

MULTIFUNCTIONALITY OF MULTIFERROIC-BASED EUTECTIC COMPOSITES

Krzysztof Orliński

Institute of Electronic Materials Technology, Wólczyńska Street 133, 01-919 Warszawa
e-mail: krzysztof.orlinski@itme.edu.pl

The present work is dedicated to the functional description of eutectic composites containing rare earth ferrite – REFeO₃. Materials that fall under this category exhibit the spontaneous dielectric and magnetic polarization – they behave as ferroelectrics and ferromagnets and can be “tuned” by small additions of other rare earth elements without causing large crystal lattice distortions. Special attention was paid to multifunctionality that, in the majority of cases, comes from the control of the structural refinement with the supercooling of the crystallizing liquid.

Key words: composite, eutectic, multiferroic, ferromagnetism, ferroelectric, perovskite, catalyst, green, energy

Wielofunkcyjność w kompozytach eutektycznych na podstawie multiferroicznej

Niniejsza praca poświęcona jest opisowi funkcjonalności eutektycznych kompozytów na podstawie ferrytów metali ziem rzadkich – REFeO₃. Materiały należące do tej grupy wykazują jednocześnie spontaniczną polaryzację dielektryczną (ferroelektryczność) i magnetyczną (ferromagnetyzm) a ponadto dają się „stroić” za pomocą domieszek innych metali ziem rzadkich nie powodując silnych zniekształceń sieci krystalicznej. Szczególną uwagę zwrócono na wielofunkcyjność wynikającą w dużej mierze z możliwości sterowania rozdrobnieniem struktury za pomocą zmiany przechłodzenia krystalizującej cieczy.

słowa kluczowe: kompozyt, eutektyka, multiferroik, ferromagnetyzm, ferroelektryczność, perowskit, katalizator, energia, zielona

1. INTRODUCTION

During recent years we have witnessed the emergence of a variety of faster and more efficient optoelectronic and photonic elements. The introduction of optical fibres was one of the those improvements enabling more rapid as well as more effective information transfer. The next step, leading to the substitution of electricity with light is nevertheless, far more complex and cannot be achieved without special materials. As photons are the quanta of electromagnetic waves, both: electric and magnetic force is needed to influence their trajectory. The research

in a branch of photonic composite materials called metamaterials is dedicated to demonstration of special properties, not found in nature, such as negative refraction [1 - 2] or invisibility in certain wavelength spectrum – *cloaking* [3 - 4].

Moreover, along with the development of technology standards, the demand for energy has increased and we found ourselves in urgent need finding its novel sources, as well as increasing the efficiency of the existing ones. Better low-cost catalysts of combustion processes are also required since the production of large amounts of energy usually follows the release of the following greenhouse gases: carbon, nitrogen and sulfur oxides. Thus, apart from concentrating on materials for low-cost catalysis⁵, much effort is being put into green energy sources for instance solid oxide fuel cells [6 - 8], or photovoltaics) and environmental monitoring including chemical sensing [9 - 10], as well as purification [11 - 12].

To rise to the challenge, the 21st century materials should possess all, or at least most, of these properties. In this work, I would like to focus on how to achieve the multifunctionality by applying the simple rules of material science and physics. Such distinct set of characteristics was found in a group of materials referred to as multiferroics.

2. MULTIFERROICS

The materials, which exhibit both: ferroelectric and ferromagnetic behaviour are called multiferroics. The typically materials crystallize typically in two types of structures. The first one, termed the spinel structure, although described by cubic symmetry, is very complex and as such, will not be the subject of further discussion. Instead, the second structure, known as perovskite compounds shall be introduced in detail.

The amount of the charge stored inside the material is highly dependent on its dielectric permittivity

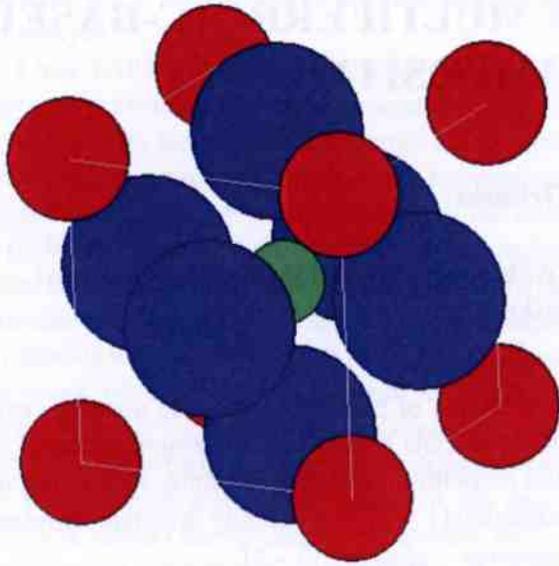


Fig. 1. ABX_3 perovskite structure is formed of cations A (red ones) in dodecahedral coordination (surrounded by 12 X anions (blue ones) e.g. oxygen) and cation B (green one) in octahedral coordination (surrounded by 6 anions).

Rys. 1. Struktura związków typu ABX_3 (sieć perowskitu) uformowana jest z kationów A (czerwone) umieszczonych w położeniu dodekahedrycznym (otoczonych 12 anionami X (niebieskie), np. tlenem) oraz z kationu B (zielony) w położeniu oktaedrycznym (otoczony sześcioma anionami).

and is found to be the highest in a group called ferroelectrics. In the case of these materials, spontaneous polarization of dipoles in certain direction, takes place, as does in ferromagnetics. Moreover, oxide perovskites (Fig. 1) particularly often exhibit ferroelectric behaviour. They can be described as compounds with the general chemical formula ABO_3 , that crystallize in the regular system - Pm-3m space group, although sometimes distorted to either tetragonal or orthorhombic systems (the distortion is given quantitatively by the c/a ratio, where c and a correspond to cell parameters along the z and x axis, respectively). The structural stability of perovskites is well described by Goldschmidt's rule:

$$R_A + \bar{R}_{O(12)} = t(R_B + \bar{R}_{O(6)})\sqrt{2}, \text{ where } 0.8 < t < 1.0$$

R stands for the radius of a particular ion, while t is the constant, that describes the stability range for given A and B cations. By using different cations (with charges summed to +6 and radii that will fit the upper equation) one can control the whole set of physical properties, including both dielectric and magnetic behaviour, the regularity of primary cell and others. When the condition is not fulfilled (the t constant exceeds the $\langle 0.8; 1 \rangle$ range) the high-symme-

try structure (e.g. cubic, tetragonal or orthorhombic) is considered unstable and gets distorted to low-symmetry forms (e.g. monoclinic).

In the case of perovskites every single cell acts as a dielectric dipole. The structure itself enables the dielectric polarization. The magnetic momentum can appear when a magnetic ion (like Fe^{+3} or Co^{+3}) is placed in the octahedral position. Icosahedral positions are much larger, so there are very few magnetic cations that can match their size e.g. Dy^{+3} or Yb^{+3} , and usually their part in the effective magnetic momentum is smaller than that Fe^{+3} or Co^{+3} cations.

The A cation will stand for a rare earth trivalent lanthanide ion (widely used, e.g. in the form of active dopants such as Nd, Pr and Yb or YAG, GdCOB, YbAG compounds). Its spectroscopic properties can be modified very easily and the similarity between their radii should prevent high structural distortions, which may cause the increased absorption of the material. The $REFeO_3$ group of perovskites were found to act as weak ferromagnets (Tabl. 1.) and ($\epsilon' \approx 1000 \text{Fm}^{-1}$; $GdFeO_3$, $f = 10 \text{MHz}^{13}$) ferroelectrics.

Table 1. Magnetization values of selected rare earth orthoferrites (14).

Tabela 1. Wartości namagnesowania wybranych ortoferytów metali ziem rzadkich (14).

RE	La	Nd	Gd	Dy	Yb
$4\pi M$ [Gauss]	83	62	94	128	143

The stability of $REFeO_3$ structure can be derived from Goldschmidt's equation, which gives the maximum deviations of the A^{+3} ionic radius:

For $\bar{R}_{Fe^{+3}} = 0.78 \text{ \AA}$, $\bar{R}_{O(2)} = 1.4 \text{ \AA}$ [SHANNON], we have: $1.07 \text{ \AA} < R_{RR(+3)} < 1.68 \text{ \AA}$

Typical rare earth ferrites, such as $LaFeO_3$, $GdFeO_3$ or $NdFeO_3$ are characterized by very good structural stability ($\bar{R}_{N(12)} = 1.36 \text{ \AA}$, $\bar{R}_{N(6)} = 1.27 \text{ \AA}$ and $R_{O(12)} = 1.11 \text{ \AA}$). A smaller radius was found to increase the c/a factor (1.415 – $LaFeO_3$, 1.424 – $NdFeO_3$, 1.431 – $GdFeO_3$) and to decrease the unit cell volume (242.93 \AA^3 – $LaFeO_3$, 236.42 \AA^3 – $NdFeO_3$, 230.07 \AA^3 – $GdFeO_3$). The denser packing can be easily distinguished macroscopically once the hardness of such materials is enhanced. It is more difficult to polish $GdFeO_3$ than $LaFeO_3$.

An exact $REFeO_3$ stoichiometry is very difficult to achieve, due to the partial reduction of iron to divalent Fe^{+2} . In consequence, this causes the appearance of oxygen vacancies and raises the ionic conductivity of the material as well as increases its absorption. Crystals are often opaque with reddish-brown or black colouration.

It turns out that REFeO_3 perovskites give away oxygen very easily as long as the loss is quickly compensated for. For example when one side of the sample is partially reduced, (due to the combustion of a gas with the help of the “lattice” oxygen) oxygen vacancies are generated and by the means of diffusion travel through the lattice until they reach the other side of the sample, where they recombine with oxygen absorbed from the air. This property is used mainly in the field of solid oxide fuel cells (SOFC), chemical sensors (CS) and low-cost catalysts.

3. EUTECTICS

Aeutectic is a set of two or more substances that mix completely in the liquid state but separate during crystallization. In Fig. 2 a phase diagram is shown with one mixture composition that melts congruently, is shown. That is the eutectic point. The eutectic mixture, or simply a *eutectic*, has another set of attractive properties: a) its melting temperature is lower than the melting points of its component phases, b) its microstructure may show a periodic pattern, the refinement of which can be tailored by the cooling rate (Fig.5).

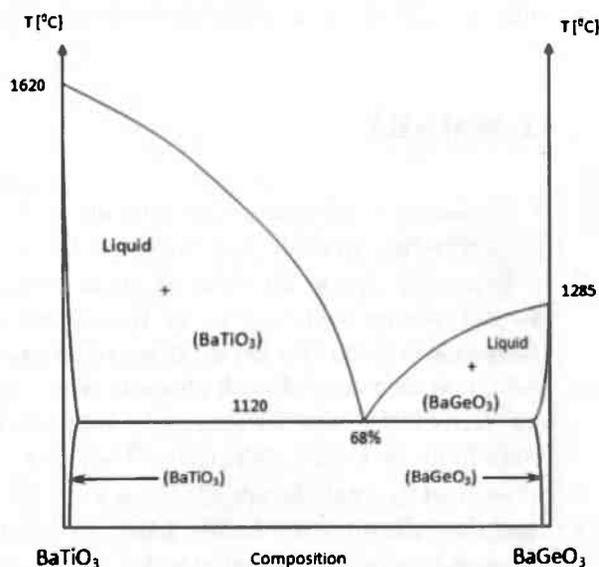


Fig. 2. Binary phase diagram with an eutectic reaction. The substances written in brackets are solid solutions of one compound in the crystal lattice of another one. The eutectic point is at ~68 mol.% BaGeO_3 and 32 mol.% of BaTiO_3 at $T = 1120^\circ\text{C}$.

Rys. 2. Układ podwójny z reakcją eutektyczną. Substancje zapisane w nawiasach są roztworami stałymi jednego związku rozpuszczonego w sieci krystalicznej drugiego. Punkt eutektyczny odpowiada ~ 68% mol. BaGeO_3 i 32 %mol. BaTiO_3 oraz temperaturze $T_e = 1120^\circ\text{C}$.

Along with the size of the phases reduction, grain boundaries occupy more and more volume percentage of the eutectic material space. Macroscopically, these crystal lattice distortions enable easier diffusion, therefore being more suitable for the use in SOFC, CS and catalysts. The same distortions influence the magnetic/electric field in the perovskite phase. When the magnetic/dielectric phase is more refined grain boundaries act as additional obstacles for domain walls movement, leading to higher magnitudes of the demagnetization/depolarization energies. The phenomenon is observed also in the presence of precipitates and is being referred to as domain wall pinning [15] (Fig. 3).

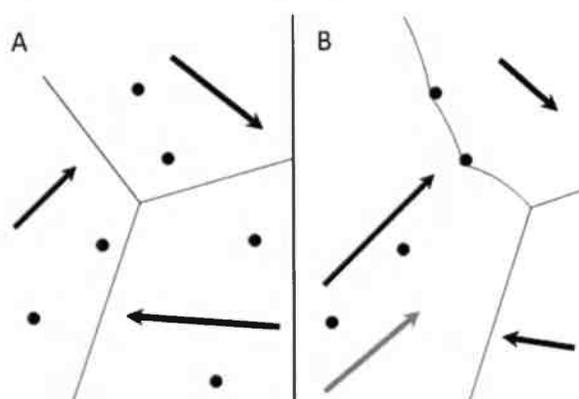


Fig. 3. Domain structure of a two-phase magnetic material without (A) and under (B) external magnetic field (blue arrow). Pinning of the domain walls decelerates their movement. Black arrows indicate the magnetization in a particular domain.

Rys. 3. Struktura domenowa dwufazowego materiału magnetycznego przed (A) i po (B) przyłożeniu zewnętrznego pola magnetycznego (niebieska strzałka). Zakotwiczenie ścian domenowych spowalnia ich ruch. Czarnymi strzałkami oznaczono namagnesowanie na obszarze konkretnej domeny.

There are two well described $\text{REFeO}_3\text{-RE}_2\text{O}_3$ eutectic phase diagrams: $\text{LaFeO}_3\text{-La}_2\text{O}_3$ and $\text{GdFeO}_3\text{-Gd}_2\text{O}_3$. In both, the perovskite phase is in the majority of about 70 mol. %. The eutectic may be considered as a two-phase composite basis for a hole range of materials. Gadolinium orthoferrite is semitransparent with red tint colour but when the thickness of the material is higher than 100 microns it appears black and nontransparent. Both gadolinium and lanthanum sesquioxides are transparent in the visible region ($E_{\text{La}_2\text{O}_3} \approx 4.3 \text{ eV}$, which corresponds to $\lambda \approx 288 \text{ nm}$ – near the ultraviolet region). The physical properties of the phases can be modified depending on the dopant. The use of different co-

oling rates gives the control over the dispersion of the component phases.

4. TECHNOLOGY

The idea of growing well structured eutectics cannot be satisfactorily introduced by the means of neither Czochralski nor Bridgeman method. Due to convection movements of the melt, near the growth region, the eutectic microstructure gets distorted. Lately however, Fukuda [16] have proposed a method called micro-pulling down, where the melt travels through a capillary and crystallizes in the form imposed by the shaper. The crystallization process begins with touching the melt appearing at the shaper bottom (via the capillary) with a seed crystal (Fig. 4) The use of small diameter nozzles (0.6 mm at most) and the appropriate length of the capillary enables lateral flow in the capillary and helps to avoid convection at the crystal/melt interface. This allows obtaining well ordered eutectic microstructures. The crystal is moved to cooler regions depending on the pulling rate.

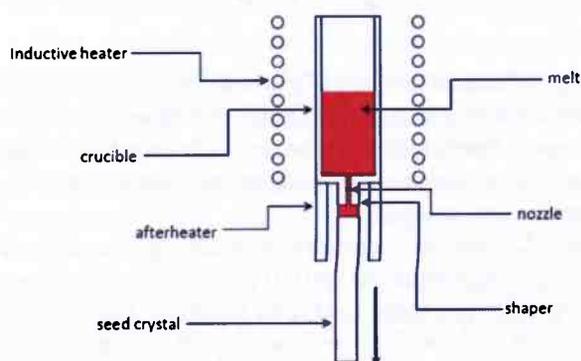


Fig. 4. Crystallization of a rod-shaped material by the micro-pulling down method. The arrow indicates the growth direction.

Rys. 4. Krystalizacja materiału w postaci pręta za pomocą metody mikrowyciągania. Strzałką zaznaczono kierunek wzrostu.

The anisotropy of the method (growth in one preferable direction) demands the formation of the phases in elongated forms, such as plates or rods (Fig. 5). Both compound- and composition dependent cross section of the eutectic is usually specific for each system.

The idea of growing fine eutectic structures, where an in situ composite mixture comprising the multiferroic medium is formed directly from the melt, was used in the “Self-organization approach towards photonics and optoelectronics” Project.

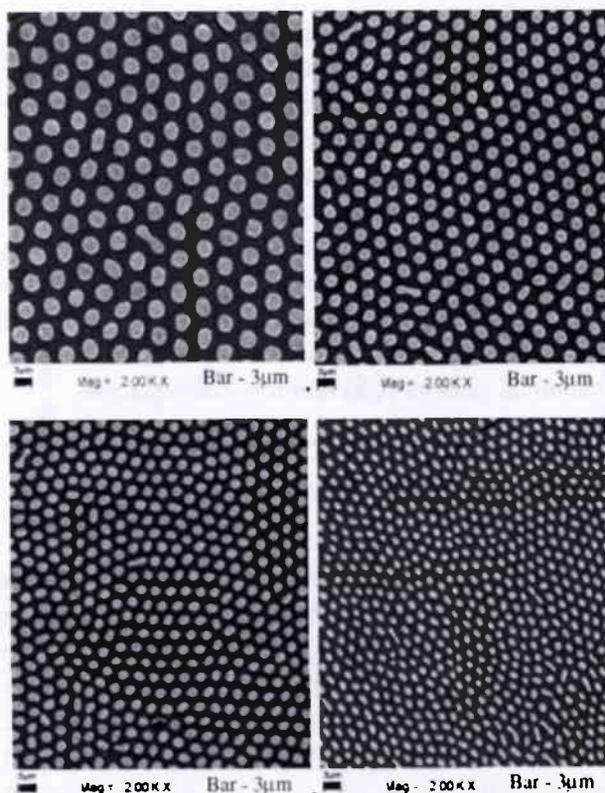


Fig. 5. Structural refinement in a rod-like eutectic caused by the change of the pulling rate. The diameter of the rod decreases with higher cooling rates [17].

Rys. 5. Rozdrobnienie struktury w eutektyce włóknistej wywołane zmianą szybkości wyciągania. Średnica włókien zmniejsza się wraz ze wzrostem szybkości chłodzenia [17].

5. SUMMARY

In conclusion, multifunctional materials should exhibit properties suitable not only for the use in photonics but also in the field of green energy sources and environment monitoring. It was proved that lanthanide orthoferrites fits the description since they have a wide range of such characteristics, including ferroelectric and ferromagnetic properties, catalytic ability or ionic conductivity. They can be easily modified by small dopant additions, especially Ln^{+3} and Co^{+3} , for they are hardly likely to distort the crystal structure. The use of eutectic bicomposites extends the above mentioned properties further when adding second phase to the grain boundaries, the volume fraction of which (as a result of structure refinement) can be controlled with the pulling rate. For the enumerated reasons $\text{REFeO}_3\text{-RE}_2\text{O}_3$ systems have recently become the subject of high interest for the manufactures of low cost, multifunctional materials.

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STRESZCZENIA ARTYKUŁÓW PRACOWNIKÓW ITME

Nucleation mechanism of 6H-SiC polytype inclusions inside 15R-SiC crystals

Y. Zhang¹, H. Chen¹, G. Choi¹, B. Raghochamachar¹, M. Dudley^{1,5}, J. H. Edgar², Krzysztof Graszka³, Emil Tynicki³, L. Zhang⁴, D. Su⁴, Y. Zhu⁴

¹ Department of Materials Science and Engineering, Stony Brook University, Stony Brook, NY, USA

² Department of Chemical Engineering, Kansas State University, Manhattan, KS, USA

³ Institute of Electronic Materials Technology, ul. Wólczyńska 133, 01-919 Warszawa

⁴ Center for Functional Materials, Brookhaven National Laboratory, Upton, NY, USA

⁵ e-mail: mdudley@notes.cc.sunysb.edu

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A model is presented for the nucleation mechanism of 6H-SiC polytype inclusions inside 15R-SiC boules. Inhomogeneous densities of screw dislocations lead to uneven growth rates, resulting in com-

plex step overgrowth processes which can partially suppress the Burgers vector of a 15R 1c screw dislocation through the creation of Frank faults and Frank partial dislocations. Combined with stacking shifts induced by the passage of basal plane partial dislocations, it is shown that the partial Burgers vector suppression can leave behind a residual 6H 1c dislocation, which then acts as a nucleus for reproduction of 6H-SiC structure in the 15R-SiC crystal.

Polytypism study in SiC epilayers using electron backscatter diffraction

Kinga Kościwicz^{1,2}, Włodek Strupiński², Wojciech Wierzchowski², K. Wieteska³, A. Olszyna¹

¹ Faculty of Materials Science and Engineering, Warsaw University of Technology, ul. Wołoska 141, 02-507 Warszawa

² Institute of Electronic Materials Technology, ul. Wólczyńska 133, 01-919 Warszawa

³ Institute of Atomic Energy, 05-400 Otwock-Świerk