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Application of the sol-gel method to deposition of thin films

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A method for synthesizing ferroelectric thin films of lead zirconate-titanate (PZT) and lead-lanthanum zirconate-titanate (PLZT) by a modified sol-gel technique is reported. The following chemical compositions with the Zr/Ti ratio were obtained: PZT 65/35 and PLZT 6.5/65/35. Thin films, prepared from acetate and alkoxide precursors of La, Pb, Zr and Ti, were deposited on stainless steel and MgO substrates by spin coating. Crystallization of PZT-based electroceramic thin films was performed by thermal annealing at the temperature range of 550–700 °C. The structure of the thin films was investigated by X-ray diffraction. The formation of the perovskite-type structure was confirmed. Microstructure was investigated by the optical microscopy. Technological conditions of the preparation of thin films were optimized.

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

1. Introduction

Metal oxides with the perovskite structure are very important materials for technological applications due to their ferroelectric properties. An increasing interest in lead zirconate-titanate $Pb(Zr_x Ti_{1-x})O_3$ (PZT) thin films has been observed for such applications as nonvolatile ferroelectric memory elements, sensors and optical devices. These applications are possible due to a high capacity of load storage, low coercive field and large thermal stability of PZT with compositions near the morphotrophic phase boundary (MPB). In practice, the MPB of PZT ceramics exists over a defined range of x ($x \sim 0.53$) and involves a coexistence of the tetragonal and rhombohedral phases due to variations of the composition. These variations give rise to local differences in the lattice parameters, which have a strong influence on the ferroelectric properties [1].

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The method of the sol-gel fabrication of ferroelectric thin films gained much interest because of its simplicity, low processing temperature, stoichiometry control and its ability to produce uniform, chemically homogenous films over large areas that can provide integration with other circuit elements. The sol-gel method can be successfully used for preparation of pure oxides applied in electronics, optics, as ceramics for utilization of radioactive wastes as well as filters in chemical and food industries. During the last few years, this method has also been applied to the synthesis of high-temperature superconductors (HTSC). Lead zirconate-titanate films have a wide range of applications, which include pyroelectric sensors [1, 2] and infrared thermal imaging devices, micro-electromechanical devices and ferroelectric random-access memories (FeRAM). Thin films for these applications must have a reproducible stoichiometry, fine homogeneity of compact structures and good electric properties. Moreover, processing of thin films must be compatible with the planar technology of semiconductors. These properties can be obtained for ferroelectric thin films deposited by the sol-gel technique [3].

The purpose of the research presented in this paper was to grow perovskite-type PZT and PLZT thin films on both, metal and single crystal substrates by the modified sol-gel technique, as well as to identify their crystal structures and microstructures.

2. Experimental

For the preparation of PZT material, metal organic precursors such as lead(II) acetate $Pb(CH_3COO)_2{\cdot}3H_2O$, zirconium(IV) propoxide, $Zr(OCH_2CH_2CH_3)_4$, titanium(IV) propoxide, $Ti(OCH_2CH_2CH_3)_4$ were used. For the preparation of PLZT material, a lanthanum containing metal-organic precursor, lanthanum(III) acetate, $La(CH_3COO)_3{\cdot}H_2O$, was also used. In the latter case, the chemical reaction can be written as:

$$(1-x)\mathrm{Pb(OAc)_2} + x\mathrm{La(OAc)_3} + (1-0.25x)[(1-y)\mathrm{Ti(O{-}}n\mathrm{Pr)_4}] \rightarrow (\mathrm{Pb}_{(1-x)}\mathrm{La}_x(\mathrm{Zr}_y\mathrm{Ti}_{(1-y)})_{(1-0.25x)} + n\mathrm{PrOOAc} \tag{1}$$

where the coefficient $0.25x$ comes from the demand for the electrical neutrality of PLZT. The electrical neutrality is maintained by the creation of $0.25x$ of (Zr, Ti) vacancies (x is the mole fraction of La used for ceramic preparation). The ratio y of Zr/(Zr + Ti) may take any value from 0 to 1 (y is the mole fraction of Zr used for ceramic preparation).

n-Propanol was used to dissolve all compounds and to form a solution. The synthesis was carried out in the argon atmosphere by heating the solution for 2 h below the solvent boiling point to form alkoxide complexes. The by-product obtained (propyl acetate ester) was removed from the solution by distillation. After cooling the reaction mixture to room temperature, *n*-propanol and acetyloacetone were added. The mixture was then hydrolysed (distilled water was used to activate the hydrolysis reaction) and a colloid solution was formed. In few minutes, the sol-gel system was formed. The PZT and PLZT thin films were deposited on stainless steel and MgO substrates by spin coating. Crystallization of PZT- and PLZT-based ceramics thin films was performed by thermal annealing at temperatures ranging between 550 and 700 °C [4–6]. The whole process is presented in Fig. 1.

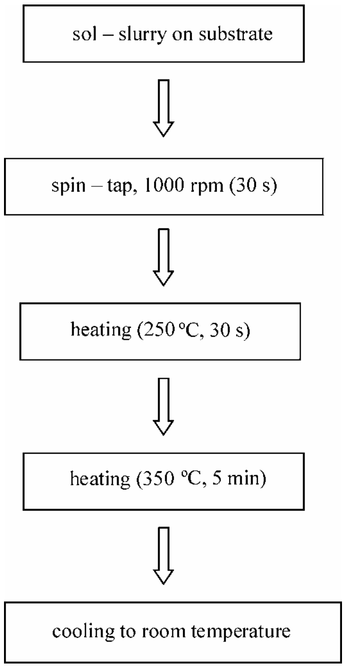

Fig. 1. Flow chart of preparation of PZT and PLZT thin films

2. Results

The crystal structure of the thin films was investigated by the X-ray diffraction method (X′ Pert Philips PW 3710 diffractometer, Θ–2Θ geometry, CuK_α radiation). Figure 2 shows the X-ray diffraction pattern recorded for a PLZT thin film grown on an MgO substrate. The strong line at $2\Theta = 43°$ originates from the MgO substrate. The other experimental diffraction lines correspond well to the assumed *R*3*m* space group. Parameters of the unit cell have been found as follows: $a_h = 0.5781$ nm, $c_h = 0.7081$ nm.

In Figure 3, the XRD pattern of the PZT thin film deposited on a stainless steel substrate is presented. The pattern was identified as a mixture of the rhombohedral *R*3*m* phase with the following parameters of the elementary cell: $a_h = 0.5802$ nm, $c_h = 0.7085$ nm and the tetragonal *P*4*mm* (group No. 99) unit cell with: $a_t = 0.4047$ nm, $c_t = 0.4132$ nm.

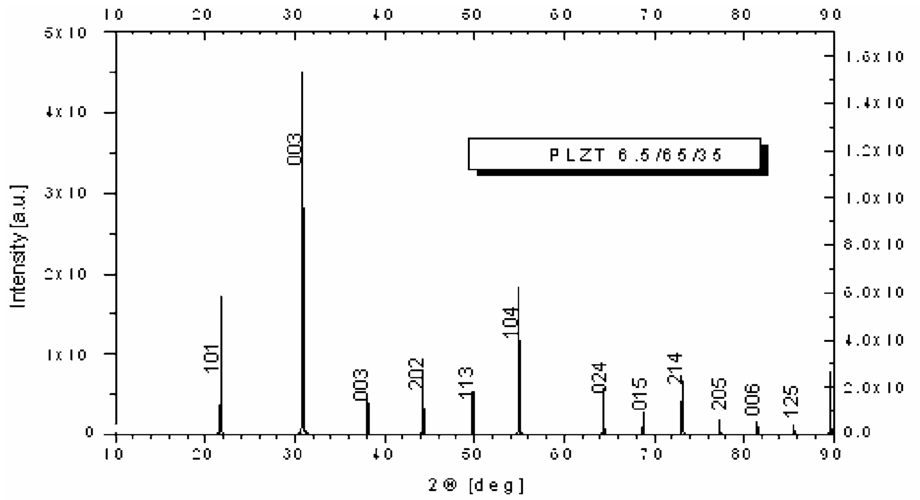

Fig. 2. X-ray diffraction pattern of PLZT on MgO

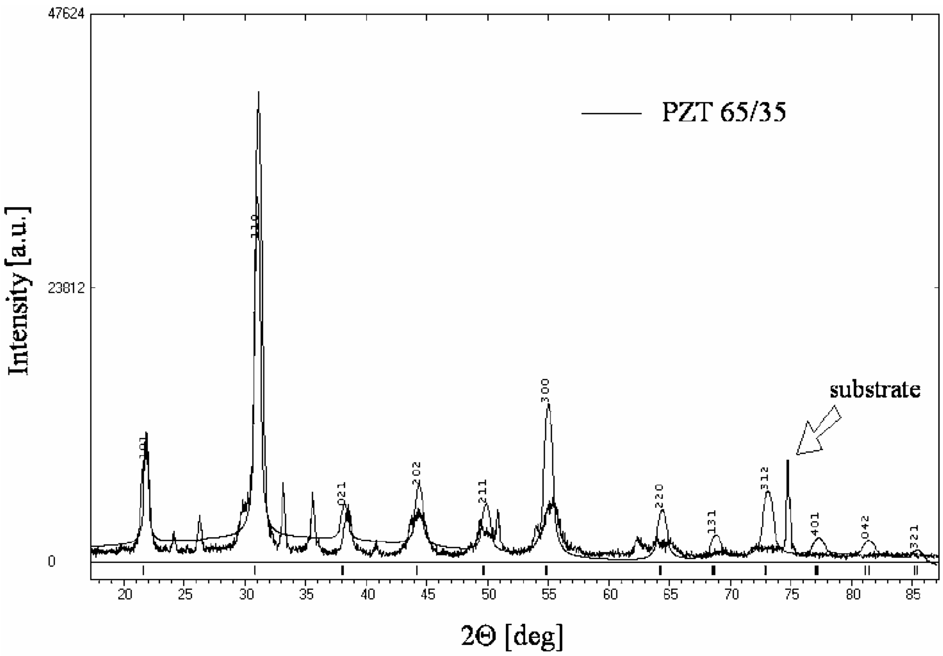

Fig. 3. X-ray diffraction pattern of PZT on stainless steel

The structure was identified as a mixture of the tetragonal and rhombohedral phases, their amounts depending on the technology of fabrication. The rhombohedral (101) (110) peaks were detected in the PLZT and PZT thin films. This indicates that the morphotropic phase boundary moved toward the Ti-rich composition and the PZT 65/35 film contained only the rhombohedral structure [5].

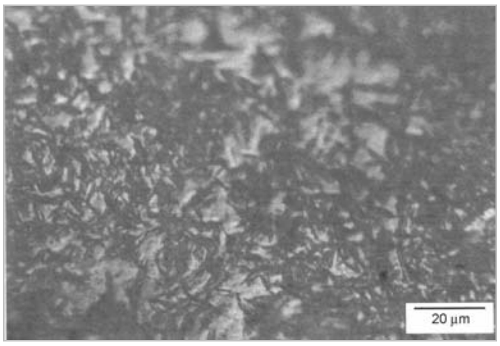

Fig. 4. Microstructure of PLZT film on MgO

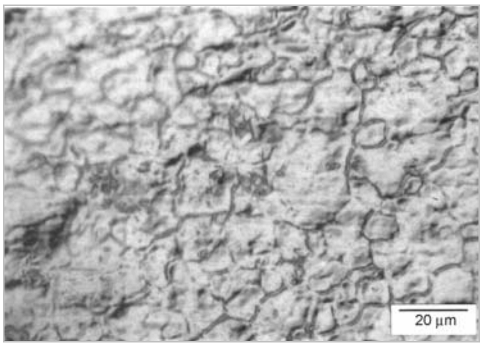

Fig. 5. Microstructure of PZT film surface on stainless steel

Both films exhibit a dense microstructure with no cracks (Figs. 4 and 5). The results of the investigations suggest that our modified sol-gel technique can prevent the formation of cracks and yield dense microstructures of the perovskite type for both PZT and PLZT thin films on metal and single-crystal substrates [7].

3. Conclusions

The purpose of the present research was to grow perovskite-type PZT and PLZT thin films on both metal and single-crystal substrates by a modified sol-gel technique, as well as to investigate their crystal structures and microstructures.

All the preparation steps, including the coating procedure, are relatively simple and can be carried out in the air. The fabricated films are dense and crack-free. The crystal structures of PZT and PLZT depend on the process of fabrication. A mixture of tetragonal and rhombohedral structures was identified for PLZT, whereas PZT thin films contained only the rhombohedral phase.

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