Rare-Earth-Doped PbTiO₃-PbZrO₃ Solid Solutions

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Abstract—(Pb_{1-x}Ln_x)(Zr_{0.53}Ti_{0.47})O₃ and (Pb_{1-x}Ln_x)(Zr_{0.65}Ti_{0.35})O₃ (x = 0.02, 0.06; Ln = La, Pr, Gd, Yb) solid solutions have been prepared by modified solid-state synthesis using organic-ligand precursors. The solid solutions have been characterized by thermal analysis, IR spectroscopy, x-ray powder diffraction, and atomic force microscopy. All of them have a rhombohedrally distorted perovskite structure (sp. gr. *R*3*c*).

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INTRODUCTION

Lead zirconate titanate (PZT) solid solutions are noted for their advantageous physicochemical properties. Owing to the morphotropic transition in the PZT solid-solution system, the morphotropic phase boundary (MPB) compositions exhibit a stronger piezoelectric response. The study of MPB solid solutions is not only of scientific interest but also of technological importance in creating novel memory devices [1]. PZT solid solutions are commonly prepared by solid-state reactions [1]. Considerable research effort has been concentrated on the MPB and dielectric properties of PZT ceramics [2, 3]. Of particular interest are materials doped with donors, such as La³⁺, Nb³⁺, Bi³⁺, Nb⁵⁺, and W⁶⁺, which typically increase the remanent polarization, dielectric permittivity, piezoelectric sensitivity, and pyroelectric coefficient of PZT-type materials. On the other hand, acceptor doping (e.g., with Mg^{2+} , Fe^{2+} , K⁺, Mn²⁺, or Mn³⁺) reduces the dielectric loss and impairs the mechanical and electrical properties of PZT. In view of this, use has been made of codoping with two or more elements [4]. The properties of PZT can be controlled both by varying the Zr/Ti ratio and by overstoichiometric doping. In a number of recent studies, the physicochemical properties of PZT-based materials were investigated in greater detail and attempts were made to optimize the synthesis of PZT-based polycrystals and films [5–7]. Efimov et al. [7] studied phase relations in the lanthanum-doped PZT system $(Pb_{1-x}La_x)(Zr_{0.65}Ti_{0.35})O_3$ (X/65/35 PLZT). Roy et al. [8] described a single-step synthesis of ultrafine PLZN powder from polymer precursors.

In this work, rare-earth-doped PZT solid solutions were prepared by a modified solid-state technique. As precursors, we used a combination of inorganic and organic metal derivatives that are widely used in thin film technology. In our opinion, particular attention should be paid to modified solid-state synthesis from mechanically activated raw materials, with no additional solvents, which makes it possible to considerably reduce the formation temperature of the resulting solid solution and the reaction time. To produce multicomponent heteronuclear compounds, we took advantage of several synthetic approaches: solid-state synthesis using both inorganic and organic metal derivatives or only organic metal derivatives.

The main purposes of this work were to select conditions for the preparation of rare-earth-doped PZT ceramics with various Zr/Ti ratios, to clarify the mechanisms underlying their formation, and to study the structure and microstructure of the solid solutions.

EXPERIMENTAL

Synthesis

Rare-earth-doped PZT solid solutions were synthesized from reagent-grade lead carbonate, PbCO₃; puregrade lead acetate trihydrate, Pb(CH₃COO)₂ · 3H₂O; pure-grade zirconium acetylacetonate, $Zr(C_5H_7O_2)_4$ · 10H₂O; titanium dichlorodiacetylacetonate; lanthanum acetate trihydrate; praseodymium acetate; gadolinium acetate trihydrate; and ytterbium acetate tetrahydrate. The solvents were dehydrated and purified in an argon atmosphere. The starting reagents *n*-hexane, acetic acid, pure-grade and reagent-grade acetylacetone, pure-grade benzene, and petroleum ether were purified as described in [9]. After distillation, they had standard physicochemical properties.

Zirconium acetylacetonate was synthesized as described in [10], with a 57% yield and standard melting point: 194.5–195°C.

Synthesis of titanium dichlorodiacetylacetonate. To a 500-ml two-neck flask were added $TiCl_4$ (0.105 mol), acetylacetone (0.45 mol), and anhydrous benzene (300 ml). The mixture was refluxed for 3 h, and then two-thirds of the benzene was distilled off. The resultant orange-red precipitate was filtered off, washed with petroleum ether, and vacuum-dried to a constant weight. Quantitative yield was achieved, and the softening temperature was 230°C [10].

Synthesis of the rare-earth acetates (general procedure). To a 500-ml four-neck flask fitted with a reflux condenser, dropping funnel, and stirrer were added a rareearth (lanthanum, praseodymium, gadolinium, or ytterbium) oxide (0.159 mol), glacial acetic acid (250 ml), and water (40 ml). The reaction was stirred while heating to 80–90°C until complete dissolution of the rare-earth oxide. After all of the rare-earth oxide was dissolved in acetic acid, the reaction mixture was cooled, and the rare-earth acetate was collected on a filter. The filtrate was boiled down to near dryness in a rotary evaporator, and the rare-earth acetate thus obtained was added to the precipitate. Next, the rare-earth acetate was washed with hexane, filtered off, and dried, first on the filter and then under a dynamic vacuum of 1 Pa for 3 h (to remove the residual acetic acid).

The Ln(CH₃COO)₃ · xH₂O acetates (x = 3 for La, x = 0 for Pr, x = 3 for Gd, and x = 4 for Yb) were isolated with a 70 to 80% yield. Their compositions were checked by chelatometric titration [11].

Synthesis of Pb(Zr_xTi_{1-x})O₃ solid solutions. The Pb($Zr_{0.53}Ti_{0.47}$)O₃ and Pb($Zr_{0.65}Ti_{0.35}$)O₃ solid solutions were synthesized from reagent-grade lead carbonate, PbCO₃; pure-grade zirconium acetylacetonate decahydrate, $Zr(C_5H_7O_2)_4 \cdot 10H_2O$; and titanium dichlorodiacetylacetonate, Ti($C_5H_7O_2$)₂Cl₂. To more rapidly pulverize and homogenize the raw materials, these were ground in the agate mortar of a Retsch micromill at 40 rpm for 12 min.

Synthesis of the $Pb_{0.98}Ln_{0.02}(Zr_{0.53}Ti_{0.47})O_{3+\delta}$, $Pb_{0.98}Ln_{0.02}(Zr_{0.65}Ti_{0.35})O_{3+\delta}$, $Pb_{0.94}Ln_{0.06}(Zr_{0.53}Ti_{0.47})O_{3+\delta}$, $Pb_{0.94}Ln_{0.06}(Zr_{0.65}Ti_{0.35})O_{3+\delta}$ (Ln = La, Pr, Gd, Yb) solid solutions. The solid solutions were prepared by a modified solid-state technique. The starting chemicals used were reagent-grade lead carbonate, PbCO₃, or reagent-grade lead acetate, Pb(CH₃COO)₃ · 3H₂O, and presynthesized zirconium acetylacetonate, $Zr(C_5H_7O_2)_4 · 10H_2O$; titanium dichlorodiacetylacetonate, $Ti(C_5H_7O_2)_2Cl_2$; lanthanum(III) acetate, Pc(CH₃COO)₃ · 3H₂O; pure-grade praseodymium acetate, Pr(CH₃COO)₃; pure-grade gadolinium(III) acetate, Gd(CH₃COO)₃ · 3H₂O; and pure-grade ytterbium acetate, Yb(CH₃COO)₃ · 4H₂O.

Appropriate starting mixtures were ground into fine powder in a Retsch micromill. The powders were fired in Nabertherm furnaces in several steps. The first step was performed at temperatures from 180 to 250°C. Next, the powders were fired in the range 400–650°C. At each temperature, the firing time was 2 h. The heattreated powders were ground and pressed at 10 MPa into 10-mm-diameter pellets. The final firing step was performed at 750° C for 3 h.

Thermal analysis[of the powders was carried out using the sample holder of a Netzsch STA-409 system. The samples were heated from 290 to 1020 K at a rate of 10 K/min in air.

IR spectra were measured on a Specord M82 spectrophotometer in the range 600–4000 cm⁻¹ after each firing step, using KBr pellets.

X-ray diffraction (XRD) studies were performed on a DRON-3 diffractometer with CuK_{α} radiation. XRD patterns were collected in step-scan mode between 10° and 100°. The phases present were identified using ICDD PDF-4 data.

Surface morphology of ceramics. The surface morphology of ceramics was examined by contact mode atomic force microscopy (AFM) on an NT MDT SOLVER-PRO47, using an NSG 10/20 crystalline silicon cantilever probe.

RESULTS AND DISCUSSION

The $(Pb_{1-x}Ln_x)(Zr_{0.53}Ti_{0.47})O_3$ and $(Pb_{1-x}Ln_x)(Zr_{0.65}Ti_{0.35})O_3 (x = 0.02, 0.06; Ln = La, Pr,$ Gd, Yb) solid solutions were prepared by modified solid-state synthesis using inorganic and organic metal derivatives as precursors. Carboxylates and some other organic metal derivatives are attractive precursors owing to their good solubility and the ability to form homogeneous mixtures and decompose at relatively low temperatures without metal volatilization or release of toxic substances. These requirements are met by zirconium acetylacetonate and lead acetate. Modified solid-state synthesis included the use of various powder reagents: metal oxide mixtures and organic and inorganic salts. Mechanical activation made it possible to enhance the reactivity of the starting reagents owing to the water of crystallization.

The initial stage of thermolysis in the range 70–180°C was represented by endothermic peaks due to dehydration and decarboxylation processes and also to the formation of intermediate carbonates, which decomposed above 500°C. Heating led to structure breakdown, which was caused by both the dehydration of metal-hydroxide groups (above 200–250°C) and the decomposition of carboxylates and other inorganic derivatives. These processes follow a complex mechanism, with active release of CO₂, CO, CH₄, C₂H₆, and other gaseous species in the range 300–470°C. Endothermic peaks with no weight loss are due to the crystallization of an oxide phase from the amorphous matrix formed through the decomposition of the starting mixture.



Fig. 1. AFM images of undoped and rare-earth-doped PZT solid solutions: (a) $Pb(Zr_{0.53}Ti_{0.47})O_3$, (b) $Pb_{0.94}Yb_{0.06}(Zr_{0.53}Ti_{0.47})O_{3+\delta}$, (c) $Pb_{0.94}La_{0.06}(Zr_{0.53}Ti_{0.47})O_{3+\delta}$.

The processes that took place during firing were also elucidated by IR spectroscopy. In the spectra of the organic precursors to the solid solutions, the intensity of the absorptions due to carboxyl and OH groups drops sharply above 200°C. In particular, the IR spectra of the thermolysis products demonstrate that raising the decomposition temperature markedly reduces the intensity of the absorption bands at 1605–1620 (–COO_{as}), 1385–1395 (–COO_s), and 3400–3600 cm⁻¹ (–OH). This points to the decomposition and removal of both the organic and metal-hydroxide components. After the final firing step, the IR spectra show a strong background absorption, characteristic of a metallic state.

The solid solutions were phase-pure as determined by XRD: no peaks from impurity phases were detected within the accuracy limits of this technique.

The surface micro- and nanostructure of several ceramic samples were examined by AFM. Polished pellets were treated with a 1 : 1 water–alcohol mixture in order to remove insoluble impurities. Next, the pellets were purified in ether and hexane.

Figure 1 shows AFM images of ceramic samples of undoped and rare-earth-doped solid solutions: $Pb(Zr_{0.53}Ti_{0.47})O_3$ and $Pb_{0.94}Ln_{0.06}(Zr_{0.53}Ti_{0.47})O_{3+\delta}$ with Ln = La and Yb.

The surface layer of the undoped sample (Fig. 1a) is composed of two types of grains: anisotropic micrograins of different habits, on the order of $1 \times 4 \mu m$ in size, and agglomerated nanograins ranging in size from 100 to 200 nm. No substructure was detected in the micrograins.

Rare-earth doping influences the surface morphology of the ceramics (Figs. 1b, 1c). We observe micrograins ranging in size from 1.5 to 2.5 μ m in Pb_{0.94}Yb_{0.06}(Zr_{0.53}Ti_{0.47})O_{3+∂} and nanograins on the order of 300–500 nm in size in Pb_{0.94}La_{0.06}(Zr_{0.53}Ti_{0.47})O_{3+δ}, evenly distributed over the surface layer. In both samples,



Fig. 2. AFM image of the $Pb_{0.94}La_{0.06}(Zr_{0.65}Ti_{0.35})O_{3+\delta}$ solid solution.

there is a substructure: the micrograins consist of 200- to 500-nm nanograins (Fig. 1b), and the nanograins, in turn, consist of finer nanograins, 30 to 100 nm in size (Fig. 1c). The doped samples are identical in grain habit.

For comparison, we also examined the surface of a ceramic sample of the $Pb_{0.94}La_{0.06}(Zr_{0.65}Ti_{0.35})O_{3+\delta}$ solid solution (Fig. 2). The grain size in this ceramic is nearly the same as in $Pb_{0.94}La_{0.06}(Zr_{0.53}Ti_{0.47})O_{3+\delta}$, and there is also a substructure, but the ceramics differ in grain habit. Moreover, the grains in the $Pb_{0.94}La_{0.06}(Zr_{0.65}Ti_{0.35})O_{3+\delta}$ ceramic are partially oriented.

Thus, rare-earth (La and Yb) doping has a significant effect on the surface morphology of ceramic samples of the Pb($Zr_{0.53}Ti_{0.47}$)O₃ and Pb($Zr_{0.65}Ti_{0.35}$)O₃ solid solutions: it reduces the grain size (by a factor of 2–8 and 3 for La and Yb doping, respectively), changes the grain habit, and results in a substructure and partial grain orientation.

The lattice parameters of our samples are listed in the table. All of the compounds studied have a rhombohedrally distorted perovskite structure.

Composition	<i>a</i> , Å	α, deg	<i>V</i> , Å ³
Pb(Zr _{0.65} Ti _{0.35})O ₃	4.9764	89.326	123.214
$Pb_{0.94}La_{0.06}(Zr_{0.65}Ti_{0.35})O_{3+\delta}$	4.9343	88.733	120.047
$Pb_{0.98}La_{0.02}(Zr_{0.65}Ti_{0.35})O_{3+\delta}$	4.8756	88.948	115.844
$Pb_{0.94}Yb_{0.06}(Zr_{0.65}Ti_{0.35})O_{3+\delta}$	4.9719	88.746	122.817
$Pb_{0.98}Yb_{0.02}(Zr_{0.65}Ti_{0.35})O_{3+\delta}$	4.8453	88.916	113.692
$Pb(Zr_{0.53}Ti_{0.47})O_3$	4.9339	88.828	120.031
$Pb_{0.94}La_{0.06}(Zr_{0.53}Ti_{0.47})O_{3+\delta}$	4.8695	87.798	115.215
$Pb_{0.98}La_{0.02}(Zr_{0.53}Ti_{0.47})O_{3+\delta}$	4.8679	89.094	115.309
$Pb_{0.94}Yb_{0.06}(Zr_{0.53}Ti_{0.47})O_{3+\delta}$	4.9162	88.910	118.758
$Pb_{0.98}Yb_{0.02}(Zr_{0.53}Ti_{0.47})O_{3+\delta}$	4.9017	88.371	117.633

Rhombohedral cell parameters of $(Pb_{1-x}Ln_x)(Zr_{0.53}Ti_{0.47})O_3$ and $(Pb_{1-x}Ln_x)(Zr_{0.65}Ti_{0.35})O_3$ solid solutions

CONCLUSIONS

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