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NEW CERAMIC FUNCTIONAL MATERIALS AND TECHNOLOGIES

Key words

microfabrication processes, biomimetic materials, smart materials and systems, materials for information storage and transmission.

Abstract

A short overview of the developments of functional materials featuring miniaturisation and integration is illustrated by examples taken from the field of ceramic functional materials. To obtain advanced materials new methods are required. Most of them are microfabrication processes developed by the "top-down" approach.

Streszczenie

Krótkie omówienie rozwoju materiałów funkcjonalnych, a głównie ich miniaturyzacji i integracji przedstawiono na podstawie przykładów z obszaru ceramicznych materiałów funkcjonalnych. Otrzymywanie zaawansowanych materiałów wymaga wykorzystania nowoczesnych metod ich wytwarzania. Większość z nich to procesy w skali mikro, polegające na zastosowaniu nowoczesnych osiągnięć techniki do modernizacji konwencjonalnych technologii.

1. Introduction

Advanced materials are conventionally divided into structural and functional ones. Development of the first group of materials has been characterized by an increase of phase complexity, from single-phase materials over surface-modified materials to fiber re-inforced composites, laminates and functional gradient materials. A decrease of size of constituent grains and particles down to nanometers has been found to be sometimes advantageous. Development of functional materials has featured a miniaturisation of the components and their integration. In both cases the development has stemmed from known laws of physics and chemistry but owing to small size and specific shape of components the new materials may acquire properties which are not easily, if ever, attainable in classic materials.

The present short overview deals mainly with functional materials because their development is more dynamic than this is the case with structural materials. Researchers who are interested in basic problems find here still large areas of the unknown as a challenge. Another challenge for basic research is to approach nature with its perfect way to perform various functions. Strong driving forces exist in this field also for applied research namely, the changes in social life associated with introduction of information and telecommunication technologies, with smart houses and cars, with requirements of the health service a.s.o.

Because the field is a broad and quickly developing one it has been necessary to impose some restrictions on the content of the paper. In agreement with what has been said before the main stress has been put on materials/material systems mimicking nature and on materials for information technology. A further restriction has been a confinement to the fields of earlier and present research activity of the author, namely to ceramic materials. On the one hand, this should permit to convey rather certain and not misleading information in a field where the opposite is not rare. On the other, the rich variety of shapes and functions performed by ceramic materials permits to illustrate well the main lines of development of functional materials in general.

2. Nano and microfabrication methods

In the field of new functional materials there has been a need for new fabrication methods. One could divide them in nano- and microfabrication methods, according to the resolution of the smallest features of the products, equal to several nanometers and few micrometers, respectively. The new fabrication methods typically have put to use electronics and photonics and have been developed by the "top-down" approach, i.e. by a modification of methods used earlier for producting classic materials. Table 1 shows, after [5], some more important microfabrication methods for producting ceramic materials. The methods permit to obtain objects of a resolution of their smallest elements ranging from a few to some hundreds of micrometers. Most of them deploy suspensions of ceramic powders (including nanopowders) in liquids, polymers, polymer solutions a.s.o. to make either final products or templates of a specific shape next filled with powders and powder suspensions.

Table 1. Microfabrication methods of ceramic materials

Method	Smallest feature resolution [μm]	2D layers or 3D bodies
RP- micropen writing	250	3D
RP-ink-jet printing of binder solution (3DP process)	200	3D
RP-ink-jet printing of suspensions	100	2D
Screen printing	70-170	2D
Direct ceramic machining of presintered bodies	50	3D
LTCC	25-100	3D
Lithography, eg. LIGA	10-20	2D/3D
Microstereolithography	2	3D
Soft lithography	1-5	2D/3D

Remarks: LTCC – low-temperature co-fired ceramic multilayer technology; RP- rapid prototyping; LIGA- X-ray lithography (Litographie-Abformung-Galvanotechnik)

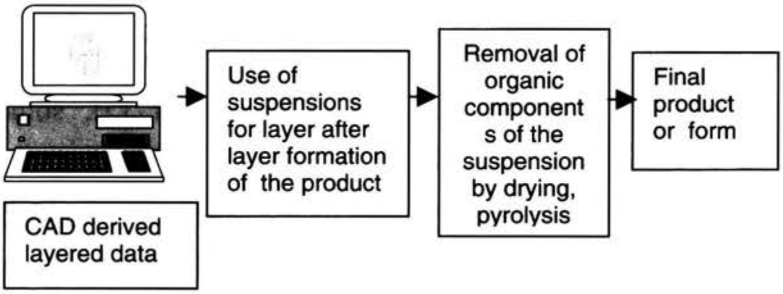


Fig.1. Schema of rapid prototyping (for ceramic materials and templates)

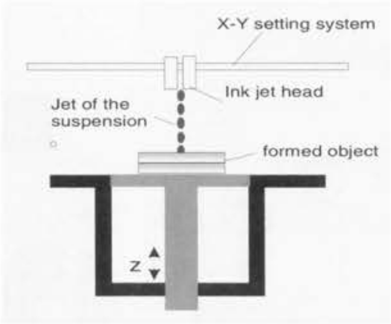


Fig.2. Rapid prototyping;, ink-jet printing of suspensions

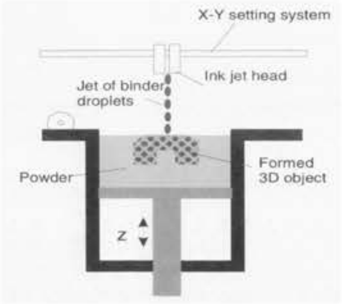


Fig.3. Rapid prototyping; ink-jet printing of binder solutions (3DP process)

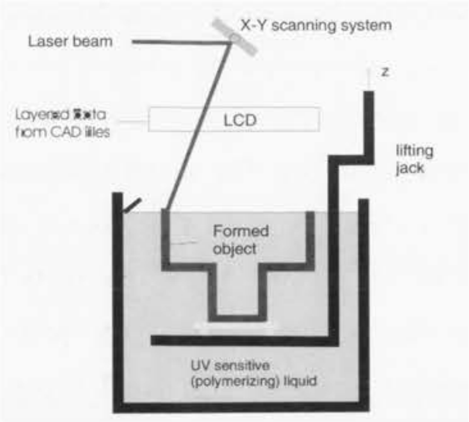


Fig.4. Microstereolithography. The layered data from CAD successively displayed on the liquid crystal display serve as masks for the laser beam; the product (composed of ceramic powder with binder) is formed in a liquid polymerising under the action of laser radiation

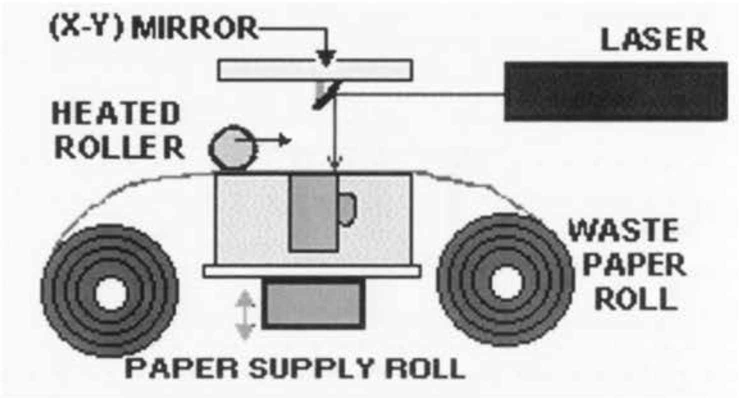


Fig.5. Laminated object manufacturing; in case of ceramic materials the rolls of ceramic green tapes are used

To more important methods belong variations of rapid prototyping (Fig. 1), such as printing with binder solutions and powder suspensions, respectively (Figs. 2 and 3), stereolithography (Fig.4). A great potential for producing microobjects has the method called laminated object manufacturing (LOM) which uses ceramic green tapes (Fig.5). The tapes are powder suspensions constituted by powder, binder, dispersing agent and solvent. Typical constituents of suspensions used in classic ceramic technology are described in [6]. The green tapes are used, e.g., in the LTCC process. In a classic form of the process, after stripping off a carrier tape, the tapes are divided in discrete parts by cutting, and are shaped by making vias, channels a.s.o. The parts are next stacked, laminated under pressure and, finally, sintered. Figure 6 shows, after [7], a typical product obtained by this method, a telecommunication micromodule constituted by several ceramic layers containing embedded passive elements such as resistors, conductive paths, induction coils a.s.o.

One-dimensional (1D) nano- and micromaterials require specific fabrication methods. Some of them shall be referred to in a proper context in part 4.

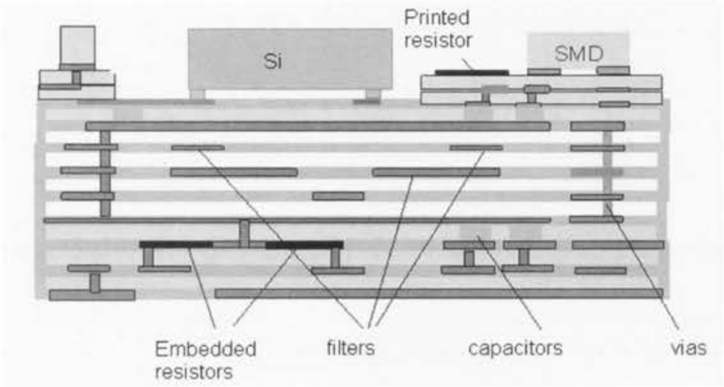


Fig.6. Micromodule for telecommunication in the microwave and radio frequency range

In the future, technologies developed by the "bottom up" approach, should probably become equally important. These are the methods which utilise processes where replicating and self-organising nanostructures grow to larger, more or less complex, ones [8] .The general idea of such an approach is illustrated in Figure 7. The idea has been partly realised in soft lithography [9] where elastomeric stamps are used to organise the structure of products.

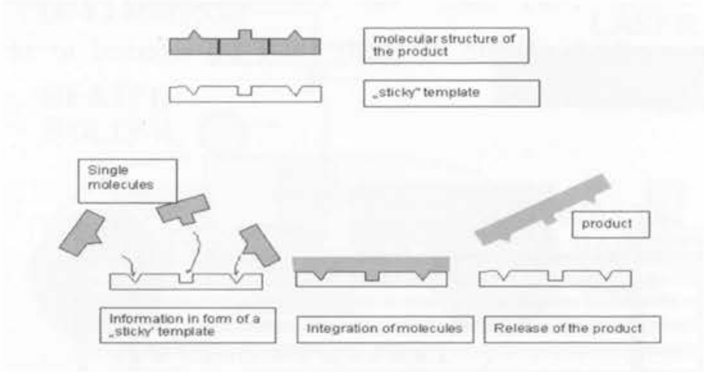


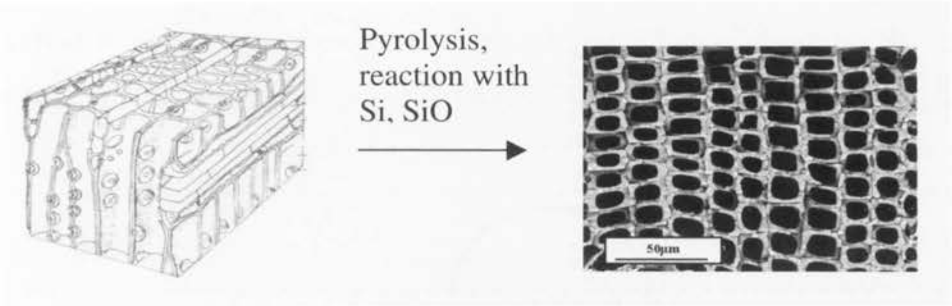
Fig.7. The idea of self-replication in materials manufacturing; after [8]

2. Materials and systems mimicking nature

3.1. Biomimetic materials

Biomimetic materials constitute an obvious link to nature. Already the fibre re-inforced composites and laminates mimic some features of the structure of organic systems performing mechanical functions, such as muscles and bone. The former may be described as a fibrous network while the hard bone constists of alternating layers of hydroxyapatite and of a soft organic issue. The mimicking can be accomplished to a limited extent only. Namely, the structure of organic systems is a hierachical one which could not be fully realised in synthetic composites until now [10]. Consequently, the properties of the latter do not approach the flexibility observed with organic systems.

Another direction is a transformation of natural objects to their pseudomorphoses by changing their chemical composition. Due to this the advantageous structure of natural objects is preserved but their resistance to high temperatures, aggresive environment a.s.o. may be increased. One of the better known examples is silicium carbide pseudomophoses of wood (Fig. 8).



wood cellular SiC

Fig.8. Cellular silicon carbide produced by pyrolysis of wood and subseqent reaction of the carbon residue with silicon and/or SiO

The pseudomorphoses are obtained in a process which involves carbon pyrolysis, followed by reaction of the carbon residue with gaseous or liquid silicon or gaseous SiO [11][12]. Producing pseudomorphoses of natural objects may also help to lower production costs of complex ceramic shapes.

Namely, conventional ceramic technology for complex shapes uses machining as a final step which is very expensive and time-consuming.

If natural objects have an appropriate shape they may be transformed by reaction in useful ceramic components. An example purvey MgO pseudomorphoses of frustules (silicized walls of diatomite cells) which are obtained by reaction of the frustules with magnesium vapour at 900 ^{0}C [13].

3.2. Smart materials and systems

Materials and systems are called smart when they the two basic ways in which living systems react to the environment. Namely, a recognition of the nature of the environment and an adequate reaction to stimuli from the environment. In other words, the living systems play a role of both a sensor and an actuator. Such a behavior may be mimicked by active smart systems, the schema of which is given in Fig. 9.

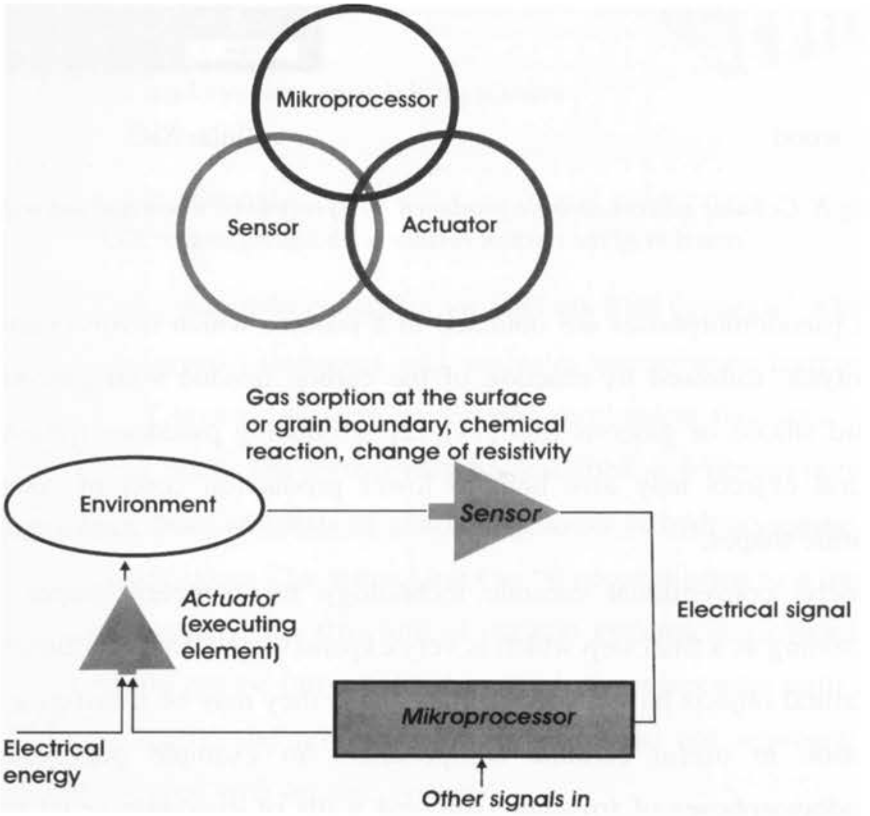


Fig.9. Active smart systems and example of an active smart system for monitoring the chemical composition of gases

The actuator and sensor usually form a feedback loop over a microprocessor. Information in the loop are transmitted by electrons. Tables 2 and 3 collect, respectively, the most commonly used sensors and actuators. In order to decrease the response time sensors, actuators and microprocessors have to be integrated.

Table 2. Currently used sensors

Exchanged energies	Effect utilised	Typical material	Some applications
Mechanical-electrical	Piezoelectric effect $\rho = f(\varepsilon)$	PZT	Sensors of position, of displacement
Mechanical-magnetic	Inverse magnetostrictive effect $B = f(\varepsilon)$	Fe, Co, Ni	Sensors of force, twist, displacement,deformation
Optical-electrical	Pyroelectric effect $E = f(E_{h\nu})$	PLZT	Night vision devices, temperature sensors
Thermal-electrical	$\rho = f(T)$	AB_2O_4 , $BaTiO_3$	NTCR and PTCR sensors
Chemical-electrical	$\rho_{surf} = f$ (chemical reactions at the surface)	SnO_2	Sensors of chemical composition of gases

Symbols used: ρ -resistivity; ρ_{surf} – surface resistivity ε -deformation; B-magnetic induction;
E- electric field intesity; $E_{h\nu}$ - photon energy, T- temperature

This has been realised in microelectromechanical systems (MEMS), an example of these systems being illustrated in Figure 10.

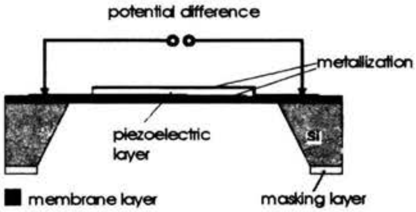


Fig.10. An example of integrated micromechanical system – acting as a piezoelectric actuator

Table 3. Currently used actuators

Energies exchanged	Effect utilised	Typical material	Some applications
Electrical-mechanical	Converse piezoelectric effect; $\varepsilon = f(E)$	$Pb(Zr_{1-x}Ti_x)O_3$	Actuators of position, of valves, of ink-jet heads
Magnetic-mechanical	magnetostriction $\varepsilon = f(H)$	Fe, Co, Ni, $Tb_xDy_{1-x}Fe_y$, Ni_2MnGa	Actuators of position, of shock absorbers, of fuel injection devices
Electrical-optical	$n = f(E)$	$LiNbO_3$	Electrooptical modulators
Electrical-thermal	$E = Uit$; $\rho = f(T)$	SiC, Si_3N_4 AB_2O_4, $BaTiO_3$	Heaters, NTCR and PTCR actuators
Electrical-chemical	$O^{2-} \rightarrow \frac{1}{2}O_2(g) + 2e^-$(at the electrode facing a lower O_2 concentration	Concentration cells based on ZrO_2	Oxygen pumps

Symbols used (see also Table 2): H- magnetic field strength; U- voltage; t - time

The MEMS are produced by using silicon chips submitted to combinations of lithography and etching.

4. Materials for information storage and transmission

Because of the role played by microprocessors in modern technology, also in development new production methods, there is much interest in introducing new materials to increase the efficiency of information storage and transmission. Examples of ceramic materials used in this field are thin ferroelectric layers for random access memories (Table 4).

Table 4. Ferroelectric materials for information storage

Material	Mode of action	Effectt
Ferroelectric random access memories (FeRAM)	Microcapacitors as cells; the states "0" and "1" of binary logic realised by changing the direction of spontaneous polarisation; recording by applying + and – voltage, respectively; reading by scanning free charges on the electrodes	Shortened access time
Ferroelectric memories made up of field effect transistors	One of the electrodes of a microcapacitor is constituted by a ferroelectric layer; this structure is utilised as the gate of the field effect transistor	Non-destructive read operation

Let us turn now to new ceramic materials for information transmission. Information can be transmitted by electrons, photons or chemical molecules. According to general trends, materials serving as the medium for transmitting information by these carriers should ensure a miniaturisation of devices. In particular, they should permit to localise and direct electrons, photons and molecules in small volumes of the order of nanometers and few micrometers (see Table 5).

As far as electrons are concerned, the turning point has been the re-discovery of carbon nanotubes (as a side-effect of research into fullerenes). There are single-walled (SWCNT) and multi-walled (MWCNT) carbon nanotubes, having diameters between 0.7 to 2 nm and lengths up to 20 mm.

Table 5. Information carriers and materials serving for information transmission

Information carrier	Typical material	Mode of action
Electrons	Carbon nanotubes (SWCNT); Si, SiC, GaAs,InAs, ZnS, CdS, ZnO, MgO, SiO_2, BaTiO3 nanotubes	Localisation of electrons and restriction of their movement to the axis of the nanotubes (nanotubes are a quantum wire)
Photons	Photonic crystals (materials with an optical band gap), e.g. "holey" optical fibres	Localisation of photons and restriction of their movement to line defects in the photonic crystal structure
Gaseous and liquid molecules	Materials and devices for microfluidics	Mixing and distribution of fluxes of liquids and gases in microchannels of a diameter below 100 µm, allowing reactions and heat transfer

The latter tubes have, as far as electrical properties are concerned, mixed properties while the former are either semiconductors or metallic conductors subject to their diameter. Due to their small diameter the carbon tubes act as quantum wires, i. e. localise the electrons inside the tubes and allow their tranmission in the direction of the axis only. There are various current and potential applications of carbon nanotubes, such as miniature cathode ray-tubes, active elements and circuits in electronics. An example of the latter applications is a field-effect transistor where the carbon nanotube serves as the channel for electrons (Fig. 11) [16].

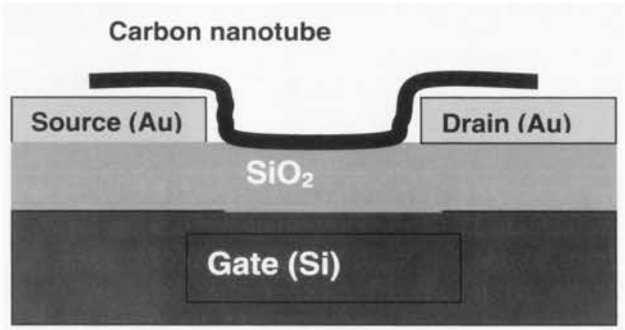


Fig.11. Field effect transistor with carbon nanotubes serving as the channel for electrons

Nanowires and nanotubes of many other semiconductors, such as Si, GaAs, InP, ZnS, CdS, ZnO, $BaTiO_3$, $PbTiO_3$, have also been obtained and their possible applications perceived for construction of electronic and photonic devices of nanometric dimensions, for example of laser diodes. It is thus reasonable to say that the 1D nanomaterials are the most important kind of nanomaterials.

Further progress in information transmission depends upon a use of photons. For example, large-scale computing requires a concerted action of thousands of microprocessors which store together enormous amounts of data. In this situation a broad-band information exchange with negligible delays and losses is necessary. Such requirement can be met when photons substitute for electrons as information carriers. The materials which may enable us to achieve this goal are photonic crystals. The term photonic crystal, or better, photonic quasi-crystal, denotes a material composed of at least two phases having different dielectric constants and thus different refractive indices. At least one of the phases has to form a 2D or 3D translational lattice with a lattice constant of the order of the length of light (near ultraviolet, visible, near infrared), i.e. from 1.10^2 to 1.10^3 nm (Fig. 12).

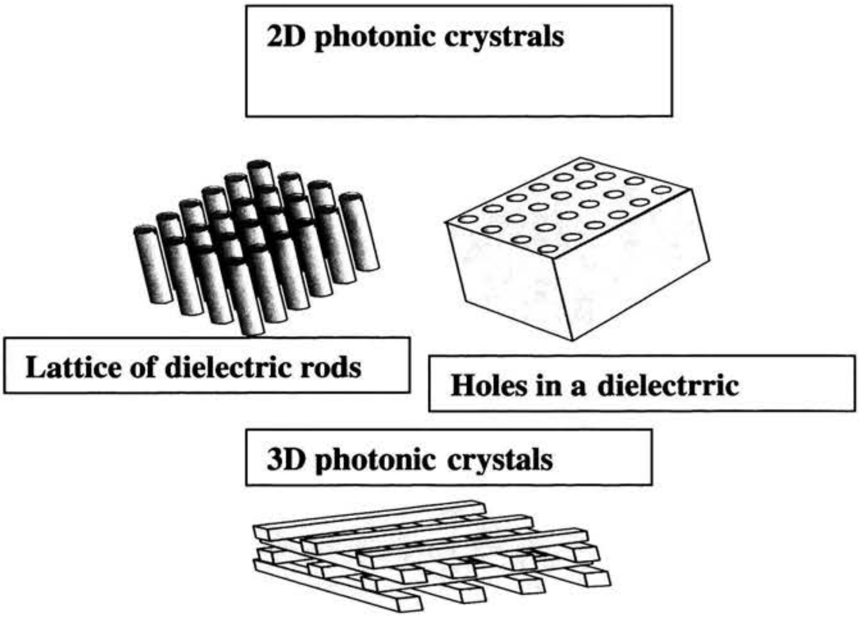


Fig.12. Various kinds of photonic crystals (optical band gap materials)

An important type of photonic crystals are the so-called "holey" optical fibres, the cladding of which is a 2D photonic crystal (of the "holes in a matrix" type) extended in one direction.Because interaction with matter of any electromagnetic radiation obeys the same rules, there occurs in the photonic crystals an energy gap at certain optical frequencies of the UV, visible and IR range (Fig. 13).

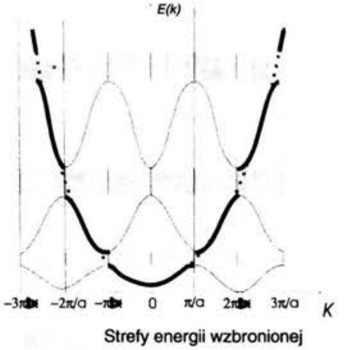


Fig.13. The dispersion relation for electromagnetic waves interacting with a space lattice of material elements; a- the lattice constant of the material

Specifically, there is a lack of allowed states of the transverse (electrical and magnetical) modes by which light is transmitted through the material. Light may, however, be transmitted via linear defects of photonic crystals. In case of the holey" optical fibres such a defect is a hollow core in the fibre axis. In order to produce the "holey" fibres rows of glass capillary tubes are extended at elevated temperature what results in diminution of their diameter and in sticking of the extended capillary tubes together (Fig. 14).

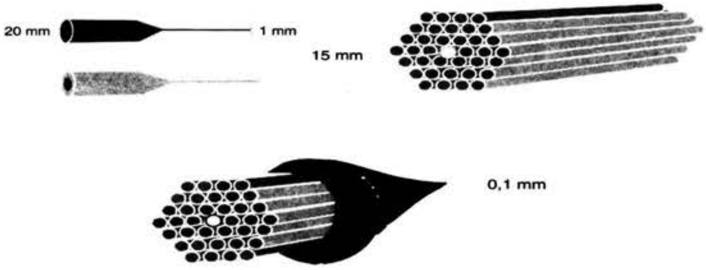


Fig.14. Production of "holey" optical fibres by drawing of glass capillary tubes

In the context of making miniaturised microprocessors based on photons it may be noted that photonic crystals in general and “holey fibres” in particular can transmit light without losses even when the light path changes by 90°. Such a situation is unavoidable in miniaturised microprocessors and not realisable even with modern conventional optical fibres.

Transmission of information by molecules in miniaturised devices has a great potential in many fields, beginning with molecular biology, biotechnology and medicine and ending with microreactors. From DNA sequencing and drug administration to high-temperature catalysed reactions producing thousands tons of product yearly. Volumes of fluids (gases, liquids) from μl to pl are tackled here. Therefore, the whole field is called microfluidics.

Our discussion of this subject shall be limited to microreactors for high-temperature catalytic reactions. Namely, ceramic materials are the obvious choice for such reactors owing to their thermal stability and resistance to aggressive environment.

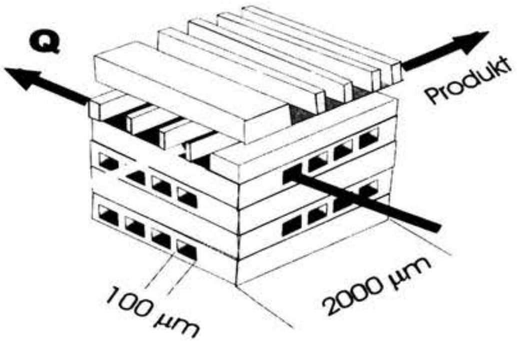


Fig.15. Ceramic microreactor; the walls of the microchannels are covered by a catalyst

Typical microreactors are constituted by piles of thin plates containing microchannels about 50-500 μm deep and up to 2000 μm long, usually covered by a catalyst. The fluids flow from one layer to another undergoing mixing, heat exchange and reactions. The flow is laminar and characterised by Reynold's numbers <100. Owing to this the resistance of flow is negligeable while the large surface to volume ratio of the fluids diminishes also the thermal resistance. This ensures a good thermal control of the reactions. These factors are advantageous for a realisation of catalysed reactions between fluids in a short time and high yields. A carrying highly exothermic reactions out near the explosion point becomes also feasible. The small volumes handled permit also a relatively safe synthesis of poisons.

References

1. Z. Bauman, K. Tester: O pożytkach z wątpliwości, transl. from English, Wyd. sic!, Warszawa (2003).
2. Z. Mróz: Nowe materiały, lecture presented at a Meeting of the Division of Technical Sciences, Polish Academy of Sciences, Warsaw, September (2003).
3. H. Tanimoto, S. Sakai, H.Mizybayash i Anelasticity of nanocrystalline metals, Materials Science and Engineering A, 370 (2004)135.
4. S. Wojciechowski, Aktualne problemy inżynierii materiałowej w obszarze nauki, techniki i kształcenia, Inżynieria Materiałowa, 23 (2003), 5.
5. M.Heule,S.Vuillemin,L.J. Gauckler, Powder-based meso- and microscale ceramic fabrication processes, Adv.Materials, 15 (2003) 1237.

6. M. Szafran, Nowe trendy w formowaniu ceramicznych mas lejnych, Prace Komisji Nauk Ceramicznych O/PAN w Krakowie, Ceramika 80 (2003) 62.
7. N. Setter, Electroceramics. Looking Ahead, Journal of the European Ceramic Society, 21 (2001) 1279.
8. S. Węgrzyn et al., Nano i kwantowe systemy informatyki, Wyd. Politechniki Śląskiej, Gliwice (2003).
9. Y. Xia, G.M. Whitesides, Soft lithography, Angew.Chemie Int.Ed. 37 (1998) 550.
10. R. Pampuch, Kompozyty ceramiczne, Kompozyty (Composites) 2 (2002) 1.
11. R. Pampuch, L. Stobierski, J. Lis, M. Rączka, Solid Combustion Synthesis of SiC, Materials Res. Bull. 22 (1987) 1225.
12. P. Greil, P. Cromme, C. Zollfrank, Biomorphous Ceramics from Cellulose Templates, Proceed. 8th Intern. Conference on Ceramic Processing and Technology, Hamburg 2002, 9.
13. K.H. Sandhage, F.M. Zalar, M.B.Dickerson, P.M. Huseman,
14. M.E.A. Schoenwaelder, Chemically-Tailored 3D Nanoparticle Structures via the BaSIC Process, Proceed. 8th Intern. Conference on Ceramic Processing and Technology, Hamburg (2002) 8.
15. S. Wojciechowski, Materiały inteligentne. Stan zagadnienia 2003 r., Inżynieria Materiałowa, 25 (2004)59.
16. R. Pampuch, L. Stoch, Materiały inteligentne: zaawansowane materiały ceramiczne i szkła, Inżynieria Materiałowa, 25 (2004) 76.
17. Information of the NEC Corporation (Japan) and IBM (USA) on the Internet, (2003) and (2004).
18. Proceed. IX. Conference “Światłowody i ich zastosowania” Krasnobród, Wyd. Politechniki Lubelskiej, Lublin (2003).