Dielectric properties of solid solutions in a PFN-based system

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Abstract. The results of X-ray diffraction analysis of the solid solutions in the (1-x)Pb(Fe\textsubscript{12/3}Nb\textsubscript{1/3})O\textsubscript{3}—xPb(Fe\textsubscript{2/3}W\textsubscript{1/3})O\textsubscript{3} systems with x = 0.0–0.5, investigating their microstructure and measurements of dielectric characteristics are presented in this paper. The critical influence of Pb(Fe\textsubscript{2/3}W\textsubscript{1/3})O\textsubscript{3} on the crystallization of solid solutions and the nature of grain boundaries is established. A sintering mechanism of the solid solutions is defined. Correlations between the dynamics of the crystalline and grain structures and the dielectric properties of investigating solid solutions are established.

1. Introduction
In recent years, special attention in the field of materials science has been paid to materials with a complex ordering of dipole and magnetic moments (multiferroics). One of the most promising multiferroics is lead ferroniobate Pb(Fe\textsubscript{12/3}Nb\textsubscript{1/3})O\textsubscript{3} (PFN). PFN has two ferroelectric phase transitions at temperatures T\textsubscript{c} ≈ 380 K and T\textsubscript{c} ≈ 350 K [1, 2] and two magnetic phase transitions (PT) at temperatures T\textsubscript{N1} ≈ 150 K and T\textsubscript{N2} ≈ 10 K [3, 4]. It is also known that the compounds having a perovskite-like structure type (AB\textsuperscript{–}B\textsuperscript{+}O\textsubscript{3}) can be completely or partially disordered in the B-position [5–6]. It contributes to the emergence of the unusual physical properties in such materials. The most promising of them can be used in such modern fields as spintronics and straiotronics [7–9].

Thus, investigations aimed to establish the patterns of structure formation and formation of dielectric responses in solid solutions based on the high-temperature multiferroic Pb(Fe\textsubscript{12/3}Nb\textsubscript{1/3})O\textsubscript{3} are relevant.

2. Experimental section
Systems (1-x)Pb(Fe\textsubscript{12/3}Nb\textsubscript{1/3})O\textsubscript{3}—xPb(Fe\textsubscript{2/3}W\textsubscript{1/3})O\textsubscript{3} with 0.0 ≤ x ≤ 0.5 were the subjects of this study. The solid solutions were prepared using a two-stage solid-state reaction at T\textsubscript{1}=1073 K for 4 h and T\textsubscript{2}=(1123–1173) K for 4–10 h followed by sintering using conventional ceramic technology at T\textsubscript{sint}=(1143÷1373) K for 2 h. The raw powders were PbO (98%), Fe\textsubscript{2}O\textsubscript{3} (99%), WO\textsubscript{3} (99.9%), and Nb\textsubscript{2}O\textsubscript{5} (98%).

X-ray diffraction was conducted using a DRON 3.0 diffractometer (using CoK\textsubscript{α} radiation with Bragg-Brentano focusing). The content of impurity phases was estimated from the relative intensity of their strong line: I\textsubscript{imp}/I\textsubscript{perovskite}·100%, where I\textsubscript{imp} is the intensity of the strong line of the impurity phase, I\textsubscript{perovskite} is the intensity of the strong line of the perovskite phase.

The microstructural measurements were performed by using a JSM – 6390L scanning electron microscope.

The dependencies of the real ϵ\textsuperscript{'} and imaginary ϵ\textsuperscript{''} parts of dielectric permittivity were measured on the mechanically free samples Ø10x1 mm in a temperature range T = 320–600 K at frequencies of 20
Hz-1 MHz using Agilent 4980A LCR meters and Wayne Kerr 6500B precision LCR meters. The samples had been annealed for 6 hours before the measurements. The measuring step was 2K.

3. Results and discussion

An X-ray phase analysis of the \((1-x)\text{Pb(Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3--x\text{Pb(Fe}_{2/3}\text{W}_{1/3})\text{O}_3\) system with \(0.0 \leq x \leq 0.5\) showed that the solid solutions had not impurity phases. All of the samples have a cubic structure at room temperature (Figure 1a).

![Figure 1. X-ray diffraction peaks (a); fragments of the microstructure (b) of the solid solutions in the \((1-x)\text{Pb(Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3--x\text{Pb(Fe}_{2/3}\text{W}_{1/3})\text{O}_3\) system.](image)

A microstructural analysis demonstrated that when a small amount of \(\text{Pb(Fe}_{2/3}\text{W}_{1/3})\text{O}_3\) \((x = 0.1)\) are added to the system the grain size is significantly increased \((d = 25 \ \mu\text{m})\). After reaching a concentration of \(x=0.2\) a liquid phase is formed. This is reflected in the appearance of the double boundaries of grains, intercrystalline interlayers that form continuous channels of the liquid phase. In doing so the habit of the grains takes the round, spherical shape \((x = 0.2, x = 0.3)\). A further increase in the concentration of \(\text{Pb(Fe}_{2/3}\text{W}_{1/3})\text{O}_3\) results in the growing number of the liquid phase. During the process, the smaller particles are dissolved and deposited on the boundaries of larger grains \((x = 0.5)\). Further, the intercrystalline interlayers completely are filled with a liquid phase and the grain boundaries become indistinguishable. Thus, it can be concluded that sintering takes place by the mechanism of surface diffusion.

The temperature dependencies of the real \((\epsilon')\) and imaginary \((\epsilon'')\) parts of the dielectric constant are shown in Figure 2. The dielectric constant \(\epsilon'\) is characterized by strong dispersion before and at the moment of the phase transition.

The analyses of the dependencies demonstrated that \(\epsilon'\) and \(\epsilon''\) pass through the maximum blurred by temperature. When \(x=0.1\) the dependencies of \(\epsilon'\) become more pronounced. However, with increasing concentration of the \(\text{Pb(Fe}_{2/3}\text{W}_{1/3})\text{O}_3\) the values of the dielectric constant in the maximum are decreased and shifted to lower temperatures.
Figure 2 (Part 1). Temperature dependences of $\varepsilon'$ (left) and $\varepsilon''$ (right) of the solid solutions in the $(1-x)\text{Pb(Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$—$x\text{Pb(Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ system at frequencies of 20 Hz-1 MHz.
Figure 2 (Part 2). Temperature dependences of $\varepsilon'$ (left) and $\varepsilon''$ (right) of the solid solutions in the 
$(1-x)\text{Pb(Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$—$x\text{Pb(Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ system at frequencies of 20 Hz-1 MHz.

The $\varepsilon'$ passes through a blurred maximum which shifted to a higher temperature at increasing frequency. However, the imaginary part is tens of times higher than the real part at low frequencies. Comparison of these values leads to the conclusion that such behavior of the temperature dependencies of the $\varepsilon'$ and $\varepsilon''$ is associated with high electrical conductivity of the solid solutions [10]. The nature of
the electrical conductivity dependence on the temperature and frequency of the field may be due to the movement of defects due to the restructuring of the structure or the movement of vacancies resulting from the reduction of variable valence ions (Fe, Nb).

4. Conclusions
The correlations between phase formation, dynamics of the microstructure, and dielectric responses of the solid solutions in the \((1-x)\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3\)\(\rightarrow\text{xPb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3\) system were established. The critical impact of a liquid phase on crystallization and macroscopic responses in the solid solutions investigated was found.

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