STUDIES OF $PbSc_{1/2}Nb_{1/2}O_3$ – $PbYb_{1/2}Nb_{1/2}O_3$ SOLID SOLUTIONS

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Introduction

The physical characteristics of compounds with chemical formula $Pb(B'_{1/2}B''_{1/2})O_3$ ($B' = Fe^{+3}$, In^{+3}, Sc^{+3}, Lu^{+3}, Yb^{+3}, Tm^{+3} etc., $B'' = Nb^{+5}$, Ta^{+5}) have been of interest due to different types of phase transition. With the degree of order between the B-site cations in the perovskites, diffuse phase transitions or sharp ones are frequently observed in these compounds [1,2]. In $PbSc_{1/2}Nb_{1/2}O_3$ B-site ions are disordered, a diffuse phase transition behavior characterized by the frequency dependence of the transition temperature and broadly distributed transition temperature in the measured dielectric constant curve are observed [3]. Particular attention has been paid to binary $PbB'_{1/2}B''_{1/2}O_3$ relaxor systems of lead titanate or zirconate. These systems are known to have a morphotropic boundaries on phase diagrams – regions of changing symmetry. A number of binary systems with morphotropic regions have been produced and studied: $PbSc_{1/2}Nb_{1/2}O_3$ – $PbTiO_3$ [4], $PbSc_{1/2}Nb_{1/2}O_3$ - $PbLu_{1/2}Nb_{1/2}O_3$ [5], $PbLu_{1/2}Nb_{1/2}O_3$ – $PbTiO_3$ [6], $PbSc_{1/2}Nb_{1/2}O_3$ - $PbYb_{1/2}Nb_{1/2}O_3$ [7,8].

$PbYb_{1/2}Nb_{1/2}O_3$ belongs to a subgroup of complex perovskites with a highly ordered arrangement of B-site cations. It undergoes a ferroelectric – antiferroelectric phase transition near $302\ ^0C$ [2,3,9]. On the degree and characteristics of ordering of ferroelectric phase transition and relaxor properties is possible to influence by annealing temperature, hydrostatic pressure and by mean of solid solutions by varying concentration of constituents [1].

Presently attempts have been made to produce ceramic samples of a number of the solid solutions (1-x)$PbSc_{1/2}Nb_{1/2}O_3$ – x$PbYb_{1/2}Nb_{1/2}O_3$ (PSN – PYbN) and to study their structure and properties.

Experimental

Powders of (1-x)PSN – xPYbN solid solutions were obtained by solid phase synthesis from high purity grade oxides – PbO, Sc_2O_3, Nb_2O_5 and chemically pure ytterbium hydrocarbonate $Yb_2(CO_3)_3 \cdot 3H_2O$.

The mixtures were homogenized and milled in an agate ball mill in ethanol for 20 – 24 h, dried and then calcined for 2 hours at $950\ ^oC$ in case of PYbN, at $1260\ ^oC$ in case of PSN and at an intermediate temperature in case of solid solutions. The calcined powders were reground, cold pressed and sintered by hot pressing for 1 – 3 h at temperatures ranging from $1100\ ^oC$ to $1220\ ^oC$, and pressures of 20 – 25 MPa depending on composition. An excess amount of PbO (1 – 3 wt%) was added to the specimens to compensate evaporation of PbO during the sintering.

The data of X-ray diffraction and differential thermal analysis (DTA) were used to select conditions for solid phase synthesis of the solid solutions.

Differential Thermal Analysis

The DTA curves of ytterbium hydrocarbonate $Yb_2(CO_3)_3 \cdot 3H_2O$ and equimolar mixtures of oxides $4PbO–Yb_2(CO_3)_3 \cdot 3H_2O–Nb_2O_5$ representing $Pb(Yb_{1/2}Nb_{1/2})O_3$ are shown in Fig.1. It was found that the endothermic effects on DTA curves of $Yb_2(CO_3)_3 \cdot 3H_2O$ (Fig.1a) tested at $130\ ^0C$ and $640\ ^0C$ are due to decomposition of hydrocarbonates. At heating, the crystallized water evaporates at the first stage (9.3 % loss of mass on the TG curve) and CO_2 is exhausted at decomposition of the carbonate, as confirmed by the relevant loss of 21.8 % of mass on the TG curve. A little exothermic effect at $600\ ^0C$ on DTA curve is due to crystallization of Yb_2O_3. The total loss of the ytterbium

hydrocarbonate mass (31.1 %) on the TG curve is in good agreement with the calculated value (32.07 %).

The endothermic effect at heating of the equimolar precursors for PbYbN (Fig.1b) is related to evaporation of crystallized water (140 ^{0}C). Decomposition of ytterbium carbonate proceeds simultaneously with formation of the first intermediate compound – $2PbO \cdot Nb_2O_5$, as suggested by a pronounced exothermic effect at 670 ^{0}C on DTA curve and a corresponding loss of mass (8.9 %) on the TG curve. The reactivity of Yb_2O_3, released at decomposition of ytterbium hydrocarbonate, is enhanced considerably, and formation of PYbN is more intensive. The endothermic effect at 850 ^{o}C on the DTA curve is due to melting of lead oxide. X-ray diffraction data and DTA curves show that the solid phase reaction is fastest in the 830–870 ^{0}C interval. About 3 phases exist simultaneously while PYbN is being formed as the main phase.
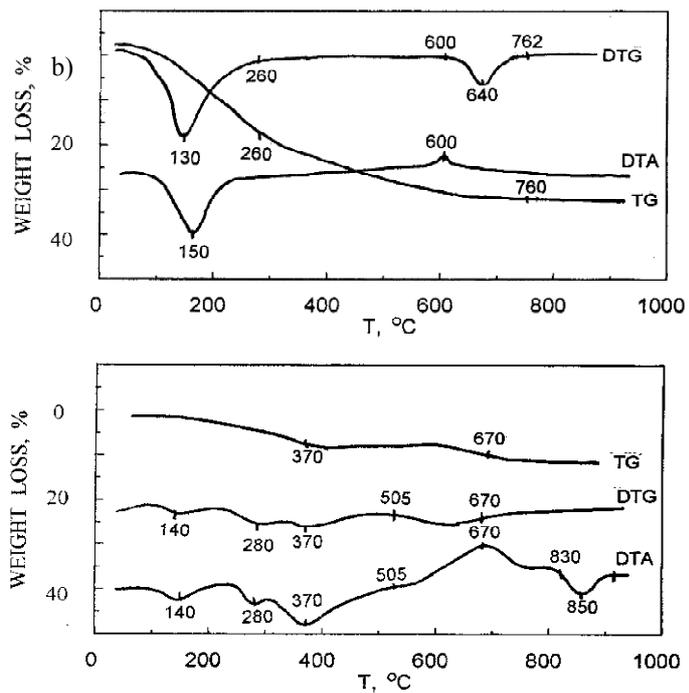

FIGURE 1. DTA curves:
a - ytterbium hydrocarbonate $Yb_2(CO_3)_3 \cdot 3H_2O$;
b – the $4PbO–Yb_2(CO_3)_3 \cdot 3H_2O–Nb_2O_5$ mixture corresponding to $Pb(Yb_{1/2}Nb_{1/2})O_3$.

X-ray Measurements

Analysis of the 200, 220, and 222 diffraction maxima of PYbN shows a monoclinic distortion of the perovskite cell at room temperature. Pure ytterbium niobate has a pronounced long-range order in the B sublattice (the X-ray diffraction pattern suggests a superstructure) and a pseudo-monoclinic cell. PYbN and compositions of higher PYbN concentrations (x=0.7–1.0) have a true orthorhombic unit cell of the Bmm2 space group. Another observed type of superlattice is associated with an AFE lattice modulation. With the increase of PSN concentration (x<0.7) the intensity of the superlattice diffraction maximums gradually decreases to zero. The crystal structure of compositions changes from orthorhombic (compositions with 0.7≤x≤1.0) to pseudocubic (0.2<x<0.7) to rhombohedric (0≤x≤0.2) and is in good agreement with other reports [7,8].

Dielectric Properties

For dielectric studies the specimens were furnished with silver paste electrodes fired for 5 min at 600 ^{0}C. Dielectric permittivity ε and dielectric loss tanδ were measured on a HP4194A instrument at frequencies 1.0, 10, and 100 kHz.

Fig.2 shows the dielectric permittivity vs. temperature curves ε(T) of the (1-x)PSN – xPYbN solid solutions. An AFE to PE phase transition is observed in pure ytterbium niobate at 300 ^{0}C. In compositions of higher PYbN concentrations (1.0≤x≤0.70) (Fig.2a), the phase transition is sharp and does not depend on the frequency of the measuring field. Broadening of the phase transition and dispersion of the dielectric permittivity characteristic to ferroelectric relaxors are observed within the 0≤x≤0.6 concentration interval.

Pure PSN has a phase transition at 90 ^{0}C where the dielectric permittivity reaches about 40000. The values of dielectric permittivity of the (1-x)PSN — xPYbN solid solutions decrease rapidly with the increase of ytterbium concentration: ε_{max}=26000 at x=0.2; ε_{max}=6000 at x=0.5; ε_{max}=1200 at x=0.7; ε_{max}=800 at x=0.8 and ε_{max}=650 at x=0.9; ε_{max}=350 at x=1.0.
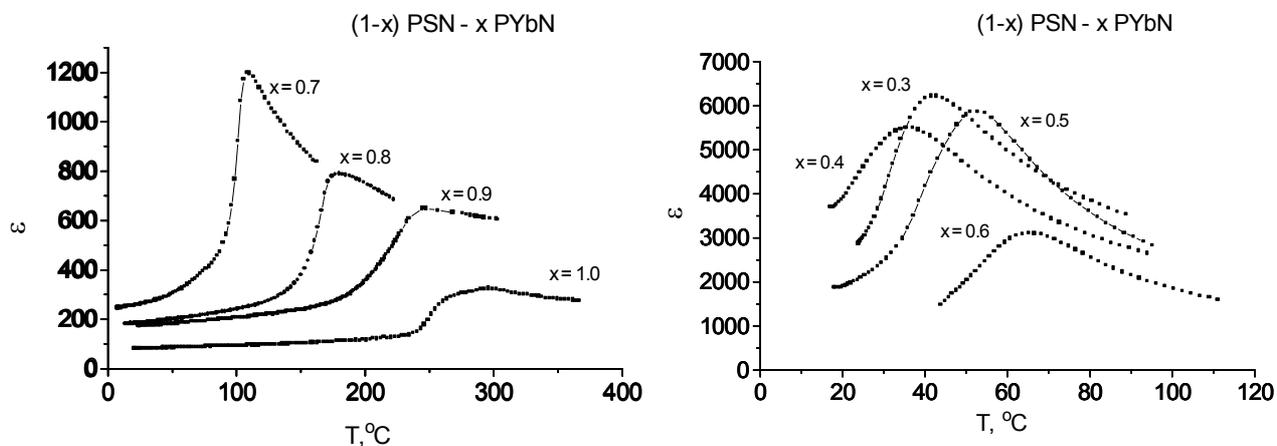

FIGURE 2. Temperature dependence of dielectric permittivity ε(T) of the (1-x)PSN — xPYbN solid solution ceramics (f = 1kHz):
a – for solid solutions x = 0.7 – 1.0; b - for solid solutions x = 0.6 – 0.3.
The numbers at curves show mole parts of PYbN.

Fig.3 shows the dependence of the temperature of dielectric permittivity maximums on the composition. The temperature $T\varepsilon_{max}$ decreases drastically from 90 ^{0}C in pure PSN to 36 ^{0}C in the 0.6PSN – 0.4PYbN solid solution, in agreement with other experimental data [7]. At farther increase of the PYbN concentration the $T\varepsilon_{max}$ increases rapidly reaching 300^{0}C in pure PYbN. A similar dependence of the temperature of dielectric permittivity maximums on composition has been noticed in the PSN – PLuN solid solution series [5].
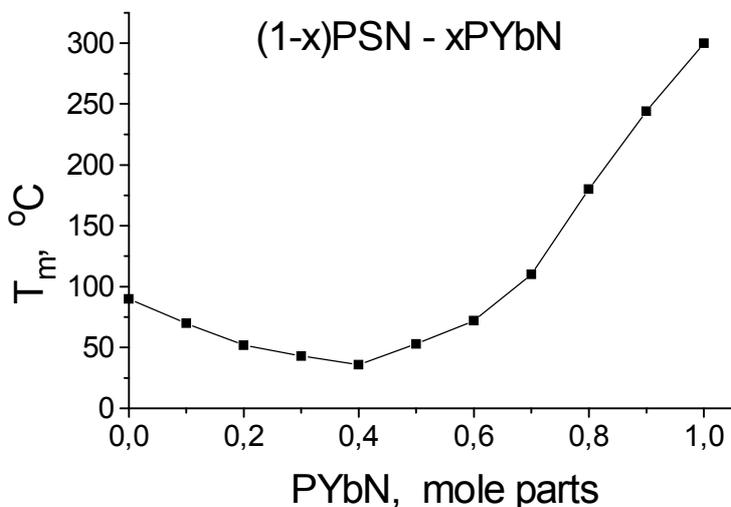
The strong dependence of the dielectric permittivity ε(T) and dielectric loss tanδ on frequency in the region of phase transition of solid solutions 0≤x≤0.6 is observed. As the

FIGURE 3. Composition dependence of the dielectric permittivity maximum's temperature T_m for solutions of (1-x)PSN - xPYbN.

frequency increases, the value of ε_{max} decreases and T_{max} shifts to higher temperatures (Fig.4). In paraelectric phase dielectric losses tanδ≤0.015.

As seen from the quasi-static loops of dielectric hysteresis of the 0.5PSN - 0.5PYbN ceramics (Fig.5), the remnant polarization P_r = 13.8 μC/cm^2 and coercive field E_c = 5.6 kV/cm at 20^{0}C.

The experimental studies of samples of the (1-x)PSN – xPYbN series show that the solid solutions 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.
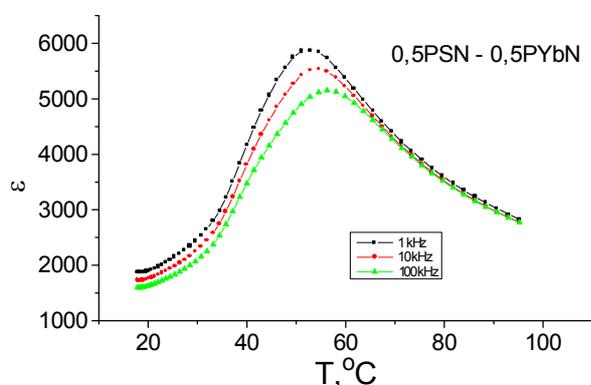

FIGURE 4. Temperature dependence of dielectric permittivity ε(T) of the 0.5PSN – 0.5PYbN solid solution ceramic (f = 1 kHz).
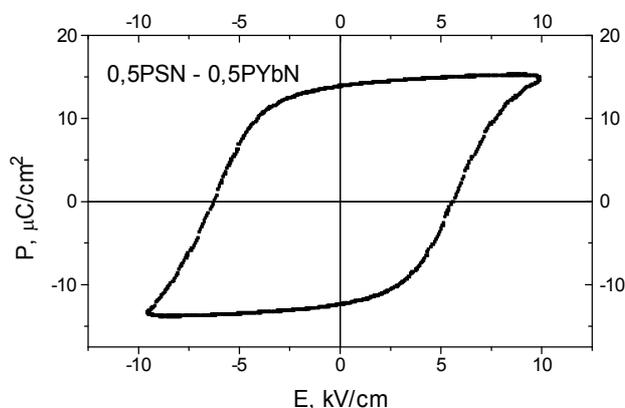
FIGURE 5. Dielectric hysteresis in 0.5PSN-0.5PYbN solid solution ceramic as function of applied field at 20 ^{0}C.

Summary

An antiferroelectric – paraelectric phase transition at ~300 ^{o}C is observed in pure lead ytterbium niobate. Solid solutions rich with PYbN (x=0.7–1.0) have a pseudomonoclinic distortion of the cubic cell. Solid solutions of 0.2<x<0.7 have a cubic structure. Broadening of phase transition and dielectric dispersion, characteristic features of ferroelectric relaxors are observed within the concentration interval of 0≤x<0.7. Solid solutions rich in PSN (x=0–0.2) have a unit cell with rhombohedric distortion. The peak values of ε decrease with increasing of PYbN: from 40000 (pure PSN) till 400 (pure PYbN). The lowest temperature of dielectric permittivity peaks ε (T$_m$=36 ^{0}C) is observed at x= 0.4.

References

[1] В.А.Исупов. Кристаллография. **49**, 5, 806 (2004).
[2] Stenger C.G.F., Burggraaf A.J.. Phys.status solidi(a). **61**, 2, 653 (1980).
[3] Ю.Я.Томашпольский, Ю.Н.Веневцев. ФТТ. **6**, 2388 (1965).
[4] Yamashita Y. Jpn.Appl.Phys.. **33,** 4652 (1994).
[5] K.Bormanis, M.Dambekalne, M.Antonova, M.Livinsh, L.Shebanovs, and A.Sternberg. J.Eur. Ceram.Soc.. **24**, 1557 (2004).
[6] А.Штернберг, Л.Шебанов, Дж.Ямашита, М.Антонова, М.Ливинш, И.Шорубалко. Кристаллография. **44,** 1, 40 (1999).
[7] И.П.Пронин, В.А.Исупов, Ч.Н. Парфенова. Сегнетозлектрики. Калинин. 125 (1982).
[8] Jai-Huun Kim and Woong Kil. Choo. Ferroelectrics. **270**, 69 (2002).
[9] Jeong Rock Kwon and Woong Kil Choo. J.Phys.Condens. Mater.. **3,** 2141(1991).