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Thermophysical properties and phase transitions of ferroelectric $PbFe_{0.5}Nb_{0.5}O_3$ at high temperatures

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The thermophysical properties of the ferroelectric $PbFe_{0.5}Nb_{0.5}O_3$ in the temperature range 300−800 K are studied. Anomalies in the heat capacity and thermal diffusion are found in the region of the diffuse ferroelectric transition $T_c \approx 380$ K, the Burns temperature $T_d \approx 670$ K, and the intermediate temperature $T^* \approx 470$ K. The dominant phonon heat transfer mechanisms in a ferroelectric with a nanopolar structure.

Keywords: heat capacity, thermal diffusion, thermal conductivity, ferroelectric, phase transitions, relaxor.

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1. Introduction

In recent years, a class of materials — ferroelectrics–relaxors, in which a magnetic structure (multiferroics) is realized, has attracted considerable interest from researchers. They have both magnetic and electrical ordering and are promising materials for solid-state electronics. One of the classic model objects for the study of such materials are lead ferroniobate $PbFe_{0.5}Nb_{0.5}O_3$ (PFN) perovskites. Three ferroelectric phase transitions are observed in PFN at temperatures of 303, 353 and 380 K [1–4] and one magnetic phase transition from the paramagnetic to antiferromagnetic state at 143 K [2]. At the Curie temperature $T_c \approx 380$ K, the transition from the cubic paraelectric phase to the tetragonal ferroelectric phase occurs in it, and the transition into the orthorhombic ferroelectric phase [5] occurs in the temperature range $T_c \approx 350$ K. The study of the electrophysical properties of the PFN multiferroic and their connection with the structural parameters was carried out in the work [6]. In a PFN, several phases with close free energies but different degrees of long-range order, Curie temperatures, directions of the polarization vector i t.e can coexist simultaneously.

As it is well known, the characteristic features of relaxors [1,2] are the smearing of the anomalies in permittivity ε (and heat capacity) in a wide range of temperatures and the significant dependence of the temperature of its maximum T_m on the frequency of the measuring field. In addition, PFN has a high dielectric constant ($\varepsilon > 10\,000$), a diffuse phase transition (usually $T_m \geq T_c$) and a low temperature synthesis, which is very important for their use in multilayer ceramic capacitors and other electronic devices. Despite the relaxor nature of the phase transition, these crystals show a very weak frequency dependence of the permittivity [7]. It is believed that polar nanozones, which are an important microscopic feature of relaxors, play an important role in various macroscopic properties. The temperature at which dynamic nanopolar zones (which break long-range order) are born is called the Burns temperature T_d, which is typically several hundred degrees higher than T_m and T_c. The Burns temperature T_d was recorded in the range of 600−700 K [8] for the known ferroelectric relaxors based on lead. Upon cooling at $T < T_d$, nanopolar zones begin to interact with each other, and at some so-called intermediate temperature T^* they merge into larger ones (corresponding to a nanoscale phase transition associated with random fields) [9,10] and long-lived polar zones [11,12]. Further cooling can lead to freezing of these dipole zones in a non-ergodic state (at a temperature T_f), i.e. to the formation of a glassy dipole phase [2].

A fairly large number of works have been devoted to the study of the physical properties of a PFN multiferroic with the use of various methods. However, the experimental results of various studies of PFN and their interpretation by different authors do not always agree with each other. Moreover, there are few studies of these materials in the literature regarding high temperatures. In particular, this may be due to the high conductivity at high temperatures, which often masks the effects of structural changes. Therefore, the question of the change in physical and structural characteristics and the existence of phase transitions in PFN at high temperatures remains open.

Heat capacity studies in a wide temperature range make it possible to record abnormal of various origin and to acquire important information regarding the nature of physical phenomena in the materials of interest. Heat transfer processes in $PbFe_{0.5}Nb_{0.5}O_3$ in a wide temperature range have not been studied to date, as far as we know. In this work, we study the thermophysical parameters (heat capacity, thermal conductivity, thermal diffusion) of PFN at high temperatures of 300−900 K in order to obtain additional information on the physical processes in these materials.

2. Sample and measurement procedure

$PbFe_{0.5}Nb_{0.5}O_3$ ceramic samples were obtained using conventional ceramic technology. Lead ferroniobate powders were synthesized from the corresponding oxides by a thermochemical reaction in the solid phase. An excess of lead oxide PbO was added to the mixture to compensate for the evaporation of PbO at synthesis. X-ray diffraction measurements at room temperature showed that the samples are single-phase and have a cubic (space group $Pm3m$) perovskite structure.

Thermal diffusion and thermal conductivity were studied by laser flash method using LFA-457 MicroFlash setup by NETZSCH (Germany). The relative measurement error did not exceed 5%. Parallel-plane specimens were used: diameter 12.7 mm and thickness 1 mm. The rate of temperature change was 5 K/min. No any additional coating was used during measurements. Thermal conductivity was calculated by the following formula: $\lambda = \eta C_p \rho$, where η — thermal diffusion (temperature conductivity), ρ — specimen density, C_p — heat capacity. Heat capacity was measured by NETZSCH DSC 204 F1 Phoenix® differential scanning calorimeter. The heat capacity measurement sample was a plate with a diameter of 4mm and a thickness of one mm.

3. Results of investigation

Figure 1 shows the results of studies of the heat capacity C_p of $PbFe_{0.5}Nb_{0.5}O_3$ solid solutions in the temperature range 300−800 K. As can be seen from the figures, the temperature dependences of the heat capacity of PFN in the temperature range $T_c \approx 380$ K exhibit an anomaly of the ferroelectric phase transition, which has a „smeared" character characteristic of relaxors. In the zone of high temperatures 670 K, the dependences $C_p(T)$ PFN exhibit an anomalous behavior characteristic of phase transformations. It is possible that nanopolar zones begin to appear in the PFN relaxor ceramics in this temperature range. E.i., at $T_d \approx 670$ K, a phase transition occurs, which leads to rhombohedral lattice distortion in local nanoscale zones and the appearance of polarization in them. However, the correlation length of such zones is very small and no macroscopic polarization occurs. In our case, the anomalous behavior of the heat capacity of PFN, which begins to be observed experimentally in the zone of 670 K, is really close to the Burns temperature $T_d \approx 603−690$ K, determined on the basis of structural and Acoustic Research PFN [8–12].

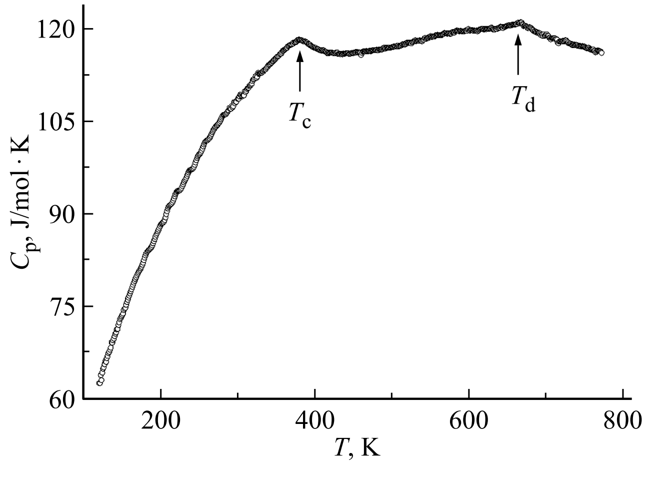

Figure 1. Temperature dependence of the heat capacity C_p of the ferroelectric $PbFe_{0.5}Nb_{0.5}O_3$.

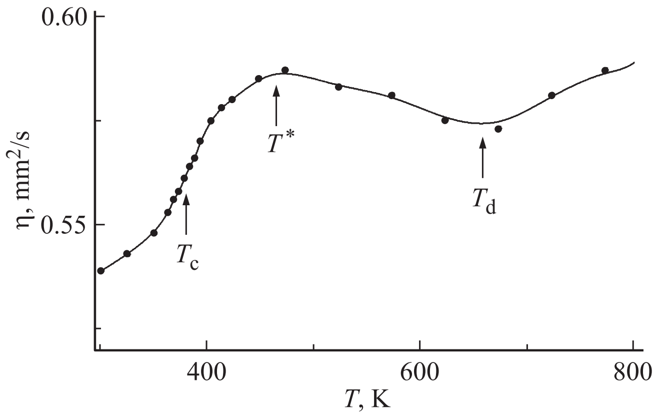

Figure 2. Temperature dependence of the thermal diffusion η of the ferroelectric $PbFe_{0.5}Nb_{0.5}O_3$.

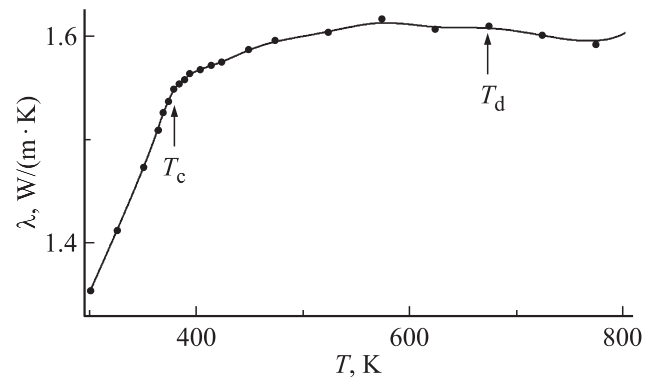

Figure 3. Temperature dependence of the thermal conductivity λ of the ferroelectric $PbFe_{0.5}Nb_{0.5}O_3$.

Figures 2, 3 show the temperature dependences of thermal diffusion η and thermal conductivity λ of PFN samples in the temperature range 300−800 K. The dependences $\eta(T)$ and $\lambda(T)$ exhibit anomalous behavior, as well as the dependences $C_p(T)$, in the temperature range of the smeared ferroelectric phase transition $T_c \approx 380$ K and $T_d \approx 670$ K. The dependence $\eta(T)$ exhibits an additional anomaly in the temperature range $T \approx 470$ K. It is possible that at this temperature $T^* \approx 470$ K, the nanopolar zones merge into larger and long-lived dipole zones (nanoscale phase transition associated with random fields), since in many well-known Pb-based relaxor ferroelectrics the temperature is T^* is in the temperature range 450−570 K [8,10].

To analyze temperature dependencies of thermal diffusion and temperature conductivity, we calculate the free path length of phonon using the known relationship $\eta = (1/3)\vartheta_s l_{\text{ph}}$ and Debye expression for phonon thermal conductivity $\lambda_{\text{ph}} = (1/3)C_\vartheta \vartheta_s l_{\text{ph}}$ (where λ_{ph} — thermal conductivity, C_v — heat capacity of unit volume). Values of η, λ_{ph} and C_{p} ($C_{\text{p}} \approx C_\vartheta$) are determined experimentally (see Fig. 1–3), the sound velocity data is taken from [13,14]. Independent estimates l_{ph} from measurements of thermal conductivity and thermal diffusion for PFN lead to the same value $l_{\text{ph}} \sim 4.0\,\text{Å}$ (at $T \geq T_{\text{room}}$). Thus, the scattering of phonons at crystal grain boundaries can be neglected, if the crystal grains have sizes are of the order of several microns, i.e. k. $l_{\text{ph}} \ll d$, where d — is the average size of the granules. From this, we can make an assumption that structural distortions (i.e. centers of scattering) limiting the free path length of phonons in PFN have values of the order of lattice constant. Defects, local distortions of the lattice, which change significantly during phase transformations, can act as such scattering centers. These distortions cam play a pivotal role in restricting the phonon heat transfer in these materials.

As can be seen from Fig. 2, 3, in the temperature range of the smeared ferroelectric transition $T_{\text{room}} < T < T^*$ ($T^* > T_{\text{c}}$) upon heating PFN, there is a slight increase in thermal diffusion and thermal conductivity, which is usually characteristic of amorphous and glassy bodies. It can be assumed that such a behavior of the thermal conductivity in the zone of 300–470 K is explained by the decay of ferrodomains into disordered dipoles (i.e., the formation of a dipole glass), which can be considered as crystal lattice defects and on which scattering occurs phonons participating in the process of heat transfer. As the phase transition is approached, their number and size decrease, which leads to an increase in the phonon mean free path and, correspondingly, to an increase in thermal conductivity and thermal diffusion.

As can be seen from Fig. 2, in the temperature range $T_{\text{c}} < T < T_{\text{d}}$, when PFN is heated, first up to a temperature $T^* \approx 470\,\text{K}$, an increase thermal diffusion, and then a slight decrease in thermal diffusion to T_{d}, which may be due to an increase in the decay above T^* of long-lived static polar zones into smaller dynamic nanopolar zones (nanosized inhomogeneous states) with an increase in temperature, which leads to an increase in phonon scattering centers. According to the structural data [10,15,16] these centers can be distortions of the lattice parameters (and changes in the lattice cell volume) caused by polar shifts of ferroactive cations Pb^{2+} and Nb^{5+} and displacements of oxygen from their initial positions in the temperature range $T^* < T < T_{\text{d}}$. At $T > T_{\text{d}} \approx 650\,\text{K}$, the nanopolar zones disappear (i.e., polar shifts of ferroactive cations Pb^{2+} and Nb^{5+}), which leads to a significant decrease in lattice distortions, i.e., scattering centers, and, accordingly, to an increase in the phonon mean free path and a noticeable increase in thermal diffusion in the $T > T_{\text{d}}$ zone (see Fig. 2).

4. Conclusion

The results of the investigations carried out and their analysis together with the literature structural data indicate that the main mechanism of phonon scattering in the relaxor PFN is local distortions of the crystal lattice caused by polar shifts of the Pb^{2+} and Nb^{5+} and displacements of oxygen from their initial positions and the resulting nanopolar zones and the glass dipole phase. On the temperature dependences of the heat capacity, thermal diffusion, and thermal conductivity, anomalies of the ferroelectric at $T_{\text{c}} \approx 380\,\text{K}$, „nanoscale" for $T^* \approx 470\,\text{K}$ and Burns for $T_{\text{d}} \approx 670\,\text{K}$. It is shown that studies of thermophysical properties allow to determine all the temperatures characteristic of ferroelectric relaxors associated with the appearance and temperature evolution of a nanopolar structure.

Conflict of interest

The authors declare that they have no conflict of interest.

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