Recent developments of electrooptic and electrocaloric materials and devices

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Characteristic features of chemical composition and structure of transparent ferroelectric ceramics and electrocaloric ceramics have been revealed from the analysis of the known materials. Recent developments of some applications are discussed.

1. INTRODUCTION

Some decades ago transparency was a property of single crystals and glasses. The recent developments in chemistry of raw materials and the production of sub-micrometer-sized and reactive powders permitted to highly improve the quality and performance of other materials (ceramics, organic compounds). Now there are four main groups of bulk optical materials [1]: (i) inorganic glasses (SiO_2) , (ii) inorganic crystals ($LiNbO_3$, $BaTiO_3$, GaAs), (iii) organic compounds and polymers, (iv) polycrystalline materials or optical ceramics.

Glasses are very useful for many applications, but most of them can only be "passive" components in a device. Single inorganic crystals of large dimensions are difficult to grow and to shape and they are expensive. Organic compounds have recently assumed a more important role as active and passive materials in optics. However, the lower thermal stability, lack of hardness and poor optical transparencies are the negative features of organic materials.

The optical ceramics may be divided according to application into the following groups:(i) the passive ceramics (MgF_2 ,Al_2O_3 , MgO, used in infrared techniques for lenses, windows and other optical elements); (ii) luminescent ceramics (ZnS + Ag - for luminescent diodes) ; (iii) wavequide ceramics (TlBr - TlJ, AgBr-AgCl - for optical guides); (iv) scintillator ceramics (YAG + Ce (Gd) - for detectors of great size in industrial and medical tomography); (v) electrooptic ceramics (PLZT - used for modulators, switches, displays, etc).

The electrooptic effect is most pronounced in ferroelectrics and the electrooptic ceramics , as a rule, are based on ferroelectric (FE) materials and hence are often called transparent ferroelectric ceramics (TFC). Hereafter we regard TFC as a solid obtained by ceramic technology (in most cases hot-pressing), transparent in the visible and near infrared region and presenting either a spontaneous or induced electrooptic effect at room temperature.

TFC was first presented by C. Land and P. Thacher more than 20 years ago [2]. Now excellent book and rewiew articles about TFC are available [3-6].

The present report is an attempt to reveal common and specific features of TFC based on the ideas presented in Ref. [4]. We are paying attention mainly to the optical properties of TFC to understand why some compositions produced by hot-pressing become transparent and some do not. In addition we reveal recent most interesting trends of TFC applications. In the last section we give short revue about electrocaloric ceramics, which exhibit a distinct first order ferroelectric phase transition and are not transparent.

2.LIGHT TRANSMITTANCE OF CERAMICS

Generally single crystals or glasses are transparent in certain regions of the spectrum depending on their optical gap. Because of their polycrystalline structure and existence of pores ceramics scatter light more than most of the single crystals and glasses. This scattering effect is so high that conventional ferroelectric ceramics cannot be transparent. There are three main reasons for this [4].

2.1. Scattering on pores

Remaining pores due to a poor densification of the ceramics are strong scattering centers, because of the large gradient of the refraction index at the grain-pore boundary (Δn). According to the Ref. [7] the scattering index S is determined by

$$S = p \ a \ (\Delta n/n)^2 , \qquad (1)$$

where p is the bulk porosity, a- the mean size of pores, n- the mean refraction index.

2.2. Scattering on grain boundaries

An amorphous layer of the thickness 10 nm and more is observed at grain boundaries in conventional PZT ceramics. The amorphous phase is really not a ferroelectric and, thus,it has a small refractive index ($n \leq 1,5$). Because of the gradient of the refractive index at the boundaries of the grains with $n \approx 2,5$ and the amorphous layer, considerable reflection and refraction takes place causing a loss of light.If the number of such boundaries in fine-grained ceramics are taken into account, it is clear why the presence of amorphous phase make a ceramic material non transparent.

2.3. Scattering on anisotropic regions

As the orientation of the grains in a ceramics is randomly distributed, the optical axes of the grains are not aligned. The same occurs for domains, the size of which is much smaller as in single crystals. To describe a macroscopically homogeneous case of scattering we use a model, where the micro structure of the ceramics is described as a periodic sequence of layers of crystalline domains [8]. The model shows, that light transmission is determined by the domain size and spontaneous birefringence of a domain - Δn_s. For many TFC compositions with sub micron domains the transparency is provided by [4]:

$$\Delta n_s \leq 0,01. \qquad (2)$$

Since $\Delta n_s \sim P_s$, where P_s - the spontaneous polarization, the scattering at optically anisotropic regions essentially depends on the temperature decreasing to zero at $T = T_c$, where $P_s = 0$.

All these facts show that obtaining transparent ceramics is difficult goal to reach.Generally light transmittance of the ce-

ramics depends on the choice of material and its production technology.

2.4. Choice of the composition

With a choice of the material we can eliminate the reason 2.3. and decrease the reason 2.1. to a certain amount.

Really, if we use composition whose FE phase transition temperature T_c is below the room temperature, than $\Delta n_s = 0$ - there are no optically anisotropic regions at 20°C. Polar micro regions, obtained in relaxor materials at $T \geq T_m$, have very small size [9] and cause no scattering. Further we replace T_c with T_m - the temperature of $\varepsilon(T)$ maximum, which is correct for materials with a sharp FE phase transition.

More than 700 compositions of TFC of oxygen octahedra FE with perovskite or tungsten bronze structure, which are already known to us, are characterized by $T_m \leq 100 °C$ (see Fig. 1 in Ref. 4 and Table 1)

The typical way to get TFC from the PZT system is shown in Fig. 1. By introducing a second component x to PZT the FE phase transition temperature decreases and the transparency of the sample, measured at room temperature, increases due to decreasing of Δn_s.
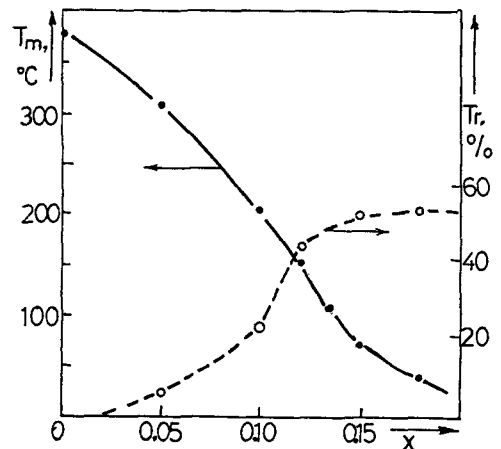

Figure 1. The temperature of $\varepsilon(T)$ maximum and transparency at 450 nm of 0,25 mm thick sample at room temperature versus concentration x for solid solution (from data rep. in [10]) $xBa(Sr_{1/3} Nb_{2/3}) O_3 - (1-x) Pb(Zr_{0,5} Ti_{0,5})O_3$

Table1
New compositions of TFC (supplement to the table 1 from Ref. [4])
MO - mixed oxide method; HP - hot pressing; Ω - order parameter for heterovalent ions.
Other compositions, not based on PZT ceramics

Composition and technology	T_m, °C	Transp. λ =600nm	References
$Pb(Mg_{0,3}Nb_{0,6}Ti_{0,1})O_3$; sol gel; 1200 °C	40	32	11,12
0,93 $Pb(Mg_{1/3}Nb_{2/3})O_3$ - 0,07 $PbTiO_3$; by columbite method with HP: 1100°C;+2% PbO	34	2	13
900°C; +2% PbO; +1%La_2O_3	15	35	
1100°C; +2%PbO; +1%La_2O_3	13	42	
$xPbSc_{1/2}Nb_{1/2}O_3$- (1-x) $PbMg_{1/3}Nb_{2/3}O_3$; from MO; HP : 1200 - 1300 °C x=1,0	93	43	14
x=0,9	85	46	
x=0,7	54	50	
x=0,3	18	41	
$xPbSc_{1/2}Nb_{1/2}O_3$ - (1-x) $PbZn_{1/3}Nb_{2/3}O_3$; from MO; HP: 1200 - 1300 °C x=0,9	79	50	14
x=0,7	58	45	
$PbSc_{1/2}Ta_{1/2}O_3$; from $ScTaO_3$; Ω=0,9 ; HP:			13
1050 °C; +10%PbO	23	45	
1200 °C;+ 2%PbO	22	1	
1250 °C;+ 2%PbO	22	22	
0,875 $PbSc_{1/2}Ta_{1/2}O_3$ - 0,125 $PbZrO_3$; from $ScTaO_3$;Ω=0; HP: 1200 °C; +5%PbO	64	70	15
$(Pb_{1-y}Ba_y)La_xNb_{2-x/5}O_6$; from MO; HP; x=0,08; y=0,58	30	64	16
x=0,09; y=0,55	40	48	

The most of TFC compositions are build up by the use of heterovalent dopants or from the compounds containing heterovalent ions at equivalent lattice points (see Table 1 in [4] and in this paper).There are two common ways of modification: (i) modification by donor dopants when the valence of dopant is higher than the valence of ions to be substituted; a typical example is PLZT ceramics, where Pb^{2+} is substituted by La^{3+}; (ii) modification by compensated heterovalent dopants, e. g. half of Pb^{2+} ions is substituted by Li^{1+} and half by La^{3+} . In the first case, at the introduction of donors only , the region of solvability is determined by vacancy formation providing quasyneutrality. The region of solvability is essentially increased by simultaneous introduction of several dopants with compensated valence. A characteristic result of modification by all these dopants is lowering of the T_m and spontaneous deformation of the lattice at room temperature (see Fig. 1 and 5 in [4]). Both the factors decrease Δn_s - the transparency being increased (Fig.1).

On the other hand, if the concentration of dopants increases, FE phase transition changes from the normal (sharp) to the diffused one. Therefore the most of TFC compositions have diffused FE phase transitions and relaxor properties. The only exception to this general rule is ordered $Pb(Sc_{1/2}Ta_{1/2})O_3$ (PSN), which has 45% transparency (Table 1). Samples of PSN ceramics, produced in our laboratory for electrocaloric experiments with order parameter $\Omega=0,88$, was not transparent. The main reason why relaxor materials favour the transparency is the absence of macroscopic phase change below T_m, therefore $\Delta n_s=0$ and the reason 2.3 do not work.

The other mechanism which favours eliminating of pores (reason 2.1) and depends on the choice of composition is an increase in the vacancy concentration. According to Ref. [17] the one of the basic mechanism of pore healing is the vacancy by vacancy solution of a pore in the surrounding medium followed by a diffusion of the vacancies to the nearest sink (surface, grain boundary). The concentration of vacancies is increased by heterovalent modification and by use compounds containing heterovalent ions at equivalent lattice points [18], therefore ceramics, containing heterovalent ions, are more transparent. Multicomponent compositions are characterized by a large set of ions and a higher concentration of point defects (vacancies included) as compared with simple compositions. For this reason the former are more transparent. It is essential to note, that we have not succeeded in obtaining TFC with a simple composition as $SrTiO_3$ and $BaTiO_3$.

Individual properties of dopants do not have large influence on the properties of TFC. So in the case of PLZT, PZT is modified by La^{3+} ions and vacancies, while in the case of $[xBa(Ca_{1/3}Nb_{2/3})O_3-(1-x)PZT]$ PZT is modified by Ba^{2+}, Ca^{3+} and Nb^{5+} ions. It was found that this two kinds of dopants play nearly the same roles in modifying PZT and determining dielectric and optic properties in phase transition region [19,20].

On the other hand PLZT ceramics has an outstanding place between other TFC compositions. First at all it is presently the only electrooptic ceramics sold commercially, and second - it is a model material for TFC and relaxors.

2.5.Production technology.

The processing of a TFC consists of two main steps: powder preparation and densification. The powder preparation methods can be traditional mixed oxide (MO) and chemical co-precipitation (CP) [5]. CP materials generally provide a purer, more homogeneous, smaller particle size and more reactive powder than the MO counterpart. However CP processing is more expensive.

The densification is controlled consolidation of the powders into a dense ceramics with little or no pores and a highly uniform microstructure. The densification is achieved by hot-pressing [5,6] or atmosphere sintering [5,6,21,22]. Hot-pressing still seems to be used worldwide and is the most practical method for achieving high optical transparency and high reliability and reproducibility. Its disadvantages include high initial capital costs and higher product costs.

Production technology allow to avoid the amorphous phase on the grain boundaries (reason 2.2) and sufficiently decrease the size and concentration of pores (reason 2.1).

Really, the forming of the amorphous phase is avoided by the use of high purity raw materials [23].High resolution electron microscopy pictures show that there are no amorphous phase on the grain boundaries in PLZT ceramics [24,25]. The grain boundaries in TFC may be regarded as dislocation network with an increased impurity concentration and shared atoms [25].

Besides the vacancy mechanism of pore healing, mentioned in section 2.4., there are other mechanisms of densification. The main idea is that porosity must be eliminated before it becomes trapped within the grains. Therefore factors inhibiting grain growth at the initial stage favours densification. One of those factors is hot-pressing: the stress in hot-pressing inhibit grain growth. The second one is excess PbO, which forms a liquid phase on

grain boundaries and inhibit grain growth. In lot of lead containing compositions excess PbO gives higher transparency (Table1).

It is interesting to note, that all technological tricks used in order to increase the dielectric constant ε simultaneously increase the transparency too [13,14,26].

The characteristic features of electrooptic effect and phase transitions of TFC have been reported in [37].

3.RECENT APPLICATIONS OF TFC

Hereafter we report on new applications, not described in rewiews [5,6].

Variable focal-length lens on the base of large electrooptic effect in PLZT 9/65/35 (the notation refers to atomic % La/Zr/Ti) is presented in [27]. The lens is composed of a rectangular parallelepiped with stripe electrodes formed on both surfaces and a laser beam is incident on the lens along the stripe electrodes. The one-dimensional lens have a high frequency response up to about 400 kHz, verifocal length ranging from infinity to about 5 cm. The two-dimensional lens can focus the laser beam into a spot.

In the University of Latvia a cheap PLZT 9,75/65/35 laser beam modulator - small in size, with short optical length (1,5mm),simple in adjusting and use were offered mostly for didactic purposes - e. g. for the demonstration of the Kerr transversal quadratic electrooptic effect [28]. Till now Kerr-effect in schools have been demonstrated with the cell containing dangerous chemical agent (nitrobenzene). Beside this nitrobenzene cell has a high half wave voltage ($U_{\lambda/2}$=3000V), but for PLZT $U_{\lambda/2}$ is 600V only. Experimental setups for the use of PLZT modulator for the measurement the speed of light and the transmission of acoustic signals trough laser beam are given in [29].

Next device, developed on the base of this modulator, is computer controlled laser illumination system [30]. For this system modulator [28] is improved with optical feedback. Computer simulates the control signal - how the intensity of laser beam must change in time. New set-up together with the improved PLZT modulator gives optical

response adequate to the computer control signal. Technical characteristics: gray scale levels - not less than 40, the minimum step duration - 1mS. The system can be used in medicine and biology.

A special field concerns optical sensors. The acoustic pressure was detected in silicone oil utilizing birefringence change of PLZT9/65/35 [31]. A linear relationship between the output signal and acoustic pressure was obtained in the range of acoustic pressure from 146 to 186 dB.

It is discovered unusual form of optical bistability in hot-pressed ceramic $Pb(Mg_{0,3}Nb_{0,6}Ti_{0,1})O_3$ (PMN) in which the thermal focussing of laser light at very low power densities (kW/cm^2) oscillates between two metastable states [12,32]. The oscillation event times are strongly dependent upon convection from sides of the PMN thermal lens. Therefore the device acts as an optical sensor for pressure and flow rate of the surrounding atmosphere.

The micro miniaturization of devices and the needs in integrating different types of materials (FE and semiconductor) are creating more interests in the preparation of PLZT thin films. Recently *Sandia* has developed some optical devices [33]: optical comparator with high resolution(1 pixel/μm^2) and rapid response time; erasable/rewritable optical disc, which uses PLZT film with a stable antiFE phase and field induced metastable FE phase; spatial light modulator which works by electrically controlled reflection in thin PZT film.

4. ELECTROCALORIC MATERIALS

The electrocaloric effect (ECE) is a general property of dielectrics to change their temperature under applied electric field and adiabatic conditions. A possible application is in cascade EC refrigeration [34].A large value of ECE ($\Delta T \geq 1°C$) is expected at the field-induced 1-st order phase transition in FE [35], the temperature change ΔT being evaluated from thermodynamic relation:

$$\Delta T = T_c/C_e \; dE_{cr}/dT \; \Delta P_s , \qquad (3)$$

where C_e is specific heat capacity, ΔP_s - jump of spontaneous polarization at $T=T_c$,while

derivative describes the shift of T_C due to electric field. From (3) it follows that one can find ECE materials among FE, characterized by a large jump of ΔP_S. Precision X-ray investigations show that structural phase transition from cubic to rhombohedric R3m phase in $Pb\,Sc_{1/2}\,Ta_{1/2}O_3$ (PST) with a high degree of ordering of scandium and tantalate ions ($\Omega=0,85-0,90$) has large ECE. With values $dE_{cr}/dT=0,638$ kV/(cmK) and $P_S=0,21Cm^{-2}$ the calculation of the contribution of the 1-st order phase transition to the ECE gives the value of $\Delta T=1,6K$, which justifies the choice of the PST as an active element of the EC cooling devices [34].

Characteristic dependencies of ECE on the temperature and electric field are shown in [35,36] . To do a cascade of ECE elements it is necessary to change T_C for every element. This is achieved by simultaneous or separate introducing Sb and Co ions in B-sites of the lattice [36], as well as by annealing (~1500°C) with very slow cooling.

ACKNOWLEDGEMENTS

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