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New ferroelectric materials on the basis of $PbSc_{1/2}Nb_{1/2}O_3$–$PbLu_{1/2}Nb_{1/2}O_3$ solid solutions

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Abstract

Original binary solid solutions $PbSc_{1/2}Nb_{1/2}O_3$–$PbLu_{1/2}Nb_{1/2}O_3$ (PSN-PLuN) have been produced. First of all nominally pure PSN and PLuN were synthesized by solid state reaction from oxides and carbonates. These compounds were mixed in different proportions to obtain $(1-x)$PSN$-x$PLuN solid solutions. Ceramic samples were hot-pressed at gradual change of the temperature. Solid solutions have the perovskite structure and are completely soluble in each other. Differential thermal analysis and X-ray diffraction were used to examine the synthesis and phase constitution. Dielectric properties—dielectric permittivity ε and dielectric loss tanδ of ceramic samples of originally synthesized $PbSc_{1/2}Nb_{1/2}O_3$–$PbLu_{1/2}Nb_{1/2}O_3$ (PSN$-$PLuN) solid solution series were measured as functions of temperature. In $(1-x)$PSN$-x$PLuN solid solutions the phase transition temperature drops at small values x further proceeding through a minimum.

Keywords: Calcination; Dielectric properties; Ferroelectric properties; Hot pressing; Perovskites

1. Introduction

Due to multifunctional properties lead containing perovskites of the general formula $Pb(B'B'')O_3$ (B′—Mg, Zn, Ni, Fe etc. ; B″—Nb, Ta, W) are of special interest. Particular attention is paid to binary systems comprising relaxor $Pb(B'B'')O_3$ and lead titanate or zirconate (PT and PZ, respectively). This kind of solid solutions are known to have morphotropic phase boundaries—regions of transition on the phase diagrams of two-component systems of different symmetry. Such regions of coexisting rhombohedral and tetragonal phases were observed in solid solutions of $Pb(Ti,Zr)O_3$ where anomalies of electromechanical properties are found in the morphotropic region and near its boundaries.[1] A number of binary systems with morphotropic regions on phase diagrams have been obtained and studied—$PbMg_{1/3}Nb_{2/3}O_3$–$PbTiO_3$ (PMN-PT),[2] $PbSc_{1/2}Nb_{1/2}O_3$–$PbTiO_3$ (PSN-PT),[3] $PbMg_{1/3}Nb_{2/3}O_3$–$PbZrO_3$ (PMN-PZ),[4] $PbYb_{1/2}Nb_{1/2}O_3$–$PbZrO_3$ (PYbN-PZ),[5] $PbSc_{1/2}Nb_{1/2}O_3$–$PbMg_{1/3}Nb_{2/3}O_3$–$PbTiO_3$ (PSN-PMN-PT).[6] Solid solution series of $(1-x)PbLu_{1/2}Nb_{1/2}O_3-xPbTiO_3$ have been synthesized and their crystallographic parameters and phase diagrams studied at the Institute of Solid State Physics of the University of Latvia.[7] It has been found that over 10 at.% of rare earth oxides may solve in lead scandium niobate.[8]

Presently attempts have been made to obtain ceramic samples of a number of $(1-x)PbSc_{1/2}Nb_{1/2}O_3-xPbLu_{1/2}Nb_{1/2}O_3$ (PSN-PLuN) binary solid solutions and study their structure and properties.

2. Experimental

Powders of pure PSN and PLuN were obtained by solid state synthesis from high purity grade scandium oxide Sc_2O_3, analytical grade lead oxide PbO, high purity niobium pentoxide Nb_2O_5 and chemically pure lutetium hydrocarbonate $Lu_2(CO_3)_3 \cdot 4H_2O$. The solid solutions $(1-x)PbSc_{1/2}Nb_{1/2}O_3-xPbLu_{1/2}Nb_{1/2}O_3$ were synthesized from mixtures of the pure compounds for 2 h at 900°C.

Conditions for solid phase synthesis of the solid solutions were selected upon data of X-ray and differential thermal analysis (DTA). The thermal interval 20–1000 °C, heating rate of 10 °C/min, and sample mass of 0.2 g

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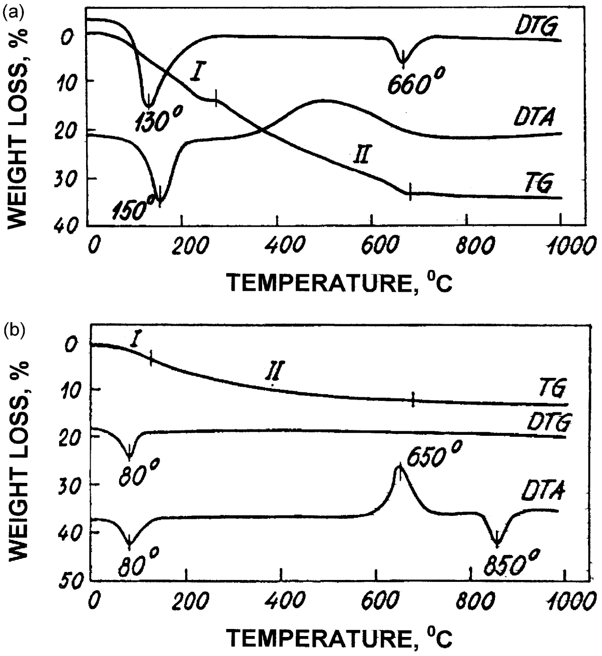

Fig. 1. DTA curves: (a)—lutetium hydrocarbonate $Lu_2(CO_3)_3{\cdot}4H_2O$; (b)—the $4PbO–Nb_2O_5–Lu_2(CO_3)_3{\cdot}4H_2O$ mixture corresponding to $PbLu_{1/2}Nb_{1/2}O_3$.

at the DTA were the same for all samples being examined.

The DTA curves of lutetium hydrocarbonate $Lu_2(CO_3)_3{\cdot}4H_2O$ and the equimolar mixture of oxides representing $PbLu_{1/2}Nb_{1/2}O_3$ are shown in Fig. 1. Evident endothermic effects related to decomposition stages of lutetium hydrocarbonate (Fig. 1a) are seen at 130 and 660 °C. They are confirmed by relevant loss of 13.8 and 19.6% of mass on the TG curve. At heating, the crystallized water evaporates first. CO_2 is exhausted at decomposition of the carbonate.

The loss of the lutetium carbonate mass (33.4%) on the TG curve is in good agreement with the calculated value (33.9%). The endothermic effect at heating of the $PbO–Lu_2(CO_3)_3{\cdot}4H_2O–Nb_2O_5$ mixture (Fig. 1b) is related to evaporation of crystallized water. Decomposition of lutetium carbonate proceeds simultaneously with formation of intermediate $2PbO{\cdot}Nb_2O_5$ compound, as suggested by the pronounced exothermic effect at 650 °C and a corresponding loss of mass on the TG curve (Fig. 1b). The reactivity of Lu_2O_3 released at decomposition of lutetium hydrocarbonate is enhanced considerably.

Compared with our earlier results of phase formation studies in the $PbO–Nb_2O_5$ oxide system,[9] $PbZn_{1/3}Nb_{2/3}O_3$, $PbSc_{1/2}Nb_{1/2}O_3$, and $PbIn_{1/2}Nb_{1/2}O_3$,[10] the thermographic and X-ray data suggest that at the first stage of the solid state reaction (500–800 °C) interacting lead and niobium oxides form intermediate compounds in molar ratios 3:2, 2:1, 5:2, 3:1 that have the pyrochlore structure of cubic (3:2), rhombohedral (2:1 and 5:2), and tetragonal (3:1) symmetry. The endothermic effect at 850°C on the DTA curve (Fig. 1b) is due to melting of lead oxide. The X-ray studies show that $PbLu_{1/2}Nb_{1/2}O_3$ is being intensively formed within this thermal interval where three phases, including the perovskite phase, coexist in a mixture. There are no principal differences in the thermal behaviour of all solid solutions suggesting that all the solid state reactions are similar.

Triple synthesis of the PSN mixture was used to facilitate the interaction and eliminate the undesired pyrochlore phase: the first was made for 2 h at 850 °C, the second—for 2 h at 950 °C, and the third—for 1 h at 1300 °C. As a result a homogeneous mixture of perovskite structure was obtained. The mixture of the lutetium niobate PLuN was synthesized through an intermediate wolframite phase $LuNbO_4$ at 1250 °C during 1 h after which PbO was introduced before firing for 2 h at 800 °C.[11] After each thermal treatment the mixture was ground in ethanol environment and the slurry was desiccated for 24 h at 250°C. Ceramic samples were hot pressed under the pressure of 20 MPa during 1–4 h the temperature being adjusted within the 1050–1280 °C interval depending on the particular component ratio.

The hot-pressed solid solution ceramics are transparent. At sample thickness of 0.3 mm the transparency is 10–20% (wavelength $\lambda = 633$ nm) and can be increased by adjusting conditions of thermal treatment.

At room temperature PSN has a rhombohedral distortion of the unit cell: $a = 4.0837$ Å, $\alpha = 89.96°$ (Table 1). Pure PLuN has antiferroelectric properties and was studied by Isupov and Krainik.[12]

Crystallographic studies were made by X-ray diffraction maxima 200, 220, 222 analysis using a DRON-UM1 diffractometer with Co K_α radiation and Fe β filter.

The pure PLuN has pseudomonoclinic cell with linear parameters $a = c = 4.1450$ Å, $b = 4.1120$ Å and an angle $\beta = 90.518°$ (Table 1); transition from antiferroelectric to paraelectric phase is observed at $T \approx 258$ °C. Lutetium niobate has a pronounced long range order in the B sublattice (the X-ray diffraction pattern suggests a superstructure). PLuN and compositions with large x has space group Bmm2 and the true unit cell is orthorhombic. The pseudomonoclinic primitive cell was used to analyse X-ray diffraction data and calculate values of unit cell parameters. The orthorhombic (a_{orth}, b_{orth}, c_{orth}) and pseudomonoclinic (a, b, β) sets of parameters are associated by relations: $a_{orth} = 2a \sin \beta/2$; $b_{orth} = 2a \cos \beta/2$; $c_{orth} = b$.

Solid solutions $(1-x)$PSN$-x$PLuN with $0 \leqslant x \leqslant 0.60$ have unit cell with rhombohedral distortion. The value of parameter a increases, but angle α changes are very small. Compositions of solid solutions with $0.75 \leqslant x \leqslant 1.0$ have pseudomonoclinic cell. The region of two coexistent phases has been observed at $0.60 < x < 0.75$.

Volume of the unit cell gradually increases from 68.1023 Å^3 (pure PSN) to 70.6455 Å^3 (PLuN) that

Table 1
Structural parameters of $(1-x)PbSc_{1/2}Nb_{1/2}O_3-xPbLu_{1/2}Nb_{1/2}O_3$ solid solutions

x	Perovskite structure							
	Rhombohedral cell		Pseudomonoclinic cell			Volume	Density, g/cm^3	
	a (Å)	α (deg)	a (Å)	b (Å)	β (deg)	V (Å^3)	$\rho_{theor.}$	$\rho_{exp.}$
0.00	4.0837	89.96				68.1023	7.9060	7.75
0.10	4.0871	89.97				68.2725	8.0416	7.88
0.25	4.0967	89.98				68.7547	8.2208	7.97
0.50	4.1161	89.99				69.7361	8.4921	8.15
0.60	4.1223	89.99				70.0517	8.6020	8.26
0.75			4.1342	4.1296	90.386	70.5822	8.7726	8.42
0.90			4.1380	4.1240	90.456	70.6132	8.9981	8.73
1.00			4.1450	4.1120	90.518	70.6455	9.1468	8.96

approve formation of solid solutions with full solubility in each other.

The density ρ of PSN-PLuN ceramics gradually increases with x as corresponds with the density values calculated from X-ray data.

3. Dielectric properties

The dielectric measurements of ceramic samples of the size of 5×8×1 mm, supplied with silver paste electrodes fired for 10 min at 700 °C, were made on a HP4284 instrument.

Temperature of $\varepsilon(T)$ maximum depends of ordering in the B sublattice. In our case pure PSN has a phase transition at 90°C where the dielectric permittivity reaches $\varepsilon_{max}=40{,}000$. The value of dielectric permittivity of $(1-x)$PSN$-x$PLuN decreases rapidly with the concentration of lutetium: $\varepsilon_{max}=6400$ at $x=0.25$, $\varepsilon_{max}=$ 4900 at $x=0.5$, $\varepsilon_{max}=2700$ at $x=0.75$, and $\varepsilon_{max}=537$ at $x=0.90$ (Fig. 2).

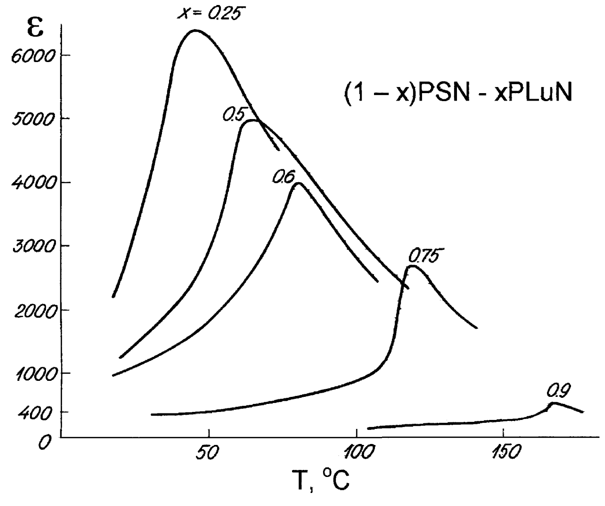

Fig. 2. Temperature dependence of dielectric permittivity $\varepsilon(T)$ of the $(1-x)$PSN$-x$PLuN solid solution ceramics, measured at frequency 1 kHz. The numbers at curves show mole parts of PLuN.

The change of temperature of the maximum dielectric permittivity of $(1-x)$PSN$-x$PLuN is rather curious: the maximum permittivity ε_{max} in 0.75PSN$-$0.25PLuN is reached at $T_{max}=42$ °C, which is considerably lower than $T_{max}=90$ °C in the case of pure PSN. However, at farther increase of PLuN concentration in the solid solution T_{max} increases: $T_{max}=118$ °C at $x=0.75$ and $T_{max}=166$ °C at $x=0.90$, due to a higher temperature of $T_{max}=258$ °C of pure PLuN. As follows from the experimental data, T_{max}(x) of the solid solution series has a minimum at $x=0.25$ (Fig. 3).

The strong dependence of the dielectric permittivity $\varepsilon(T)$ and dielectric loss tan$\delta(T)$ on frequency in the region of phase transition is characteristic to relaxor materials. As the frequency increases, the value of ε_{max} decreases and T_{max} shifts to higher temperatures (Fig. 4). Simultaneously, the maximum temperature and value of tanδ increases. In paraelectric phase dielectric losses tan$\delta \leqslant 0.03$.

As follows from the quasi-static loops of dielectric hysteresis, the remnant polarization of the 0.75PSN$-$0.25PLuN ceramics are $P_r=9.3$ μC/cm^2 and coercive field $E_c=4.0$ kV/cm at 20 °C.

The experimental studies of samples of the $(1-x)$PSN$-x$PLuN series show that the solid solutions

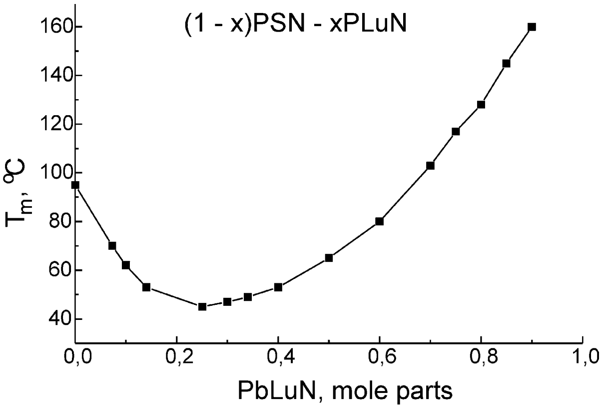

Fig. 3. Composition dependence of temperature T_{max} of solid solutions $(1-x)$PSN–xPLuN at frequency 1 kHz.

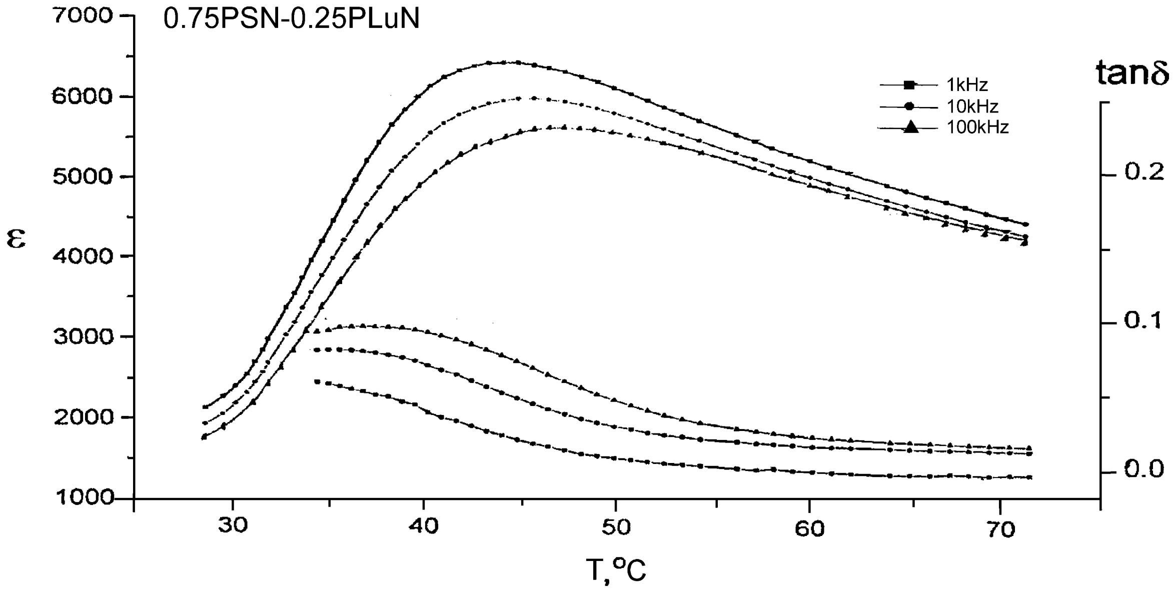

Fig. 4. Temperature dependence of dielectric permittivity $\varepsilon(T)$ and dielectric loss $\tan\delta(T)$ at different frequences of the 0.75 PSN–0.25 PLuN ceramics.

have the perovskite structure. Details of the morphotropic region and behaviour of the temperature of dielectric permittivity maximum with the component concentration are the matter of some future publications.

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