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Application of the sol-gel method to the synthesis of ferroelectric nanopowders $(Pb_{1-x}La_x)(Zr_{0.65}Ti_{0.35})_{1-0.25x}O_3$, $0.06 \leq x \leq 0.1$

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The aim of this study was to prepare pure, dense and transparent lead–lanthanum zirconate–titanate (PLZT) ceramics. The PLZT ceramics was sintered by the hot-pressing method from sol-gel derived powders. The samples obtained exhibited lack of voids, and the density close to the theoretical X-ray values. They were homogeneous from the chemical and physical points of view and exhibited stoichiometric chemical compositions. Dimensions of the crystallites depended on the temperature of sintering of the amorphous nanopowders. Dielectric and ferroelectric properties of the nanocrystalline PLZT ceramics were studied and relationships between their properties and processing conditions were revealed.

Key words: *sol-gel method; nanopowders; ceramics; PLZT; ferroelectric properties*

1. Introduction

Application of proper technological methods to the fabrication of ceramic powders is one of the factors improving the control of the stoichiometry of materials, influencing the properties of ferroelectric ceramic materials. The sol-gel method is a low-temperature process, which utilizes chemical precursors and makes it possible to obtain fine powders that exhibit high chemical reactivity, as well as better purity, homogeneity and physical properties than those fabricated by conventional high-temperature processes.

The lead–lanthanum zirconate–titanate (PLZT) ceramics is one of the ferroelectric materials, which is successfully obtained by the sol-gel method. The chemical composition of PLZT is given by the formula [1]:

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$$(Pb_{1-x}La_x)(Zr_{1-y}Ti_y)_{1-0.25x}V_{0.25x}O_3 \quad (1)$$

The formula takes into account the charge compensation, assuming that the electrical neutrality is maintained by the creation of (Zr, Ti) vacancies (*V*). The concentration of La, $x = La/(La + Pb)$, may vary from 0.02 to 0.3. The ratio *y* of Zr/(Zr + Ti) may take any value from 0 to 1. The composition of PLZT is usually represented by the notation $x/(1 - y)/y$, which denotes the amounts of La/Zr/Ti, given in mole fractions or mole per cent (i.e. mole fraction multiplied by 100). For instance, the notation 8/65/35 represents PLZT with the chemical composition $(Pb_{0.92}La_{0.08})(Zr_{0.65}Ti_{0.35})_{0.98}O_3$ [2].

Lanthanum-doped lead zirconate–titanate ceramics, with variable dopant concentration and the ratio of Zr/Ti exhibit a variety of phases such as ferroelectric (FE), antiferroelectric (AFE), paraelectric (PE) and mixed (MPh) phases, shown in the room temperature phase diagram in Fig. 1 [3, 4].

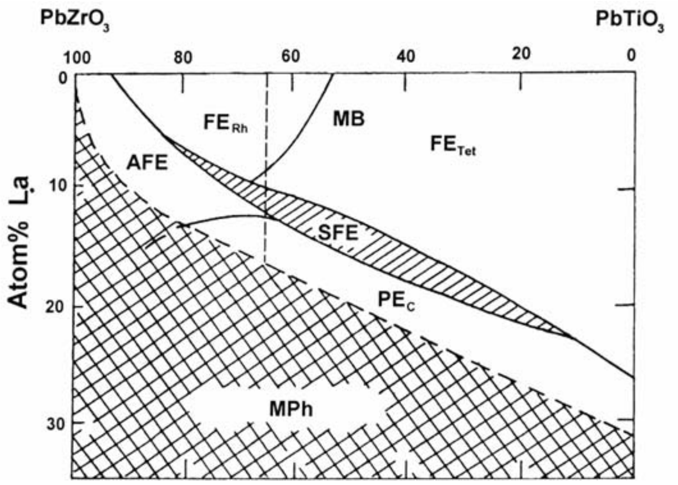

Fig. 1. Phase diagram of the PLZT system at room temperature [3]

The doping of La to the basic PZT system results in many effects such as enhanced dielectric and piezoelectric properties, increased squareness of the *P–E* hysteresis loops, decreased coercive field (E_c) and transparency [5].

The advantages of this material include not only the optical transparency, but also a fast response, multicolour capability and electrooptic properties. Solid-state nature of the material is based on the simple $PbZrO_3$–$PbTiO_3$ (PZT) solid solution system, the function of the La concentration as well as the Zr/Ti ratio, i.e., the *x*/65/35 composition yields the most transparent ceramics for La concentrations in the range of 8–16 mole per cent [2].

Nanocrystalline PLZT materials obtained from the sol-gel derived powders exhibit some features substantially increasing possibilities of their application in electronic and opto-electronic devices such as: segment displays, light shutters, coherent modulators, colour filters, linear gate arrays and image storages. As a result, they have been widely investigated [6].

The goal of this study was: (i) to utilise a modified sol-gel method for obtaining amorphous PLZT nanopowders with the chemical composition corresponding to the x/65/35 ratio, where x = 6–10 mole per cent of La, (ii) to obtain transparent ceramics by the hot-pressing method, and (iii) to study their structure and basic dielectric properties.

2. Experimental

The technological process of fabrication of the PLZT ceramics included two basic stages. In the first stage, a modified sol-gel process was employed to obtain amorphous nanopowders of the ferroelectric PLZT ceramics with the following chemical compositions:

- $(Pb_{0.94}La_{0.06})(Zr_{0.65}Ti_{0.35})_{0.985}O_3$, 6/65/35 PLZT,
- $(Pb_{0.93}La_{0.07})(Zr_{0.65}Ti_{0.35})_{0.9825}O_3$, 7/65/35 PLZT,
- $(Pb_{0.92}La_{0.08})(Zr_{0.65}Ti_{035})_{0.98}O_3$, 8/65/35 PLZT,
- $(Pb_{0.91}La_{0.09})(Zr_{0.65}Ti_{0.35})_{0.9775}O_3$, 9/65/35 PLZT,
- $(Pb_{0.9}La_{0.1})(Zr_{0.65}Ti_{0.35})_{0.975}O_3$, 10/65/35 PLZT.

The second stage involved consolidation of the prepared powders and obtaining fine-grained PLZT ceramics by the hot-pressing method.

As the initial materials, the following high-purity organometallic salts of precursors were chosen:

- lead(II) acetate trihydrate, $Pb(COOCH_3)_2{\cdot}3\ H_2O$,
- lanthanum acetate hydrate, $La(COOCH_3)_3{\cdot}H_2O$,
- zirconium(IV) propoxide, $Zr(OCH_2CH_2CH_3)_4$,
- titanium(IV) propoxide, $Ti(OCH_2CH_2CH_3)_4$,
- *n*-propyl alcohol as a solvent,
- acatyloacetone as a stabilizing agent.

The processes used for preparation of PLZT are presented in the flow chart (Fig. 2).

The stoichiometric mixture of the components was disolved in *n*-propyl alcohol and then heated for 2 h below the boiling point of the solution. As a result of the reaction the alkoxide complexes and an organic ester were formed. The by-product of the synthesis (the ester – propyl acetate) was removed by simple distillation. The condensed form of the by-product needed an addition of the solvent and the stabiliser to form a sol. Distilled water was used to activate the reaction of hydrolysis. A gradual colloidal gel formation was then observed. The colloidal sol-gel system was IR -dried and calcined at T = 873 K. The calcined powders (i.e., the powders without organic components) consisted of small particles and agglomerates of nanoparticles. The powders were ground, mixed and sintered by the hot-pressing method at the temperature verified experimentally, T_s = 1473 K for 2 h.

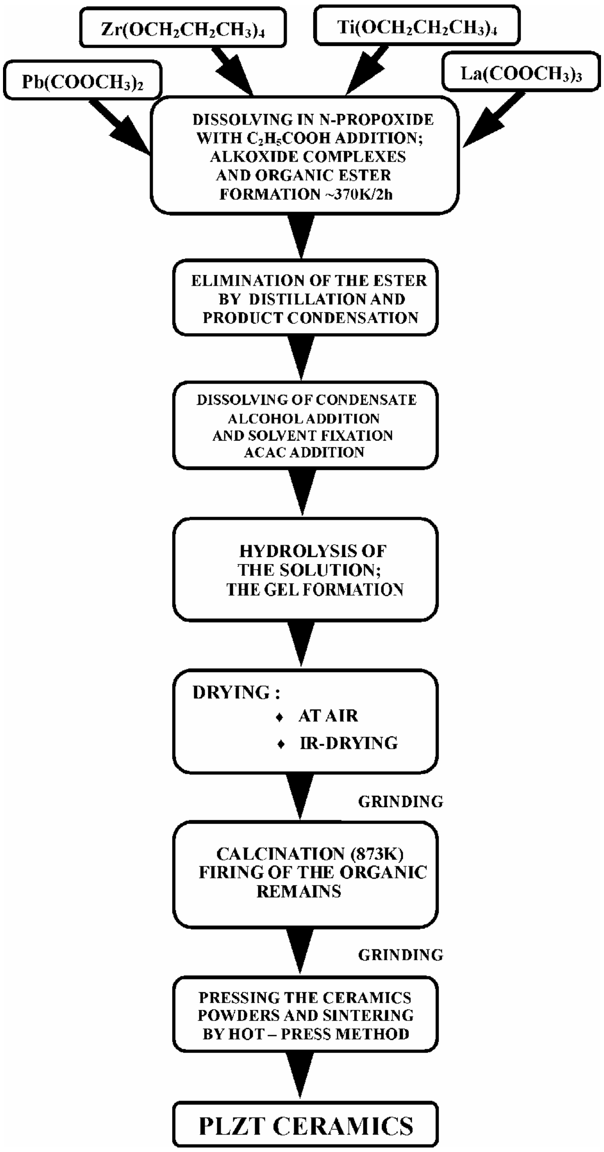

Fig. 2. Flow chart of the preparation of PLZT ceramics

X-ray analysis (Philips PW 3710 diffractometer, Θ–2Θ geometry, $CuK_{\alpha1}$ radiation) was used to characterise the structure of the PLZT samples (the calcined powders and the hot-pressed ceramics were studied). Electrodes were formed with a silver paste on disk-shaped ceramic samples. A Tesla BM 595 RLCG meter was used to perform measurements of temperature dependences of the electric permittivity ε and the dielectric loss tangent $\tan\delta$. The dielectric hysteresis loops were recorded with the Sawyer–Tower method.

3. Results and discussion

X-ray spectra were recorded for the powdered gel, the calcined powder (i.e., the powder devoid of organic remains) and the powdered PLZT ceramics obtained by the hot-pressing method. Figure 3 presents the thermal evolution of the crystal structure of the 8/65/35 PLZT material. The X-ray pattern of the IR-dried powdered gel indicates the presence of the diffraction lines originating from the organic remains. Their calcination ($T = 873$K) leads to the crystallisation of PLZT in the rhombohedral symmetry. The crystal structure was identified as a rhombohedral one with the space group $R3m$ and the parameters of the unit cell equal to $a_h = 0{,}5745$ nm and $c_h = 0{,}7060$ nm (the hexagonal setting was used for the indexing).

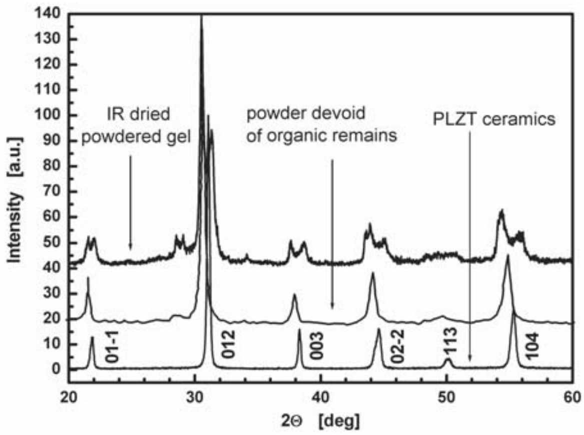

Fig. 3. X-ray powders diffraction diagrams of 8/65/35 PLZT at 3 stages of the ceramics preparation

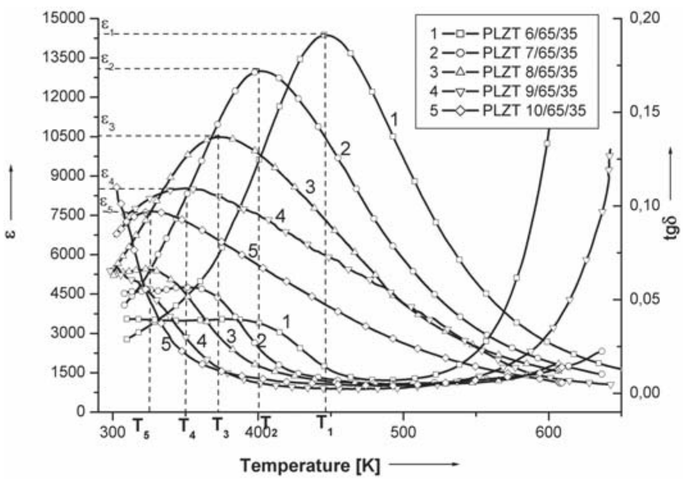

Fig. 4. Temperature dependence of the relative electric permittivity ε and the dielectric loss tangent tanδ for the selected PLZT compositions with Zr/Ti = 65/35

The dielectric parameters (the electric permittivity ε and the dielectric loss tangent $\tan\delta$ were measured by the bridge method. The results are shown in Fig. 4.

As can be seen in Fig. 4, the increase of the La content reduces the height of the dielectric constant peak and makes it more diffuse. A significant change in the maximal temperature of the peak (the table) is also observed. The loss tangent increases with the increase of the La content. It reaches the maximum values of $\tan\delta = 0.02$ and $\tan\delta = 0.06$ for x = 0,06 and x = 0.10, respectively. The results obtained are typical of materials exhibiting diffuse phase transitions.

Table. Selected properties of the PLZT ceramics

Composition	Density [g/cm^3]	T_0 [C°]	T_m [°C]	ε_m
PLZT 6/65/35	7.715	222	189	13570
PLZT 7/65/35	7.705	168	143	12590
PLZT 8/65/35	7.660	120	108	9980
PLZT 9/65/35	7.630	64	83	8550
PLZT 10/65/35	7.550	16	60	7370

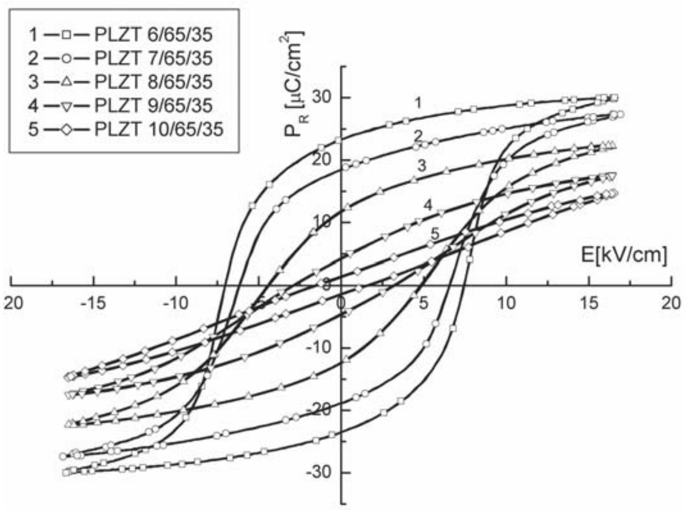

Fig. 5. *P–E* hysteresis loops of the PLZT *x*/65/35 ceramics (for x = 6–10 La mole per cent) measured for 1 Hz at room temperature

Ferroelectric properties of PLZT ceramics obtained by the hot-pressing method from the sol-gel derived powders have been proved by the ferroelectric hysteresis loops. The results of these investigations are presented in Fig. 5. Remanent polarization and coercive field have been measured at the frequency of ν = 1 Hz at room temperature. Figure 5 shows that the increase in the La mole fraction from 0.06 to 0.1

(for the constant Zr/Ti ratio) results in disappearance of the hysteresis loop. Our investtigations showed that the application of the hot-pressing method to consolidation of sol-gel derived powders and sintering of ceramics makes it possible to prepare transparent PLZT materials. Figure 6 shows a selected sample of PLZT 10/65/35 material exhibiting a good optical transparency.

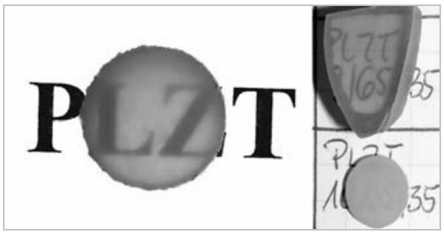

Fig. 6. Optical transparency of the PLZT 10/65/35 ceramics

4. Conclusions

By employing the sol-gel method, amorphous nano-powders of PLZT ceramics were obtained. Transparent PLZT ceramics, exhibiting rhombohedral symmetry, have been obtained by means of the hot-pressing method. The ferroelectric properties of the sintered ceramics have been proved by measurements of the ferroelectric hysteresis loop. Dielectric, ferroelectric and optical properties (i.e., transparency in the visible region) of PLZT ceramics prove high quality of the obtained ceramics.

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