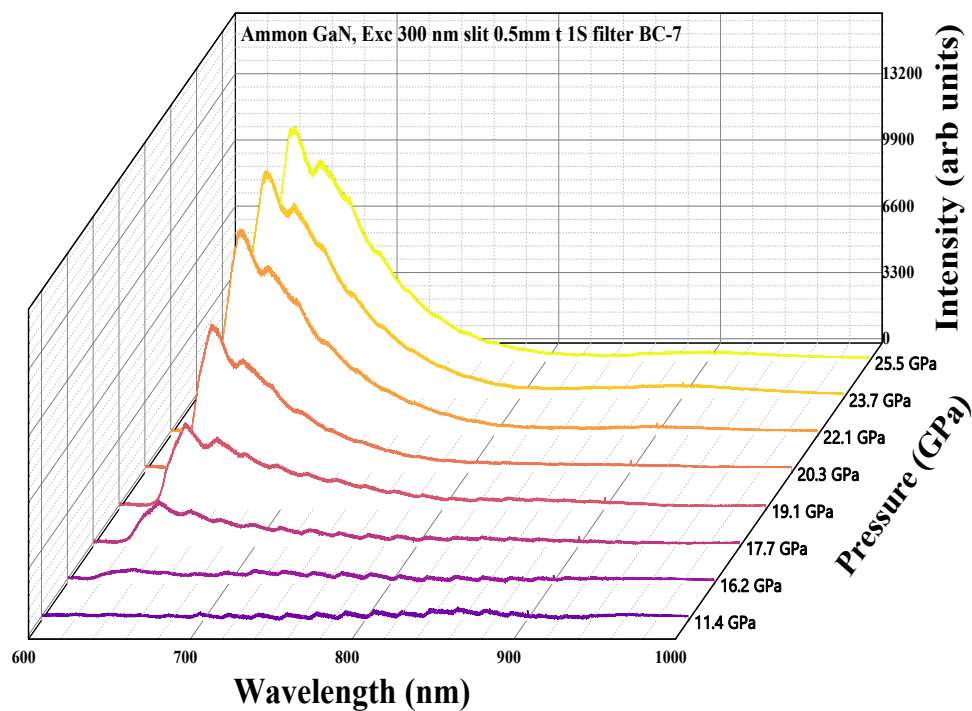


Figure 6.12.(a) Pressure-induced emission spectra of Mn^{2+} in the ammono GaN sample at low temperature, excited with 300 nm laser line. (b) The sample's luminescence shift under high pressure from blue to orange-red. (image captured from DAC using an optical microscope during the experiment).

After the gradual increase of pressure above >15 GPa, a small peak started appearing around 650 (1.9 eV) nm when excited with a 300 nm UV laser; which is related to the ${}^4T_1({}^4G) \rightarrow {}^6A_1({}^6S)$ transition of the Mn^{2+} ion. This is in the higher energy range than the Mn^{3+} absorption and emission peaks observed earlier near 1.41 eV during GaN:Mn measurements at ambient pressure [128]. Figure 6.12.(a) shows that as the pressure increases above 15 GPa, the intensity of the Mn^{2+} luminescence band gradually increases and the peak shows minor redshift with the increase of pressure compared to the pressure-dependent luminescence spectra of Mn^{2+} in some other wurtzite materials; however, most of these materials are highly compressible and reveal luminescence quenching due to a lower pressure induced wurtzite to rock salt phase transition point compared to the GaN [84]. The pressure evolution of the shape of the newly induced luminescence band is identical to the low-temperature luminescence band of Mn^{2+} in AlN material observed at ambient pressure; however, the energy of the emission peak maximum is slightly lower compared to the 2 eV (620 nm) of AlN: Mn^{2+} [80], and similar to the energy of the Mn^{2+} peak observed in the wurtzite-like LiGaO₂ material. Figure 6.12.(b) shows a photograph of luminescence observed from the DAC at various pressures through the microscope; at ambient pressure, the sample exhibits defect-related blue emission upon 300 nm excitation. As the pressure increased, the luminescence gradually shifted from blue to orange-red colour as shown in Figure 6.12.(b). The intensity of GaN host emission (blue) decreases with an increase in Mn^{2+} peak intensity, along with a rise in pressure. Additionally, the Mn^{2+} luminescence band disappears upon pressure release, returning to the blue colour of host emission. This indicates that the pressure-induced generation of Mn^{2+} luminescence in ammono GaN is reversible.

For comparison, the high-pressure luminescence studies on the AlN: Mn^{2+} sample reported by Lazarowska et al. are presented in Figure 6.13 [80]. These studies were conducted using a Merrill-Bassett type DAC with polydimethylsiloxane (PDMS) oil as the pressure-transmitting medium, with pressure calibrated by monitoring shifts in the ruby luminescence. The AlN: Mn^{2+} powder has a hexagonal wurtzite crystal structure with space group P6₃mc (186), contains less than 1% secondary phase, and has high structural purity. X-ray diffraction further confirmed that the AlN: Mn^{2+} structure remained stable after synthesis and under applied pressure, with no degradation or phase transitions observed under high pressure. High-pressure photoluminescence

spectra recorded at room temperature reveal that the broadband emission associated with Mn^{2+} shifts linearly towards lower energy as pressure increases.

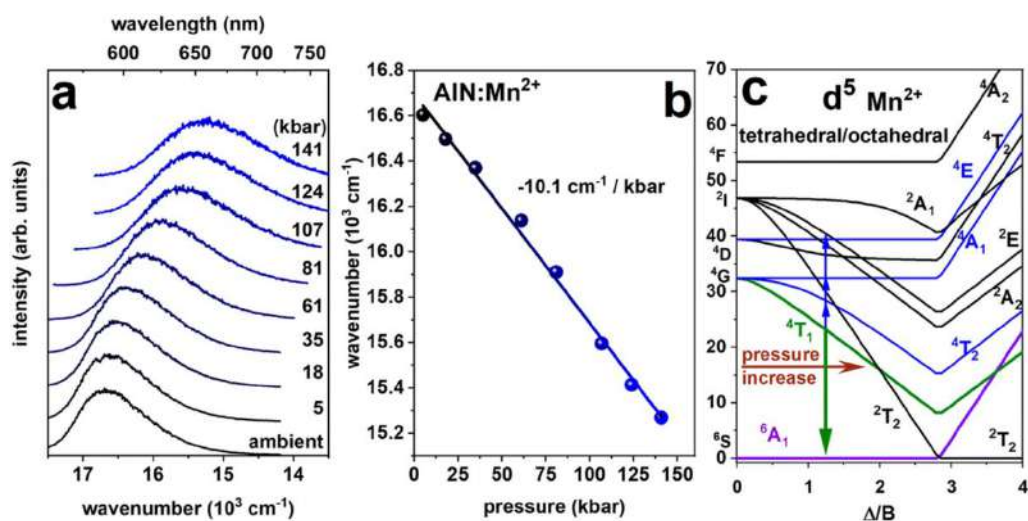


Figure 6.13. (a) Mn^{2+} emission in AlN as a function of pressure measured at 293 K, excited with a 290 nm pulse laser source. (b) Mn^{2+} emission peak energy versus pressure graph. (c) Tanabe–Sugano diagram for tetrahedrally/octahedrally coordinated Mn^{2+} . Reprinted with permission from *Dual role of oxygen-related defects in the luminescence kinetics of AlN:Mn²⁺*, Dalton Transactions, DOI:10.1039/D2DT02171D. © Royal Society of Chemistry 2022 [80].

The position of the emission maximum was plotted against pressure, demonstrating that the AlN:Mn²⁺ emission peak decreases at a rate of -10.1 cm⁻¹/kbar, consistent with values ranging from -11 to -9.6 cm⁻¹/kbar, attributed to crystal compression. This compression enhances the crystal field (Δ), resulting in a decrease in the energy of the lowest excited state ($^4\text{T}_1$) of Mn^{2+} , as illustrated by the Tanabe-Sugano diagram within the crystal field approximation (see Figure 6.13 (b)&(c)). The TS diagram was used to analyse the energetic structure under pressure, emphasising the Coulomb and exchange interactions of 3d electrons and the evolution of the crystal field strength (10Dq). Spectroscopic analysis allowed for the calculation of Racah parameters as $B = 655 \text{ cm}^{-1}$, $C = 2793 \text{ cm}^{-1}$, and $10Dq = 7043 \text{ cm}^{-1}$, compared to the free-ion Racah parameters $B_0 = 860 \text{ cm}^{-1}$ and $C_0 = 3850 \text{ cm}^{-1}$ for Mn^{2+} [80]. Overall, the high-pressure optical response demonstrates that AlN:Mn²⁺ maintains exceptional structural stability while displaying a pressure-induced red shift in Mn^{2+} photoluminescence. This shift is attributed to an increase in the crystal-field strength due to lattice compression, which modifies the energy levels of the Mn^{2+} ion, as

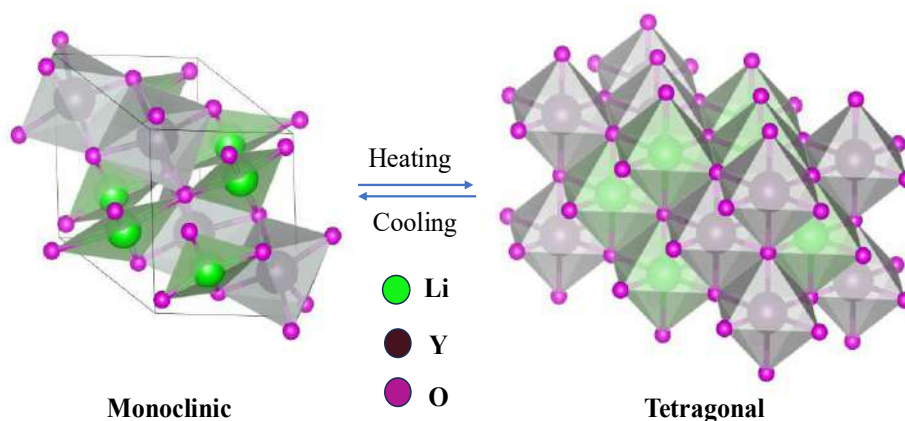
interpreted through theoretical models such as the Tanabe-Sugano diagram and Racah parameter calculations.

Moreover, the decrease in luminescence intensity in AlN:Mn is possibly due to the wurtzite to a cubic rock salt structure with space group $Fm\bar{3}m$ at pressure above 15 GPa. This first-order phase transition ranges from 15 GPa to 21 GPa according to various literature sources [129–131]. This phase transition is completely irreversible, as observed in the case of wurtzite ZnS. After the pressure is released, the AlN remains in the cubic rock salt phase [131,132].

6.6. Conclusion

A high-pressure investigation of selected manganese-doped materials was conducted, with particular emphasis on the luminescence of the Mn^{2+} charge state under pressure. The chosen materials include LiGaO₂, ZnS, and GaN, all of which are well-connected and display unique properties when doped with Mn. For these purposes, a Mn-doped LiGaO₂ material with various concentrations was successfully synthesised in-house using a vacuum-assisted method. This method had not been attempted previously with this material. Highly luminescent phosphor samples emit bright orange-red luminescence with increasing Mn concentration. Various optical, analytical, and high-pressure measurements were done. It is shown that pressure-induced luminescence quenching occurs at approximately 15 GPa in the LiGaO₂:Mn phosphor at room temperature. Similar quenching was also observed for Mn-doped zinc-blende ZnS materials at approximately 15 GPa, caused by a pressure-induced phase transition from the wurtzite to the cubic rock salt structure. Furthermore, ZnS in both zinc blende and wurtzite phases exhibits this phase transition within a comparable pressure range [133]. However, in the case of Mn-doped GaN, Mn^{2+} luminescence was observed only above 15 GPa, due to pressure-induced widening of the GaN band gap, unrelated to any pressure-induced phase transition, as previous high-pressure studies indicate that GaN remains stable up to 40 GPa.

7. LiYO₂: Eu³⁺, Gd³⁺ Phosphor Under High Pressure



7.1. Introduction

The ternary lithium metal oxides (LMO₂) made with lanthanide ions like M = Eu, Gd, Tb form γ polymorph, M = Dy, Ho, Y form β polymorph, and M = Er, Tm, Yb form α polymorph of the sample [134]. The formation of each polymorph varies with an increase in the ionic radius of the element. One of the LMO₂, LiYO₂, has complex structural, optical, and electrical characteristics essential for various technological uses. According to thermometry studies reported by Marciniak et al., the LiYO₂ sample has a temperature-dependent phase transition from β polymorph (monoclinic ($P2_1/c$)) to the α -LiYO₂ (tetragonal phase ($I4_1/amd$)) near room temperature (288 K) [135]. This transition point varies slightly with various physical properties, such as the sample's particle size, the dopant ion's ionic radius, etc.

The comprehensive temperature and high-pressure-dependent study of doped and undoped LiYO₂ host material could result in improving lithium-ion battery technology, luminescence thermometry, temperature sensors, and as an additional phosphor material for commercial phosphors based on lanthanide-doped Y₂O₃ with a monoclinic structure, since it is usually

produced at very high pressures [136]. Also, Eu^{3+} doped LiYO_2 produces better results than commercial YVO_4 phosphor under suitable excitation [8]. Furthermore, LiYO_2 material plays a crucial role in the nuclear industry as it forms as a by-product when Y_2O_3 -based ceramic anti-thermal coatings on the reactor surface react with liquid lithium in the lithium-cooled nuclear reactors. Moreover, LiYO_2 material has been widely used in carbon dioxide capturing technologies since it has better CO_2 capturing efficiency than the prominent NaYO_2 material [137].

Luminescence and powder XRD investigations on LiYO_2 samples at ambient and high pressures are crucial to a better understanding of how these materials behave structurally and optically under extreme conditions. The samples used for the high-pressure luminescence and X-ray diffraction studies are undoped and doped LiYO_2 with dual RE ions (Eu^{3+} and Gd^{3+}). The Eu^{3+} and Gd^{3+} codoped samples usually exhibit strong and efficient luminescence at varied temperatures, high colour purity, and brightness due to the energy transfer from Gd^{3+} to Eu^{3+} , making it suitable for high-resolution displays and advanced lighting solutions, potentially leading to more energy-efficient and high-performance optical devices, and thermochromic materials [138].

7.2. Sample preparation

The undoped and doped LiYO_2 with 1% europium (Eu^{3+}) and 0.5% gadolinium (Gd^{3+}) samples were synthesised by the modified Pechini method described in the paper of Marciniak et al. [135]. High-purity Li_2CO_3 , Y_2O_3 , Eu_2O_3 , Gd_2O_3 , $\text{C}_6\text{H}_8\text{O}_7$, $\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$, (PEG-200, $n = 200$, Alfa Aesar) were used as the precursor materials. Oxides of lanthanides were first dissolved in HNO_3 solution and subsequently recrystallised three times to remove residual acid. A fourfold stoichiometric excess of lithium carbonate (Li_2CO_3) and anhydrous citric acid ($\text{C}_6\text{H}_8\text{O}_7$) was then added to the aqueous solution of metal nitrates. After complete dissolution, PEG-200 was introduced, and the solution was stirred at 60 °C for 3 h. The resulting solution was dried at 90 °C for three days until a resin was formed. Finally, the resin was calcined in porcelain crucibles at 1000 °C for 6 h in air. An undoped LiYO_2 sample was also prepared for the comparisons.

7.3. Experimental techniques

The X-ray diffraction experiment at ambient pressure was performed using a BRUKER D2 PHASER with $\text{Cu-K}\alpha$ radiation, operating at 30 kV and 10 mA, as described in chapter 4.2. A

standard Differential Scanning Calorimetry (DSC) measurement (temperature range: -80 to 550 °C) of both samples was performed on a DSC 3 instrument from Mettler Toledo in a nitrogen atmosphere using an aluminium pan as the sample holder. The ambient and low-temperature luminescence and decay characteristics were measured using a Horiba Fluorolog-3 modular spectrometer equipped with a 450 W Xenon lamp as the excitation source. A Janis continuous flow liquid helium cryostat was used for low-temperature measurements. High-pressure luminescence studies were conducted using a DAC from Almax easyLab, with a diamond culet size of 0.45 μm . A methanol-ethanol mixture with a 4:1 ratio was used as the pressure-transmitting medium, and ruby balls served as the pressure gauge. The sample was excited with a pulsed laser excitation from an NT342/3 series tuneable OPO instrument from EKSPLA.

High-pressure X-ray diffraction (HP XRD) experiments on undoped LiYO_2 were carried out in a Mao-Bell type DAC at the synchrotron facility BL-11, Indus-2, RRCAT, Indore, India, using a stainless-steel gasket, along with a pressure calibrant –Ag and silicone oil as a pressure-transmitting medium. Debye-Scherrer patterns were collected on a MAR-345 image plate detector. Analysis of the XRD patterns and Le-Bail refinement were carried out using the FullProf suite [73].

7.4. Results

7.4.1. Ambient pressure XRD and DSC

The crystal structure of undoped LiYO_2 and $\text{LiYO}_2\text{:Eu}^{3+}$, Gd^{3+} samples was measured using the standard powder XRD method. The results are shown in the Figure 7.1(a) & (b). The phase composition was estimated using semi-quantitative phase analysis based on comparing reflection intensities assigned to identified phases and I/I_{cor} parameters from PDF standards cards for these phases. The preliminary powder XRD studies on both undoped LiYO_2 and doped $\text{LiYO}_2\text{:Eu}^{3+}$, Gd^{3+} samples at ambient temperature reveal that the undoped powder sample contains around 94.8 % tetragonal phase (PDF 04-008-9825) and around 3.2 % monoclinic phase (PDF 04-010-0630). However, the doped sample is in a mixed state rather than a single phase; the powder consists of crystalline particles of both monoclinic ($P2_1/c$) β phase of around 34.6% and tetragonal ($I4_1/amd$) α phase of 56.4 % percent. The β phase has point symmetry of C_1 in the octahedral yttrium site, and the α phase has D_{2d} point symmetry for the same site [139].

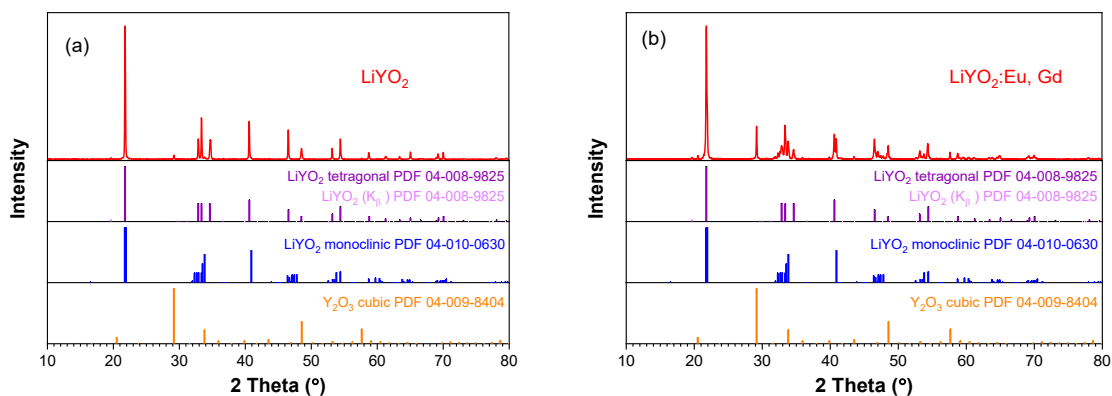


Figure 7.1. Detailed comparative phase analysis of the powder XRD spectra of (a) undoped LiYO_2 & (b) LiYO_2 doped with Eu and Gd.

The percentage of the tetragonal α phase in the doped sample is slightly higher than the percentage of the monoclinic β phase. Moreover, a minor percentage of the cubic Y_2O_3 phase (PDF 04-009-8404) with space group $I\bar{a}3$ was also observed in both samples; however, the undoped sample contains significantly less of this phase than the doped one. The percentage of Y_2O_3 in the undoped LiYO_2 is around 2 %, and in the doped sample, it is around 9 %. The Y_2O_3 percentage level mainly depends on the annealing time and the presence of carbon compounds in the sample. Table 7.1 shows the percentage of different phases observed by powder XRD in both undoped and doped LiYO_2 at room temperature and ambient pressure.

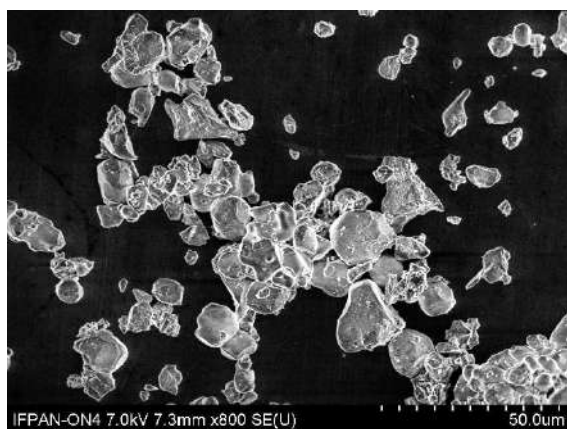
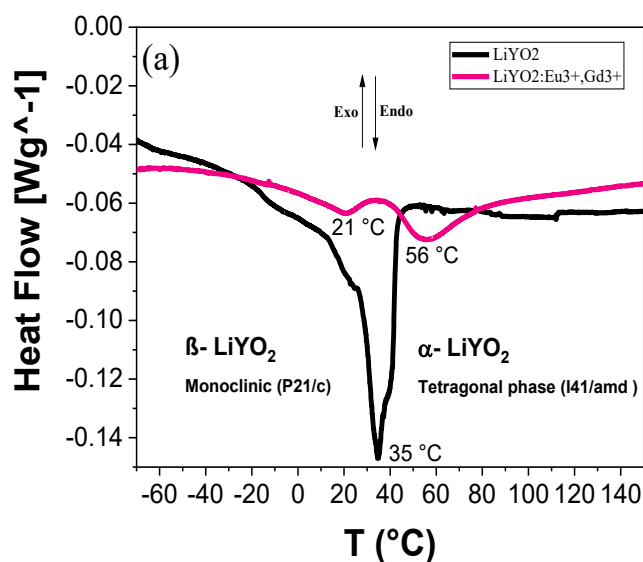
Table 7.1. Percentage of different phases observed with powder XRD in both undoped and doped LiYO_2 at room temperature and ambient pressure.

Sample	Tetragonal	Monoclinic	Cubic Y_2O_3
LiYO_2	94.8 %	3.2 %	2%
$\text{LiYO}_2\text{:Eu}^{3+}, \text{Gd}^{3+}$	56.4%	34.6%	9%

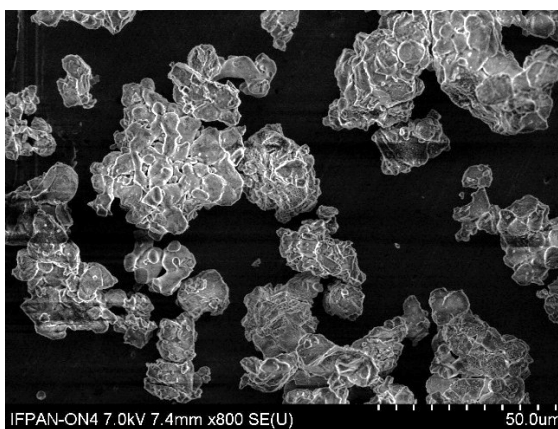
The DSC study of the doped sample was conducted over a wide range of temperatures and compared with the results obtained for undoped LiYO_2 sample. Figure 7.2 (a) shows the DSC curves of the materials in endo-up format on the Y-axis. The undoped LiYO_2 exhibits a sharp endothermic peak at 35 °C (308.15 K). For the 1% Eu^{3+} and 0.5% Gd^{3+} doped sample, two connected endothermic peaks are observed at 21 °C (294.15 K) and 56 °C (329.15 K). This indicates that the reversible phase transition from β to α polymorph in the undoped material occurs

at a faster rate than in the doped sample. This finding is consistent with the ambient-temperature XRD analysis, which showed a higher percentage of the tetragonal phase in the undoped sample. The presence of twin peaks in the doped sample is primarily associated with the sample's morphological nature; these phase transition peaks are broad, and the transition occurs more slowly than in the undoped sample. This is in good agreement with results reported for Gd^{3+} doped LiYO_2 , as the percentage of Gd^{3+} concentration increases in the LiYO_2 matrix, and the phase transition temperature also shifts from lower to higher temperatures [139]. The complete temperature-assisted phase transition occurs at a slightly higher temperature, which aligns with the powder XRD results, showing a mixed phase. The doped and undoped LiYO_2 also shows a phase-transition related negative thermal expansion behaviour, like a shrinkage in volume when moving from tetragonal, while an increase in temperature, and the addition of RE ions affects these properties significantly by the change in ion-ion distance [140].

Figures 7.2(b) and (c) show the SEM morphology of undoped and doped LiYO_2 samples. Both images show that the samples share nearly identical morphologies, despite being doped with the heavier ions of RE elements. They also illustrate that the nano-crystallites are agglomerated in irregular shapes with an average size of less than 20 μm .



(b)



(c)

Figure 7.2. (a) DSC curves, (b) SEM image of undoped and (c) doped samples [a temperature-induced reversible structural phase-transition from monoclinic to tetragonal phase with temperature is shown in the **Chapter 7** cover image].

7.4.2. High-pressure XRD

Figure 7.3 shows the high-pressure HPXRD data of an undoped LiYO_2 sample at room temperature. The pressure was measured up to 18.5 GPa. Ambient pressure phase of LiYO_2 is identified as tetragonal with space group $I4_1/amd$ (no. 141), where $a=b=4.439(3)$ Å, $c=10.339(7)$ Å, and the unit cell volume $V=203.74(31)$ Å³. This is in good agreement with ICDD

PDF No. 04-029-0215 and Ref. [141]. The pressure evolution of the XRD pattern presented in Figure 7.3 shows that new diffraction peaks (indicated by asterisks) appear at approximately 5.1 GPa, marking the onset of a structural transition. Upon further compression, the peak emerging near the tetragonal (*101*) reflection becomes comparatively more intense. Likewise, other new peaks also gain intensity, implying an increasing contribution of the high-pressure phase. Above 11.7 GPa, the tetragonal (004) peak disappears, signifying the complete disappearance of the ambient pressure phase.

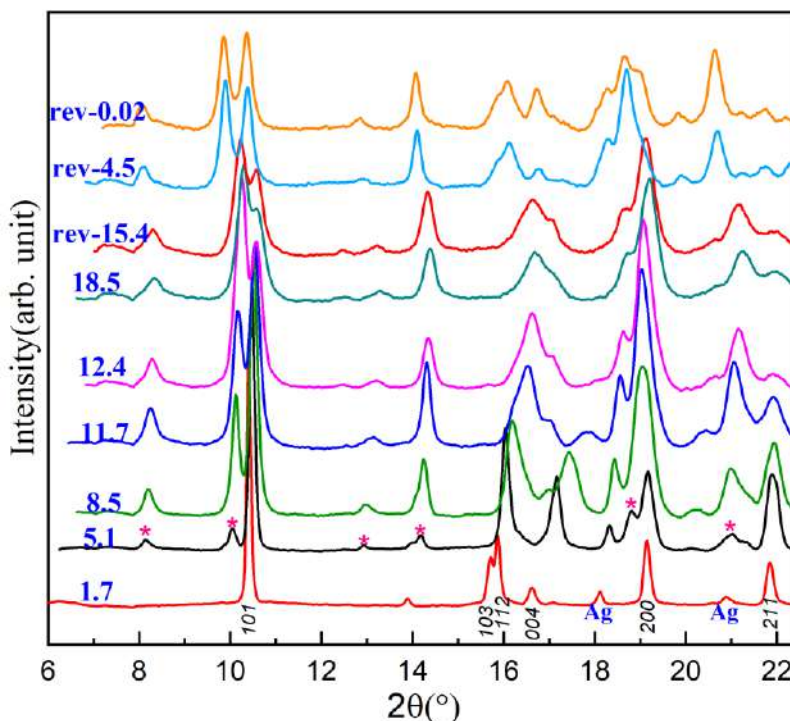


Figure 7.3. Selected high-pressure XRD data for undoped LiYO₂ (the blue-coloured numbers indicate the corresponding pressure values in GPa during increasing and decreasing pressure).

The pressure evolution of the lattice parameters, axial ratio (c/a), and unit cell volume of the tetragonal phase is shown in Figures 7.4 (a–c). The a -lattice parameter exhibits minimal compression, whereas the c -lattice parameter decreases steadily with increasing pressure. Near the transition pressure (≈ 5.1 GPa), the slope of the c/a curve changes, reflecting a modification in the unit cell geometry. The pressure–volume data were fitted to a second-order Birch–Murnaghan equation of state (BM2 EOS) [142], yielding a bulk modulus of 114(3) GPa. The newly formed high-pressure phase persists up to the highest pressure achieved in this study (18.4 GPa). It remains

stable upon decompression to ambient conditions, indicating that the structural transition in LiYO_2 is irreversible. To identify the high-pressure phase of LiYO_2 , the structural types of analogous LiRO_2 compounds ($R = \text{RE element}$) were reviewed [140]. As has been mentioned at the beginning of chapter 7.1, near room temperature the β -monoclinic structure transforms into the α -tetragonal phase, indicating that higher symmetry becomes favourable with thermal expansion [143]. This trend suggests that as the unit cell expands, the effective ionic radius appears smaller, favouring structures corresponding to smaller R . Conversely, under compression (i.e., at high pressure), the reduced cell volume favours structures associated with larger ionic radii, such as γ -orthorhombic or δ -monoclinic phases.

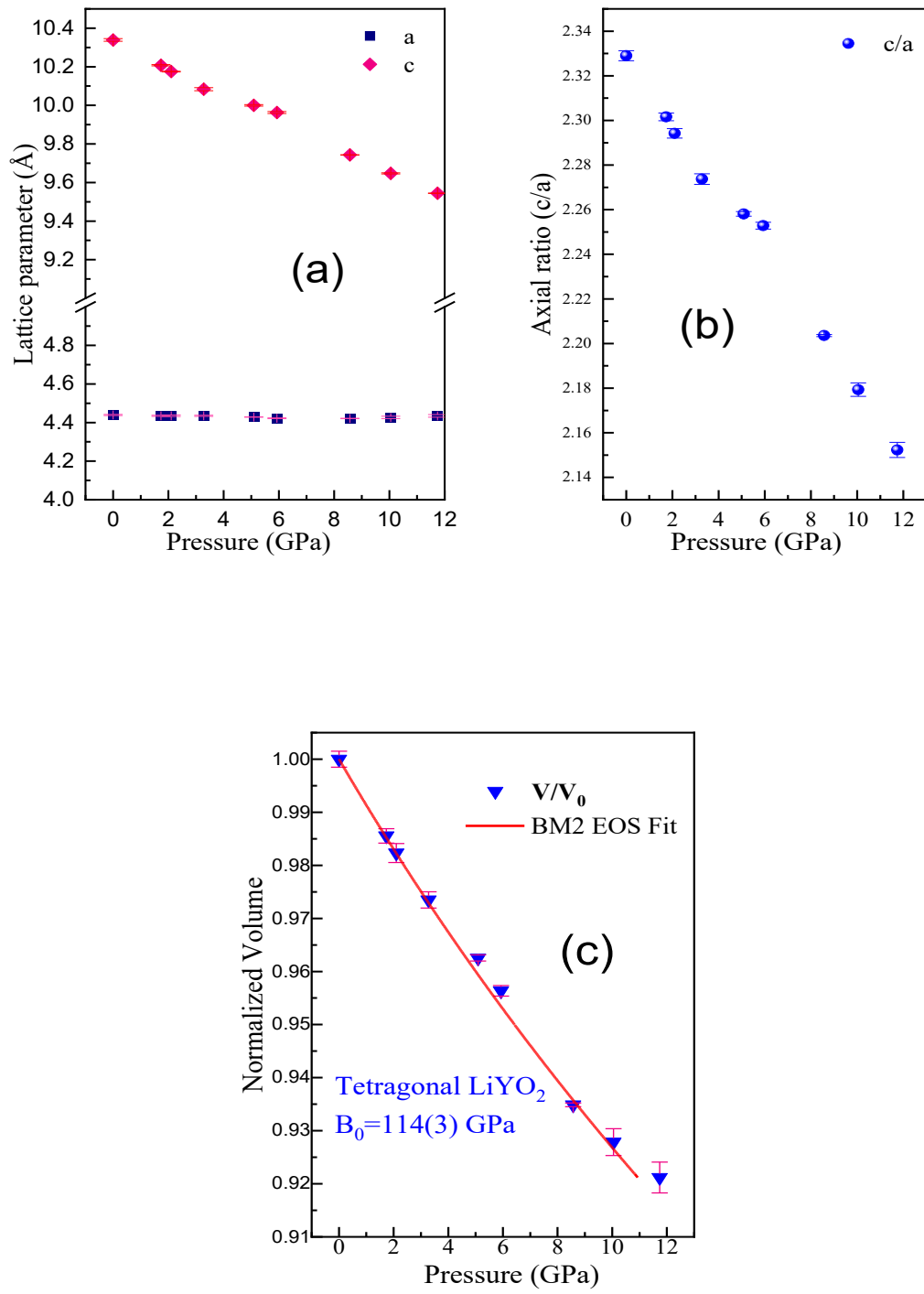


Figure 7.4: Pressure evolution of (a) lattice parameters a and c , (b) axial ratio, and (c) volume of the tetragonal phase unit cell.

7.4.3. Luminescence at ambient pressure

Figures 7.5 (a) and (b) depict the luminescence excitation and emission spectra of the undoped LiYO_2 sample at ambient temperature and pressure. The excitation spectra measured for the 405 nm emission show a broad main band centred around 332 nm and another band below 270 nm; however, the latter extends into the VUV region, which is below the detection limit of our spectrometer. When excited via the main band around 332 nm, the sample shows a broad emission band in the UV-blue region, peaked at 385 nm. Furthermore, no other prominent emission peak was observed in the visible region, except for this one.

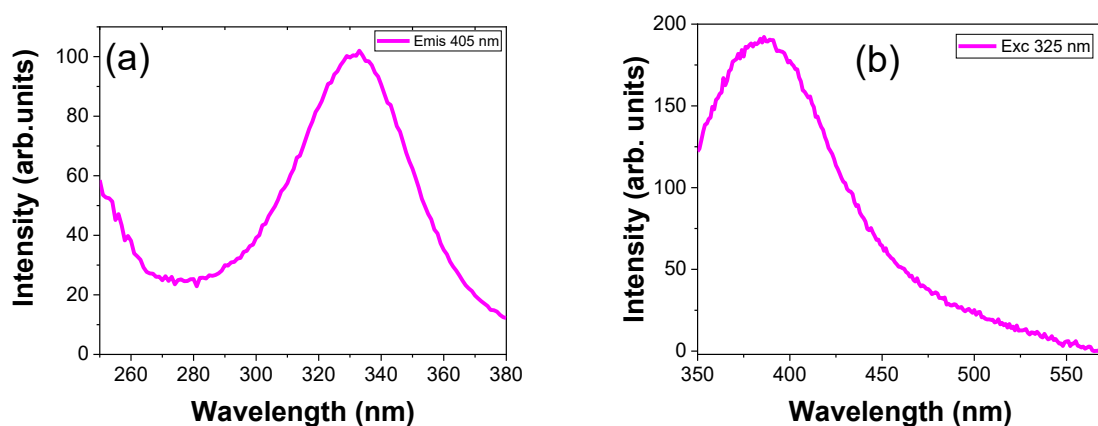


Figure 7.5. Photoluminescence excitation (a) and emission (b) spectra of the undoped LiYO_2 sample.

The luminescence excitation and emission spectra of $\text{LiYO}_2:\text{Eu}^{3+}$, Gd^{3+} sample at ambient temperature and pressure are shown in Figures 7.6 (a) & (b).

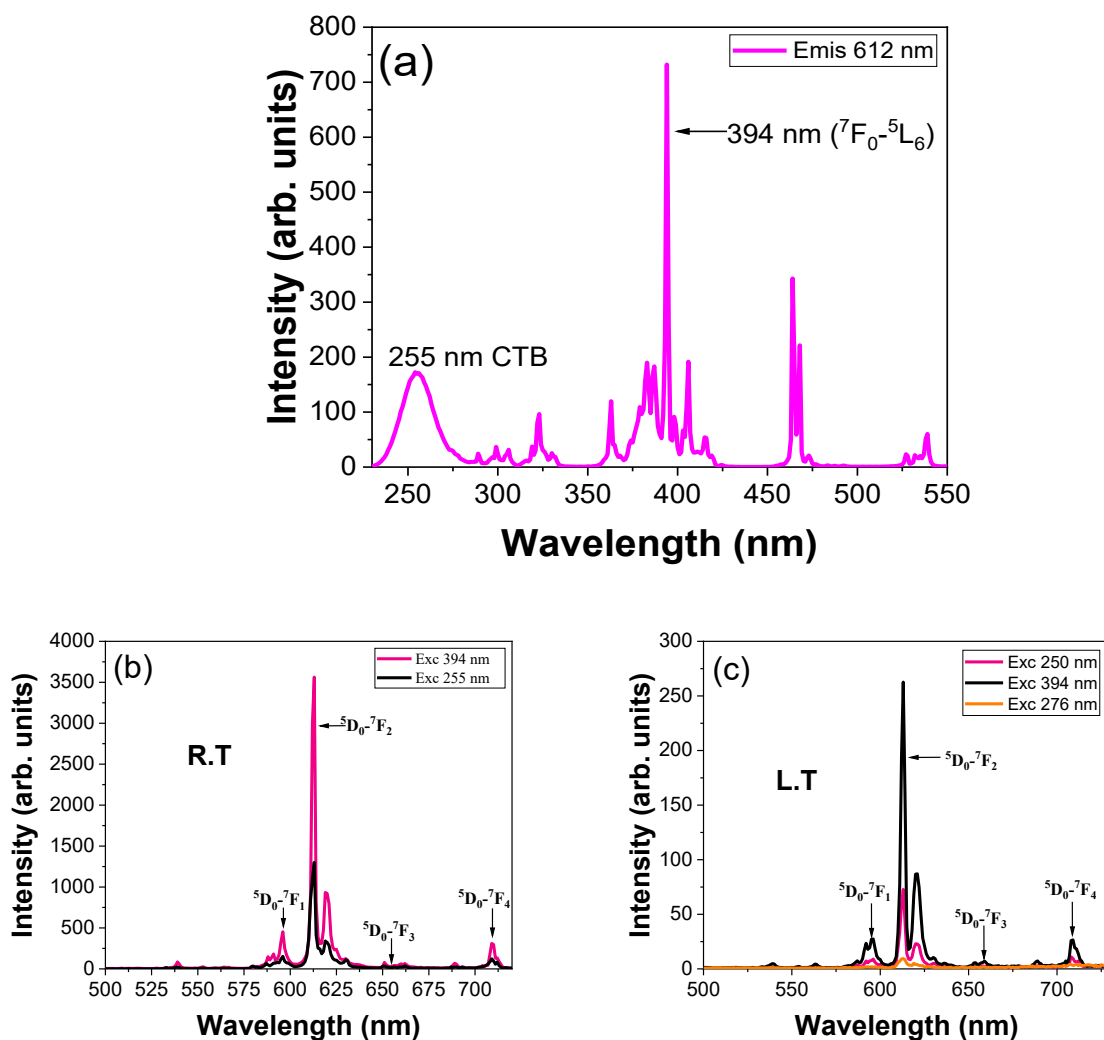


Figure 7.6. Photoluminescence (a) excitation and (b) emission spectra of Eu^{3+} ions in $\text{LiYO}_2:\text{Eu}^{3+}$, Gd^{3+} sample at ambient conditions. (c) Emission spectra at 4.5 K and various excitation wavelengths.

Figure 7.6 (c) shows the emission spectra at liquid helium temperature. At ambient temperature, the charge transfer band (CTB) intensity visible in the excitation spectrum (Figure 7.6 (a)) was weaker compared to the direct excitation peak of Eu^{3+} related to the ${}^7F_0 - {}^5L_6$ transition at 394 nm [144]. When excited from both the CTB and 394 nm direct excitation peaks, the Eu^{3+} emission spectra at 612 nm related to the ${}^5D_0 - {}^7F_1$ [8] are stronger at the low-temperature

monoclinic phase than at the room temperature mixed phase. Also, at low temperatures, this peak is slightly shifted to higher energies.

Figures 7.7 (a) & (b) show the Gd^{3+} co-dopant's luminescence excitation and emission spectra; however, the peaks are relatively weak compared to the Eu^{3+} peak. The excitation peak was centred around 275 nm, which is related to the 4f–4f intra-configurational transition between $^8S \rightarrow ^6I_1$ states of the Gd^{3+} ion, and the emission peak was centred around 314 nm, related to the $^6P_{7/2} \rightarrow ^8S_{7/2}$ transition of the Gd^{3+} ion.

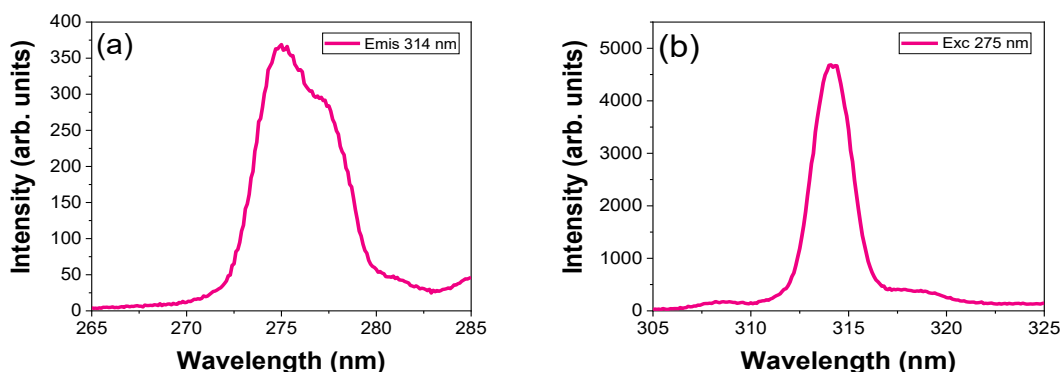


Figure 7.7. (a) Excitation and (b) emission spectra of Gd^{3+} ions in $LiYO_2:Eu^{3+},Gd^{3+}$ sample at ambient conditions.

After absorbing 275 nm UV excitation, the Gd^{3+} ion's $^8S_{7/2}$ ground state excites to the higher energy level $^6I_{7/2}$. [145]. Then, this excited $^6I_{7/2}$ state populates non-radiatively the $^6P_{7/2}$ state of the Gd^{3+} ions. Afterwards, part of the excitation is emitted as a result of the $^6P_{7/2} \rightarrow ^8S_{7/2}$ transition in the Gd^{3+} ion, and additionally, an energy transfer occurs from the $^6P_{7/2}$ of Gd^{3+} to the ^5D_J excited state of Eu^{3+} , leading to radiative emission between the $^5D_0$ and ^7F levels of Eu^{3+} , which results in bright visible red emission. However, energy transfer-related luminescence is relatively weak in the chosen matrix containing 0.5 % Gadolinium (Gd). The schematic energy level diagram of Gd^{3+} and Eu^{3+} ions is presented in Figure 7.8.

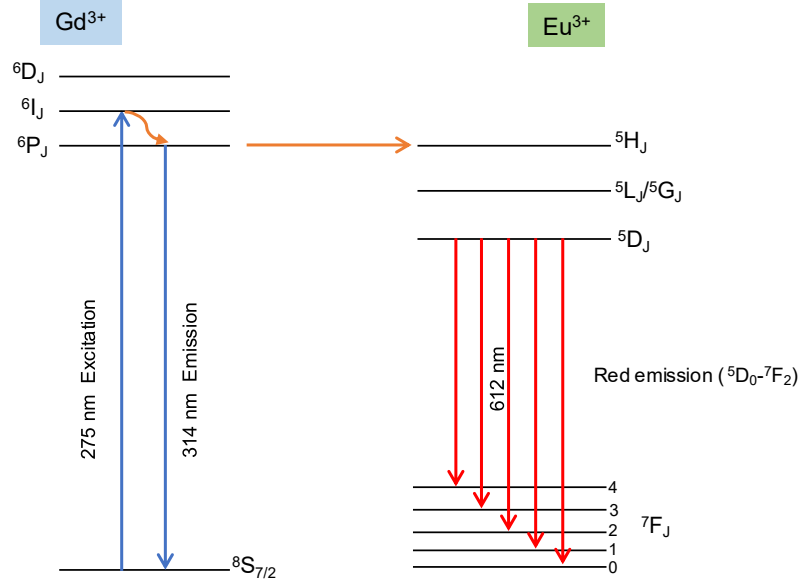


Figure 7.8. Energy transfer diagram from Gd^{3+} to Eu^{3+} with 275nm UV excitation.

7.4.4. Luminescence decay

The results of PL decay measurements of the ambient mixed phase and the monoclinic β phase of $\text{LiYO}_2: \text{Eu}^{3+}, \text{Gd}^{3+}$ phosphor is shown in Figure 7.9 (a) & (b). For the monoclinic phase, the PL decay was measured at liquid helium temperature (4.5 K). At this temperature, the sample stabilised to a single monoclinic phase without any distant influence of the trigonal phase. The PL decay of Eu^{3+} ions was recorded at the emission peak of 612 nm associated with the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition, and excited from both the charge transfer band at 250 nm and the direct excitation band at 394 nm. The decays were fitted with a single exponential equation, and the decay times at room temperature were equal to $\tau_1 = 0.990$ ms, and $\tau_1 = 1.00$ ms, and at low temperature $\tau_1 = 0.957$ ms and $\tau_1 = 0.962$ ms, respectively, for 250 nm and 394 nm excitations, which are close to 1 ms. The PL decay times are shorter than the reported decay time of Eu^{3+} ions in monoclinic Y_2O_3 , which was equal to about 2.3 ms [146]. To better understand the addition of the Gd^{3+} in the matrix and the effect of energy transfer between Gd^{3+} and Eu^{3+} , the decay measurements were also executed at the 275 nm excitation related to the $^8\text{S}_{7/2} \rightarrow ^6\text{I}_{7/2}$ transition and emission set at 314 nm peak related to the $^6\text{P}_{7/2} \rightarrow ^8\text{S}_{7/2}$ transition of Gd^{3+} and 612 nm of Eu^{3+} displayed in Figure 7.9 (c). Figure 7.9 (c) shows that the Gd^{3+} emission peak at 314 nm has a single exponential decay time of

1.9 ± 0.005 ms in the LiYO_2 matrix when codoped with Eu^{3+} ; however, when the emission peak is set at $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu^{3+} , the decay curve is fitted with a double-exponential equation

$$I_t = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + I_0 \quad (26)$$

The decay times determined in this way were $\tau_1 = 1.23 \pm 0.035$ ms, $\tau_2 = 0.58 \pm 0.025$ ms, respectively. The long Eu^{3+} decay time of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is due to energy transfer from Gd^{3+} to Eu^{3+} . Figure 7.9 (c) clearly demonstrates the double-exponential nature of the decay curve.

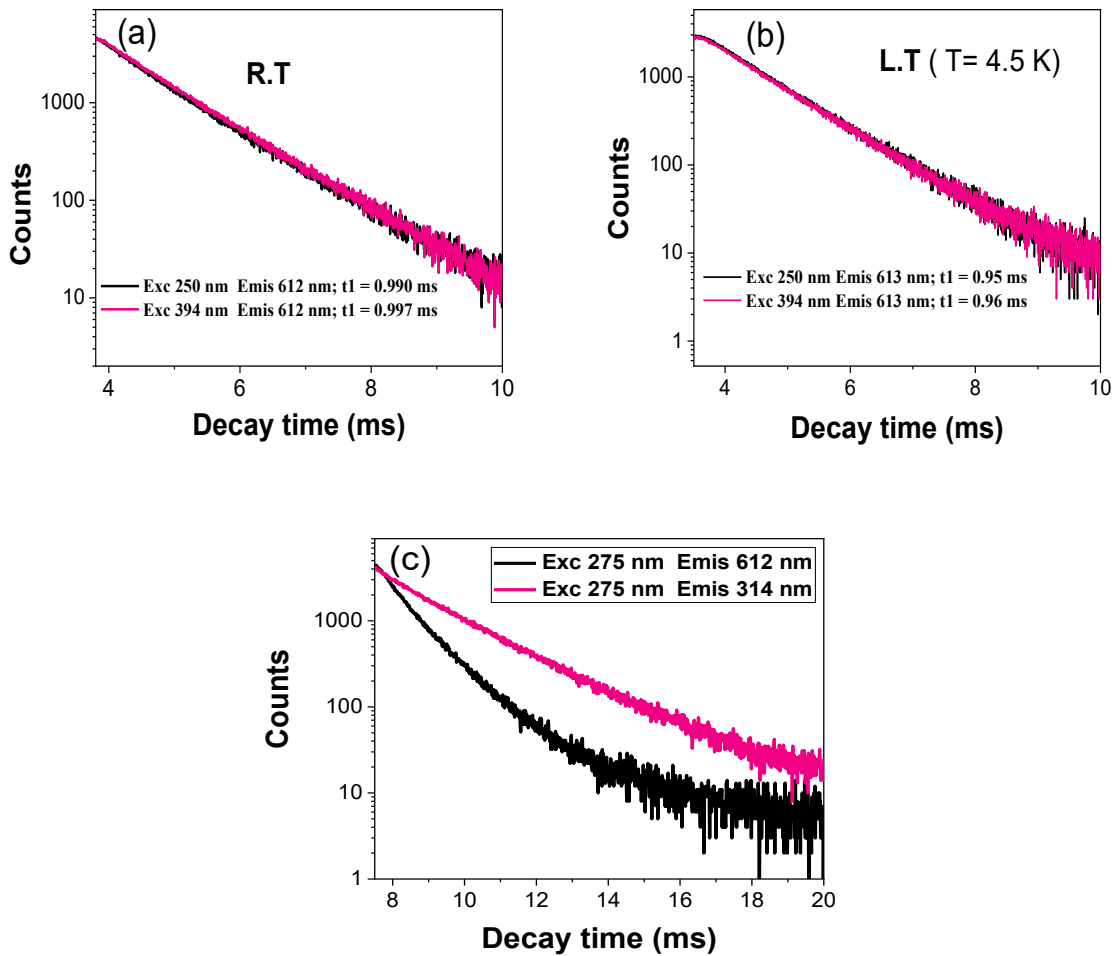


Figure 7.9. (a) Ambient and (b) low-temperature luminescence decay profiles of $\text{LiYO}_2:\text{Eu}^{3+}, \text{Gd}^{3+}$ phosphor. (c) Luminescence decays of Eu^{3+} emission (black line) and Gd^{3+} emission (pink line) excited through the Gd^{3+} excitation peak.

7.4.5. High-pressure luminescence

Figures 7.10 (a) and (b) show the high-pressure luminescence spectra of the $\text{LiYO}_2\text{:Eu}^{3+}, \text{Gd}^{3+}$ sample, measured at pressures ranging from 1 to 25 GPa at room temperature. The excitation wavelength of the OPO laser was fixed at 255 nm, i.e., in the charge transfer band. As the pressure increases, the intensity of the main Eu^{3+} peak at 613 nm (2.023 eV), related to the $^5\text{D}_0\text{-}^7\text{F}_2$ transition, initially exhibits a sudden change at a few pressure values (up to 5.8 GPa) and then gradually diminishes as pressure increases. Moreover, Figure 7.10 (c) indicates that the main $^5\text{D}_0\text{-}^7\text{F}_2$ peak shifts to lower energies with increasing pressure; however, this shift is relatively small. Figure 7.10 (d) shows an enlarged view of the same $^5\text{D}_0\text{-}^7\text{F}_2$ peak energy dependence with pressure. Figure 7.10 (a) also shows that, after exceeding 5.8 GPa, the main peak began to show anomalies in its shape, and around 9-10 GPa, a new peak started to appear alongside it. The same happened with the peak around 710 nm (1.746 eV). This hints at a possible pressure-induced phase transition above 5.8 GPa. These dual peaks shift to lower energies very slightly with further pressure increase. The other minor Eu^{3+} peaks related to $^5\text{D}_0\text{-}^7\text{F}_1$ and $^5\text{D}_0\text{-}^7\text{F}_4$ transitions also shift towards lower energies, similarly to the main peak shift shown in Figure 7.10 (c), although this shift is relatively weak. This is a typical pressure behaviour of f-f transitions in RE ions, because the f-shell is well screened from the crystal lattice, so the f-f transitions are not as sensitive to crystal field changes as d-d transitions in TM ions.

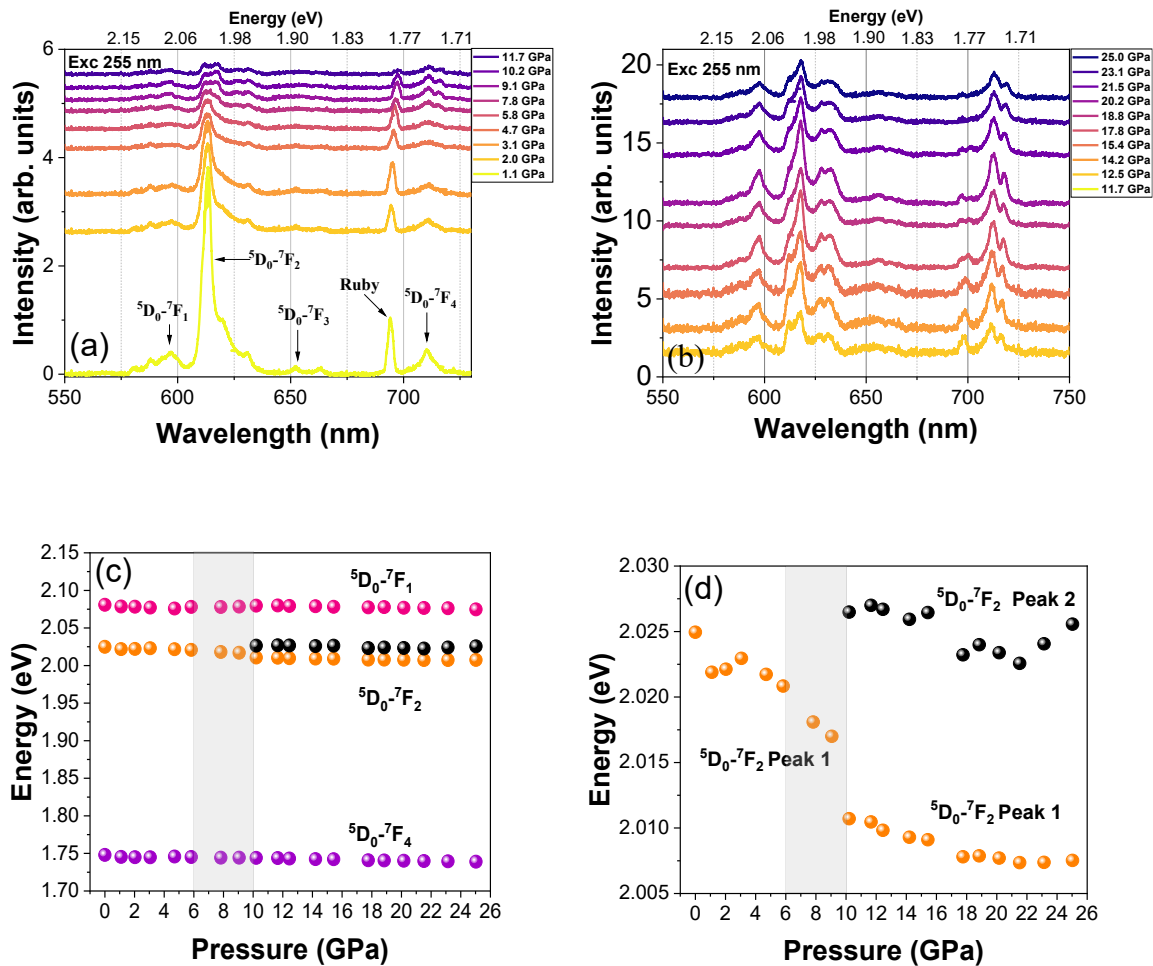


Figure 7.10. High-pressure luminescence spectra of LiYO₂: Eu³⁺, Gd³⁺ sample at room temperature, and at (a) 1-11 GPa and (b) 11-25 GPa, respectively. (c) Energy versus pressure of ⁵D to ⁷F_J transitions of Eu³⁺ emission, and (d) enlarged image of ⁵D₀-⁷F₁ transition alone.

The newly appearing peak becomes significantly more resolved than the twin peak above 10 GPa, and up to 25 GPa, no further significant changes in the emission spectrum related to phase transitions are observed. The pressure-induced changes above 5.8 GPa are likely associated with the pressure-assisted phase transition of the predominant tetragonal phase in the sample. Additionally, there is a possibility of a minor increase in the percentage of the tetragonal phase in the sample mounted inside the DAC compared to ambient conditions due to heating from the pulsed laser excitation used for the measurement. The high-pressure luminescence study of Eu³⁺ doped cubic Y₂O₃ phosphor showed a similar trend in intensity decrease and phase transition.

However, in the cubic Y_2O_3 phosphor, the phase transition from cubic to monoclinic occurs near 11 GPa [136].

7.5. Summary and conclusion

Both temperature and pressure-assisted phase transitions in doped and undoped LiYO_2 samples were investigated. Both samples exhibit a temperature-assisted reversible phase transition from the β to the α polymorph of LiYO_2 near room temperature; however, doping with RE elements significantly influences the position of this transition point. HP-XRD results of the undoped sample indicate that the predominant tetragonal phase undergoes a pressure-assisted phase transition above 5.1 GPa, completing near 11.7 GPa. At 14 GPa, the sample displays an entirely new phase, likely either the γ -orthorhombic or δ -monoclinic phase, which is currently under investigation. Further identification and validation of this new phase are required. The pressure-assisted luminescence study reveals that the $\text{LiYO}_2:\text{Eu}^{3+}$, Gd^{3+} sample also indicates this phase transition above 6 GPa, thereby confirming the presence of a novel high-pressure phase. Above 10 GPa, the $^5\text{D}_0$ - $^7\text{F}_2$ transition peak of Eu^{3+} does not exhibit notable changes. For the low-temperature (LT) monoclinic phase, both HP-XRD and high-pressure luminescence should be performed at lower temperatures, representing an area for future research.

8. Summary and Future Work

The present thesis focuses mainly on the luminescence studies of two lithium metal oxides (LMO), specifically LiGaO_2 and LiYO_2 , doped with TM and RE under high pressure and varying temperatures. Many of the experimental studies on these materials, described in Chapters 5, 6, and 7, are comparatively novel and promising for various applications. Most of the experiments were conducted under extreme conditions, including varying temperatures in the range of 4-300 K and a pressure range of up to 25 GPa. The high-pressure measurement results described in each chapter are repeated multiple times, verified, and supported by synchrotron measurements.

Chapter 5 primarily focused on the Fe^{3+} -doped stable β - LiGaO_2 polymorph of LiGaO_2 , which exhibits unique luminescence characteristics when doped with Fe^{3+} ions. The study included the structural and optical behaviour of this compound under varying temperatures and pressures, focusing on its near-infrared luminescence. The phosphor sample structure and morphology were analysed using XRD and SEM analysis. The Fe^{3+} ions effectively replaced the Ga^{3+} ions in LiGaO_2 , resulting in a remarkable emission at 746 nm associated with the ${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$ transition. At low temperatures, it also showed a sharp zero-phonon line at 709 nm associated with the same transition. The phosphor exhibited a quantum efficiency of 28% at ambient conditions. Temperature dependence studies indicated that as the temperature decreased down to the helium temperature, the luminescence intensity increased. Additionally, calculations indicated a relatively weak electron-phonon coupling in this sample, with a Huang-Rhys factor $S = 3.36$. The pressure-dependent luminescence studies showed that around 3 GPa the characteristic zero phonon line of the luminescence disappeared due to the phase transition from stable orthorhombic phase to trigonal, and further increase of the pressure resulted in the complete disappearance of the luminescence band at 14 GPa due to the loss of crystallinity. Moreover, the emission band also shifted with a pressure coefficient of $-74 \text{ cm}^{-1}/\text{GPa}$ as pressure increased. The PL decay studies under pressure showed that it exhibited three exponential decay times, with the most significant

component having a decay time of 13 ms; this value varied slightly with pressure. Also, the friction-induced ML behaviour of the phosphor was examined for the first time. The results showed that the phosphor produced significant ML in the promising NIR region.

Further studies of the same phosphor were conducted due to the observation of a few unknown peaks during the initial measurements and to investigate the minor LiGa_5O_8 impurity phase observed during XRD analysis. For this purpose, an additional sample was prepared by further annealing of the original sample. Consequently, this study investigated the multiple luminescence sites in both samples in a detailed way, and also investigated how Fe^{3+} ions integrate into these sites. The XRD and SEM studies showed that in the annealed sample LiGa_5O_8 phase increased to 28% from its initial 0.8 percentage, and the morphology changed from rod shape to flake-like shape. The multiple luminescent Fe^{3+} centres occupying distinct lattice sites were investigated using XAS, EPR, and Mossbauer studies. The XAS study revealed that the Fe ions were predominantly in a tetrahedral coordination, and didn't show any hits on octahedral coordination. However, the Mössbauer and EPR studies indicated that at least three centres were present, and the peak at 695 nm observed during the luminescence study likely arose from tetrahedral coordination. The studies of annealed samples showed that the Fe ions were not occupying the tetrahedral Li sites in LiGa_5O_8 , but rather weakly luminescent octahedral sites of Ga, as evidenced by the lack of change in the luminescence spectra despite annealing and an increase in the LiGa_5O_8 percentage. Additionally, the sample's mechanoluminescence, thermo-stimulated luminescence, cathodoluminescence, and VUV luminescence were explored.

In **Chapter 6**, the studies focused on Mn^{2+} luminescence in LiGaO_2 and other materials under high pressure, with particular attention to wurtzite-like or wurtzite materials. For this purpose, we used in-house synthesised LiGaO_2 samples doped with different manganese concentrations. We prepared six samples with varying Mn concentrations using vacuum-assisted synthesis methods. The phosphor samples exhibit excellent luminescent properties and phase purities. Of the six samples, we selected $\text{LiGaO}_2\text{:Mn 1\%}$ for detailed analysis. Ambient temperature luminescence studies revealed at least two types of Mn^{2+} sites. High-pressure studies revealed that Mn^{2+} luminescence diminished with increasing pressure, a trend consistent with previous observations. Furthermore, the research also includes the study of the nature of Mn^{2+} luminescence in other materials such as ZnS and GaN under pressure. ZnS exhibited pressure-induced luminescence

quenching near 15 GPa due to a phase transition to the rock salt structure, and literature shows that AlN also exhibits similar behaviour under high pressure. However, in GaN, the Mn^{2+} luminescence began to appear around 16 GPa, which warrants further theoretical and experimental investigation to understand the underlying phenomenon.

In **Chapter 7**, the high-pressure behaviour of another lithium metal oxide, undoped LiYO_2 and doped LiYO_2 (with RE elements such as Eu^{3+} and Gd^{3+}), is described using synchrotron HP-XRD and high-pressure luminescence. The XRD and DSC studies indicate that at ambient temperature, both samples exhibit a mixed phase rather than a single phase, comprising high-temperature tetragonal and low-temperature monoclinic phases, along with a minute percentage of Y_2O_3 . Both synchrotron HP-XRD and high-pressure luminescence studies show that the doped and undoped materials undergo a pressure-induced phase transition above 5.1 GPa and up to 11 GPa. Above this pressure, a new pressure-induced LiYO_2 phase is observed. However, further theoretical and experimental studies are required to predict the additional features of this new phase.

The promising nature of the present thesis work covering LMO materials indicates that further investigations are necessary under extreme conditions, not only in the field of phosphor-related applications but also in understanding the phenomena related to the phase transition of this class of materials. Some of these materials are listed in the introduction section; however, many of lithium-based compounds remain unexplored. Further research into the structural, electrical, and optical properties of materials from the family of lithium-based compounds is essential, particularly in light of recent high-pressure studies on LiGaO_2 , LiGa_5O_8 , and LiYO_2 . Structurally similar materials such as LiGaO_2 and LiYO_2 may also undergo pressure-induced phase transitions, amorphization, and coordination changes. Additionally, the obtained results suggest that many other uncharacterised polymorphs might exist within this class of materials, which could be uncovered through systematic pressure and temperature-dependent studies. Such research has broader implications beyond basic optical material research; it can have significant impacts in fields such as optoelectronics, energy storage, and nuclear technologies. Lithium-based compounds are also gaining renewed interest for atomic fusion/fission applications, where liquid lithium is investigated as both a coolant and a plasma-facing material due to its advantageous neutron and thermal absorption properties.

In summary, the lithium metal oxides studied in this thesis provide excellent opportunities to advance both fundamental and practical material research. Under pressure, they undergo reversible or irreversible phase transitions, as well as modifications in luminescence and structural reorganisation, indicating that they possess multifunctional properties applicable to various key technological sectors, including solid-state lighting, energy storage, stress sensing, and nuclear fission and fusion. Future research will focus on discovering new phase transitions and developing these materials for real-time, practical applications up to device fabrication.

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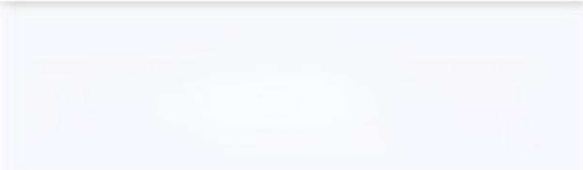
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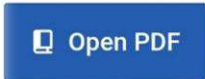
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AUTHORSHIP CONTRIBUTION STATEMENT

I declare that I am the co-author of the following publications:

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I contributed to this publication by conceptualising and visualising the scientific idea, as well as coordinating and executing all experiments described in the above article. I carried out photoluminescence and decay measurements under ambient, low-temperature, and high-pressure conditions, including data analysis and interpretation. I authored the original draft of the article from the introduction to the conclusions; prepared all figures and tables; and reviewed, edited, and drafted responses to the reviewers prior to final publication.

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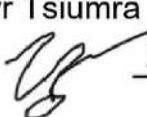
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I contributed to the publication by measuring the quantum yield and validating the results interpreted by the author Ajeesh Kumar Somakumar. I reviewed the final draft before publication.

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I contributed to the above publication through mechano-luminescence investigations, XRD analysis and validation of the results interpreted by the author Ajeesh Kumar Somakumar. I reviewed the final draft before publication.

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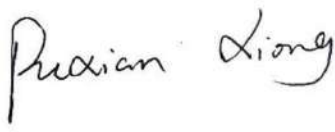
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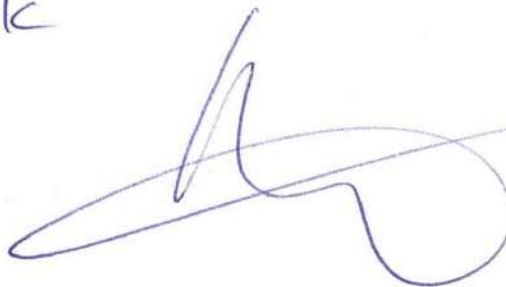
I declare that I am the co-author of the publication:

1. **Ajeesh Kumar Somakumar**, Lev-Ivan Bulyk, Volodymyr Tsiumra, Justyna Barzowska, Puxian Xiong, Anastasiia Lysak, Yaroslav Zhydachevskyy, and Andrzej Suchocki. "**High-Pressure Near-Infrared Luminescence Studies of Fe³⁺-Activated LiGaO₂.**" *Inorganic Chemistry* 62, no. 31 (2023): 12434-12444.
doi.org/10.1021/acs.inorgchem.3c01627

I contributed to the publication through the SEM measurements and the validation of the results interpreted by the author Ajeesh Kumar Somakumar. I reviewed the final draft prior to publication.

Name: Anastasiia Lysak

Signature and Date 3.03.2026



AUTHORSHIP CONTRIBUTION STATEMENT

I declare that I am the co-author of the following publications:

1. **Ajeesh Kumar Somakumar**, Lev-Ivan Bulyk, Volodymyr Tsiumra, Justyna Barzowska, Puxian Xiong, Anastasiia Lysak, Yaroslav Zhydachevskyy, and Andrzej Suchocki. **"High-Pressure Near-Infrared Luminescence Studies of Fe³⁺-Activated LiGaO₂."** *Inorganic Chemistry* 62, no. 31 (2023): 12434-12444.
doi.org/10.1021/acs.inorgchem.3c01627

I contributed to the publication by assisting in PL investigations, discussions and validation of the results interpreted by the author Ajeesh Kumar Somakumar. I reviewed the final draft before publication.

Name: 3.03.2026
Signature and Date

Head of QN4.1 Group
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11.2. Author Contribution Statements for Article 2:

Ajeesh Kumar Somakumar, Ivo Romet, Agnieszka Grabias, Marcin Kruk, Shusaku Hayama, Damian Włodarczyk, Justyna Barzowska, Yadhu Krishnan Edathumkandy, Eduard Feldbach, Puxian Xiong, Yaroslav Zhydachevskyy, Monika Trzaskowska, Hanka Przybylińska, Andrzej Suchocki. **Multisite Fe³⁺ luminescent centers in the LiGaO₂: Fe nanocrystalline phosphor.** *Molecules* 30, no. 11 (2025): 2331. <https://doi.org/10.3390/molecules30112331>

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List of Authors (Statement attached)

1. Ajeesh Kumar Somakumar
2. Ivo Romet
3. Agnieszka Grabias
4. Damian Włodarczyk
5. Justyna Barzowska
6. Puxian Xiong
7. Yaroslav Zhydachevskyy
8. Monika Trzaskowska
9. Hanka Przybylinska

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1. **Ajeesh Kumar Somakumar***, Ivo Romet, Agnieszka Grabias, Marcin Kruk, Shusaku Hayama, Damian Włodarczyk, Justyna Barzowska, Yadhu Krishnan Edathumkandy, Eduard Feldbach, Puxian Xiong, Yaroslav Zhydachevskyy, Monika Trzaskowska, Hanka Przybylińska, Andrzej Suchocki. * **“Multisite Fe³⁺ luminescent centers in the LiGaO₂:Fe nanocrystalline phosphor.”** *Molecules* 30, no. 11 (2025): 2331.
doi.org/10.3390/molecules30112331

I contributed to this publication by conceptualising and visualising the scientific idea, as well as coordinating and executing all experiments described in the above article. I carried out photoluminescence and decay measurements under ambient, low-temperature, and high-pressure conditions, including data analysis and interpretation. I authored the original draft of the article from the introduction to the conclusions; prepared all figures and tables; and reviewed, edited, and drafted responses to the reviewers prior to final publication.

Name: Ajeesh Kumar Somakumar

Signature and Date  9-3-26

AUTHORSHIP CONTRIBUTION STATEMENT

I declare that I am the co-author of the following publications:

1. **Ajeesh Kumar Somakumar***, Ivo Romet, Agnieszka Grabias, Marcin Kruk, Shusaku Hayama, Damian Włodarczyk, Justyna Barzowska, Yadhu Krishnan Edathumkandy, Eduard Feldbach, Puxian Xiong, Yaroslav Zhydachevskyy, Monika Trzaskowska, Hanka Przybylińska, Andrzej Suchocki. * **“Multisite Fe³⁺ luminescent centers in the LiGaO₂:Fe nanocrystalline phosphor.”** *Molecules* 30, no. 11 (2025): 2331. doi.org/10.3390/molecules30112331

I contributed to the above publication through thermoluminescence and cathodoluminescence measurements and the validation of the results interpreted by the author Ajeesh Kumar Somakumar. I reviewed the final draft before publication.

Ivo Romet

Signature and Date


06.03.2026

AUTHORSHIP CONTRIBUTION STATEMENT

I declare that I am the co-author of the following publications:

1. **Ajeesh Kumar Somakumar***, Ivo Romet, Agnieszka Grabias, Marcin Kruk, Shusaku Hayama, Damian Włodarczyk, Justyna Barzowska, Yadhu Krishnan Edathumkandy, Eduard Feldbach, Puxian Xiong, Yaroslav Zhydachevskyy, Monika Trzaskowska, Hanka Przybylińska, Andrzej Suchocki. * **“Multisite Fe³⁺ luminescent centers in the LiGaO₂:Fe nanocrystalline phosphor.”** *Molecules* 30, no. 11 (2025): 2331. doi.org/10.3390/molecules30112331

I contributed to the publication through the Mössbauer spectroscopy measurements of the sample and the validation of the results interpreted by the author Ajeesh Kumar Somakumar. I reviewed the final draft before publication.

Name AGNIESZKA GRABIAS

Signature and Date



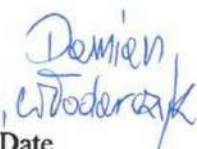
March 3, 2026

AUTHORSHIP CONTRIBUTION STATEMENT

I declare that I am the co-author of the following publications:

1. **Ajeesh Kumar Somakumar***, Ivo Romet, Agnieszka Grabias, Marcin Kruk, Shusaku Hayama, Damian Wlodarczyk, Justyna Barzowska, Yadhu Krishnan Edathumkandy, Eduard Feldbach, Puxian Xiong, Yaroslav Zhydachevskyy, Monika Trzaskowska, Hanka Przybylińska, Andrzej Suchocki. * **“Multisite Fe³⁺ luminescent centers in the LiGaO₂:Fe nanocrystalline phosphor.”** *Molecules* 30, no. 11 (2025): 2331. doi.org/10.3390/molecules30112331

I contributed to the above publication by conducting Raman measurements on the sample and validating the Raman results interpreted by the author, Ajeesh Kumar Somakumar. I reviewed the final draft before publication.

02.03.2026, 
Signature and Date

AUTHORSHIP CONTRIBUTION STATEMENT

I declare that I am the co-author of the following publications:

1. **Ajeesh Kumar Somakumar***, Ivo Romet, Agnieszka Grabias, Marcin Kruk, Shusaku Hayama, Damian Włodarczyk, Justyna Barzowska, Yadhu Krishnan Edathumkandy, Eduard Feldbach, Puxian Xiong, Yaroslav Zhydachevskyy, Monika Trzaskowska, Hanka Przybylińska, Andrzej Suchocki. * **“Multisite Fe³⁺ luminescent centers in the LiGaO₂:Fe nanocrystalline phosphor.”** *Molecules* 30, no. 11 (2025): 2331. doi.org/10.3390/molecules30112331

I contributed to the above publication through XRD analysis and the validation of results interpreted by the author Ajeesh Kumar Somakumar. I reviewed the final draft prior to publication.

Name:



Signed by / Podpisano
przez:

Justyna Maria Barzowska
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08:14

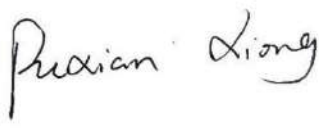
AUTHORSHIP CONTRIBUTION STATEMENT

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I contributed to the publication through the synthesis of the sample and validation of the results interpreted by the author Ajeesh Kumar Somakumar. I reviewed the final draft before publication.

Name: puxian xiong

Signature and Date 

March 5 2026

AUTHORSHIP CONTRIBUTION STATEMENT

I declare that I am the co-author of the following publications:

1. **Ajeesh Kumar Somakumar***, Ivo Romet, Agnieszka Grabias, Marcin Kruk, Shusaku Hayama, Damian Włodarczyk, Justyna Barzowska, Yadhu Krishnan Edathumkandy, Eduard Feldbach, Puxian Xiong, Yaroslav Zhydachevskyy, Monika Trzaskowska, Hanka Przybylińska, Andrzej Suchocki. * **“Multisite Fe³⁺ luminescent centers in the LiGaO₂:Fe nanocrystalline phosphor.”** *Molecules* 30, no. 11 (2025): 2331.
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I contributed to the publication by assisting in PL investigations, discussions and validation of the results interpreted by the author Ajeesh Kumar Somakumar. I reviewed the final draft before publication.

Name: 3.03.2026
Signature and Date

Head of ON4.1 Group
Institute of Physics PAS
Prof. dr hab. Yaroslav Zhydachevskyy

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I contributed to the above publication through antimicrobial studies of the sample and the validation of the results interpreted by the author Ajeesh Kumar Somakumar. I reviewed the final draft before publication.

Name *Monika Trzaskowska*

Signature and Date

*03.03.2026r.
Trzaskowska*

AUTHORSHIP CONTRIBUTION STATEMENT

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1. **Ajeesh Kumar Somakumar***, Ivo Romet, Agnieszka Grabias, Marcin Kruk, Shusaku Hayama, Damian Włodarczyk, Justyna Barzowska, Yadhu Krishnan Edathumkandy, Eduard Feldbach, Puxian Xiong, Yaroslav Zhydachevskyy, Monika Trzaskowska, Hanka Przybylińska, Andrzej Suchocki. * **“Multisite Fe³⁺ luminescent centers in the LiGaO₂:Fe nanocrystalline phosphor.”** *Molecules* 30, no. 11 (2025): 2331. doi.org/10.3390/molecules30112331

I contributed to the above publication through EPR spectroscopy measurements of the sample, data interpretation, and validation of the results. I reviewed the final draft before publication.

Name

Signature and Date

4.03.2016

Hanka Przybylińska

Dostępny do artykułów:

1. **Ajeesh Kumar Somakumar**, Lev-Ivan Bulyk, Volodymyr Tsiumra, Justyna Barzowska, Puxian Xiong, Anastasiia Lysak, Yaroslav Zhydachevskyy, and Andrzej Suchocki. "**High-Pressure Near-Infrared Luminescence Studies of Fe³⁺-Activated LiGaO₂.**" *Inorganic Chemistry* 62, no. 31 (2023): 12434-12444.
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