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Relaxation dynamics, phase pattern in the vicinity of the Curie temperature, Fe valent state and the Mössbauer effect in PFN ceramics

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Abstract

High-density lead ferroniobate, $PbFe_{1/2}Nb_{1/2}O_3$ (PFN), was prepared by the conventional ceramic technology. Its dielectric properties, phase pattern in the vicinity of transition into the polar phase, and the x-ray electron and Mössbauer spectra were studied. The relaxation dynamics discovered at the temperature exceeding the Curie temperature at the frequencies of 3×10^{-2}–10^5 Hz is described in detail. Near T_C, the following sequence of phase transitions was established: rhombohedral ($T<368$ K)→pseudocubic ($368\text{ K}<T<387$ K)→cubic ($T>387$ K). It is shown that in both the ferroelectric and paraelectric phases the Fe ions are, mainly, in a high-spin valent state Fe^{3+} in the octahedral environment.

Keywords: B. Spectroscopy; C. Ferroelectric properties; D. Ferrites; Mössbauer effect

1. Introduction

Lead ferroniobate, $PbFe_{1/2}Nb_{1/2}O_3$ (PFN), is a representative of the class of materials called “multiferroics” [1]. Its close and fairly high values of the Néel and Curie temperatures, $T_N\sim140$–170 K [2] and $T_C\sim368$–385 K [2–9], make PFN a very interesting object from the applied point of view (the use in the UHF and sensor technique [10]) as well as from the standpoint of possibilities for studying the interaction of ferroelectric and magnetic subsystems. Despite the fact that PFN has received a broad study [2–9], in a number of works there are the contradictions concerning the T_C value (according to the different reported data it ranges from 368 K to 385 K [2–9]), the phase pattern in the vicinity of transition into the polar phase [5,11–15], and so on. In addition, in Ref. [2], the anomalous behavior of the relative dielectric permittivity $\varepsilon/\varepsilon_0$ and the loss tangent tg δ in PFN near T_C was noticed but its origin was not discussed. The present work deals with a detailed study of dielectric properties of PFN in the wide temperature (293–973 K with a step of 1–2 K and frequency 3×10^{-2}–10^5 Hz) ranges and a detection of their interaction with structural and crystallochemical peculiarities of this compound.

2. Methods for the preparation and examination of the samples

The samples for studying were synthesized by the method of solid-state reactions from the high-purity oxides PbO, Fe_2O_3 and Nb_2O_5 using the two-stage annealing with the intermediate milling at the temperatures $T_1=T_2=1123$ K for 4 h ($\tau_1=\tau_2$). At each temperature the synthesized products were sintered at $T_{sint}=1373$ K for 2 h.

The x-ray structure analysis was performed by the x-ray powder diffraction method using the ADP-1 diffractometer ($Cu_{K\alpha}$ radiation; the Bragg–Brentano focusing scheme). A study was made on the powdered sample, which enabled us to preclude the effect of surface effects, stresses and texture arising in the process of preparation of the ceramics.

The complex relative dielectric permittivity ($\varepsilon^*/\varepsilon_0=\varepsilon'/\varepsilon_0+i\varepsilon''/\varepsilon_0$, where ε' and ε'' are the real and imaginary parts, respectively, ε_0—dielectric constant) was measured on non-polarized ceramic samples in the form of a disk

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coated with the end faces of silver electrodes with the help of a universal measuring bridge (Novocontrol ALPHA A High-Resolution Dielectric Analyzer) equipped with a Novocontrol-HT temperature control system for high-temperature measurements (3×10^{-2}–10^5 Hz) as well as Broadband High Voltage Booster HVB 1000 and Novocontrol QUATRO cryosystem for investigation of reversible nonlinearity, i.e. the dependency of $\varepsilon^*/\varepsilon_0$ measured in a weak AC electric field on cyclically varying DC bias electric field E.

x-Ray photoelectron spectra (XPS) were obtained using x-ray photoelectron microprobe ESCALAB 250. XPS were excited with a monochromatized AlKα-line radiation. Absolute resolved energy interval was of 0.5 eV, which was determined by the Ag3d$_{5/2}$ line. The diameter of the x-ray spot on a sample was 500 µm; it was small enough to study the samples obtained. Combined exposure to slow electrons and ions was employed to remove the positive charge on the sample. Contamination-free surface of ceramic was obtained by the diamond file scribing in vacuum within a sample preparation chamber at a pressure of about 1×10^{-8} Torr.

Mössbauer spectra were studied with the help of a MC1104Em spectrometer (designed at the Research Institute of Physics, SFU) with the gamma radiation source ^{57}Co in the Cr matrix. Model interpretation of the spectra was performed using the computer program UnivemMS. Isometric chemical shifts of spectra were assessed in relation to the metallic α-Fe.

3. Experimental results and discussion

The analysis of experimental results evidences the obtaining of high-density, impurity-free samples of the PFN ceramics (the relative density, $\rho_{\text{rel}}, > 95\%$), which enables one to consider them as reliable and trustworthy.

Ferroelectric (FE) properties of the studied ceramics, clearly manifested at room temperature in the study of dielectric hysteresis loops (Fig. 1) and reversible nonlinearity (Fig. 2). The dependences shown in figures are typical for classical ferroelectrics, and their analysis allowed us to calculate the value of the residual polarization $P_R \sim 0.2$ C/m^2 and the coercive field, $E_C \sim 1.4\times10^5$ Вм$^{-1}$.

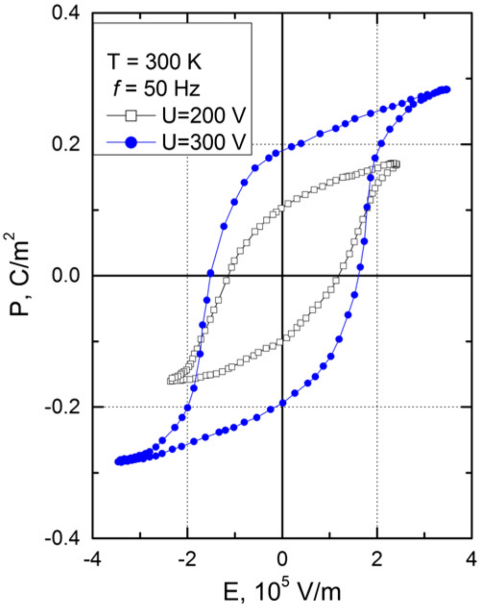

Fig. 1. A set of hysteresis loops of PFN ceramics at a frequency of 50 Hz at room temperature for different amplitudes of the voltage U.

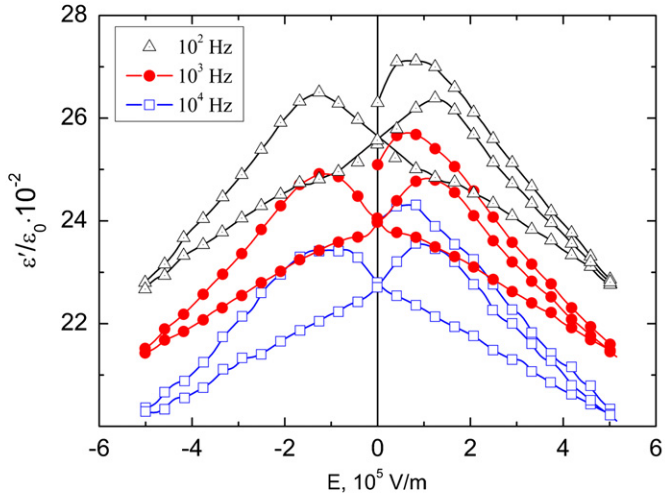

Fig. 2. Dependences of $\varepsilon'/\varepsilon_0$ on E for PFN ceramics, measured at frequencies of 10^2, 10^3 and 10^4 Hz at room temperature.

Fig. 3 presents the temperature dependences of $\varepsilon'/\varepsilon_0$ and tg δ for PFN in the range of 293–673 K measured in the frequency range of 3×10^{-2}–10^5 Hz. The well defined, independent of frequency $(f)\varepsilon'/\varepsilon_0(T)$ maximum at $T=369\pm1$ K is indicative of the fact that it is just the temperature which is T_C. At $T>T_C$, one can observe a formation of the additional $\varepsilon'/\varepsilon_0(T)$ maximum which is reversible, highly relaxing, having a remarkable dispersion, displacing to the high-temperature side ($\Delta T_m=222$ K; T_m is the $\varepsilon'/\varepsilon_0(T)$ maximum temperature in the range above T_C) and decreasing in the case of the increase of f from 2×10^2 Hz to 10^5 Hz ($\Delta\varepsilon'/\varepsilon_{0\max}=49{,}661$) in the temperature range of 400–673 K; one observes a growth of tg δ as well. It is well seen that at the frequencies of 2×10^2–10^5 Hz the $\varepsilon'/\varepsilon_0$ values in maxima at $T=T_C$ exceed those at $T=T_m$ while in the case of decreasing frequency this difference decreases and at $\sim$25 Hz frequencies these values become, practically, equal. The following decrease of f leads to a progressively more remarkable role of the mechanism(s) responsible for the formation of a highly relaxing process in the range of $T>T_C$, and as a consequence, in the low-frequency range with the increase of temperature $\varepsilon'/\varepsilon_0(T)$ behaves as follows: after the maximum corresponding to T_C one can observe only a negligible decrease of $\varepsilon'/\varepsilon_0$ (and, at $f=1$–6 Hz, a kink on the $\varepsilon'/\varepsilon_0(T)$ curve) followed by its increase (see Ref. [4]) and a formation of the maximum at T_m corresponding to the measuring frequency. At $f<1$ Hz, a "temperature" separation of contributions from the different mechanisms of the formation of $\varepsilon'/\varepsilon_0$ maxima in the recorded dielectric response becomes impossible because there occurs their complete merging. As a result, there takes place a formation of only one, highly diffuse $\varepsilon'/\varepsilon_0(T)$ maximum at the temperatures exceeding T_C.

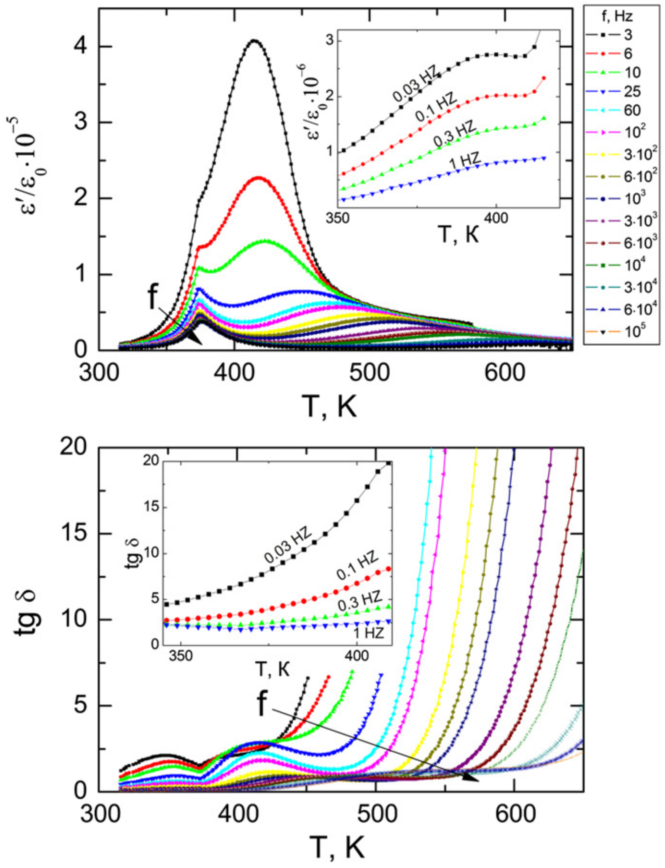

Fig. 3. Temperature and frequency dependences of $\varepsilon'/\varepsilon_0$ (top) and tg δ (bottom) for PFN in the range of 293–673 K and 3×10^{-2}–10^5 Hz.

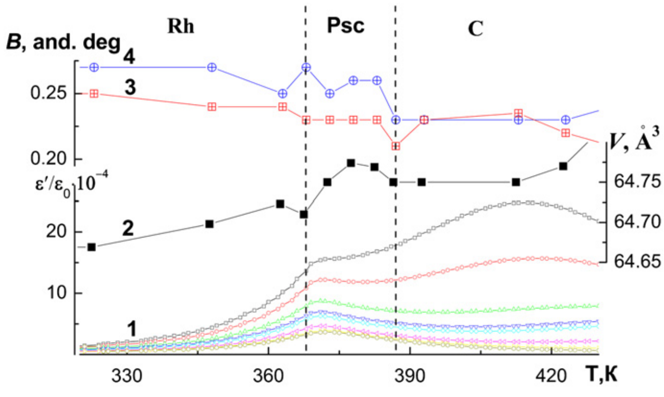

Fig. 4. The region of the F→P phase transition in PFN and the temperature dependences of $\varepsilon'/\varepsilon_0$ (1), V (2), half-widths of the x-ray lines B 200 (3) and B 220 (4).

Fig. 4 shows the temperature dependences of $\varepsilon'/\varepsilon_0$, the unit cell volume ($V$) and the half-widths of x-ray lines B_{200} and B_{220} for PFN at $T=293$–423 K.

In the range of 293 K $\leq T \leq$ 363 K is situated a rhombohedral (Rh) phase. At 363 K $\leq T \leq$ 387 K, a jump-like change of the B_{220} line, a step of V at $T=368$ K, a domed change of V with a maximum at $T=378$ K and a minimum at $T=387$ K are indicative of the rearrangement of structure in this temperature range. At the same time, the decreased half-width of the 200 line does not give any reasons for identification of temperatures of the tetragonal (T) phase in this range disclosed in Ref. [15] in the process of studying the PFN single crystals, and therefore, we defined this phase as pseudocubic (Psc). The first V step temperature (368 K) precedes T_C determined from the electrophysical measurements in the present work. The maximum V temperature (378 K) corresponds, practically, to a transition into the cubic (C) phase reported in Ref. [5] (376 K). At the minimum V temperature (387 K) PFN undergoes a transition into the C phase in accordance with the results obtained in Ref. [7].

The analysis of Figs. 3 and 4 has shown that the relaxation PFN dynamics detected in the temperature range above T_C is not related to the change of its phase state. It is probably due to the change of its real (defect) structure, namely: the motion of oxygen vacancies, interlayer (Maxwell–Wagner) polarization [16] a formation of which may be due to the variable valency of Fe, that is, the presence of some amount of Fe^{2+} in addition to Fe^{3+}. To clarify this question the XRE study and a study of the Mössbauer effect in PFN were carried out.

The results of XPS studies on the PFN ceramics at room temperature presented in Figs. 5 and 6.

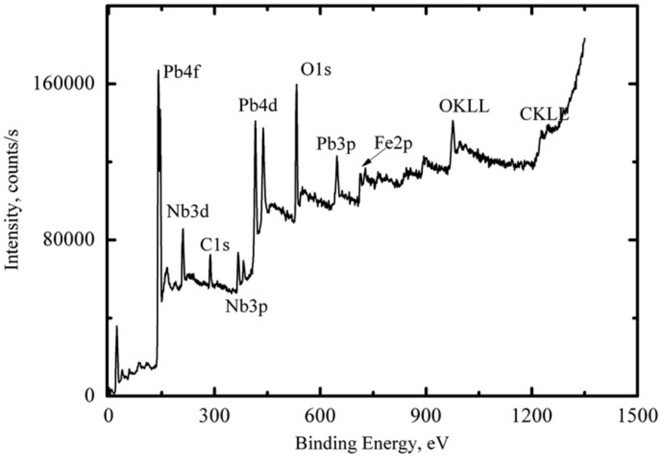

Fig. 5. Review x-ray electron spectrum from the surface of PFN ceramics.

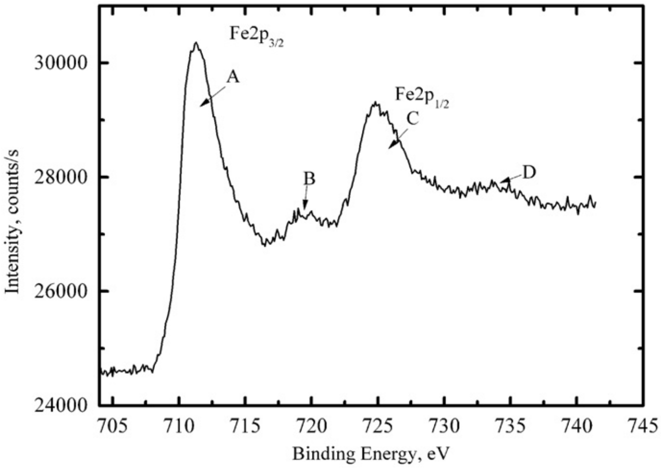

Fig. 6. x-Ray electron Fe2p spectrum from the ceramic PFN sample.

The survey PFN spectrum (Fig. 5) giving an idea of the qualitative elemental composition of the ceramic layer under study (of the order of 5 nm) shows only the lines referring to the compound elements. As seen from Fig. 6, the Fe2p-spectrum has four special features: A, B, C, D. The A peak is the Fe2p$_{3/2}$ line from the electron level of Fe2p. Its energetic position with calibration on the 1s line of carbon accepted as 285 eV is at 711.3 eV. The C peak is the Fe 2p$_{3/2}$ line from the electron level of Fe2p (energetic position is at 724.8 eV). The B and D peaks in the Fe2p spectrum refer to the charge transfer satellites (their energetic positions are at 719.6 eV and 734.2 eV, respectively). The energetic position of the A peak being at 711.3 eV [17,18] and the presence of charge transfer satellites with the above mentioned energies may be considered evidence that in the ceramics under study ions Fe is only in the Fe^{3+} state.

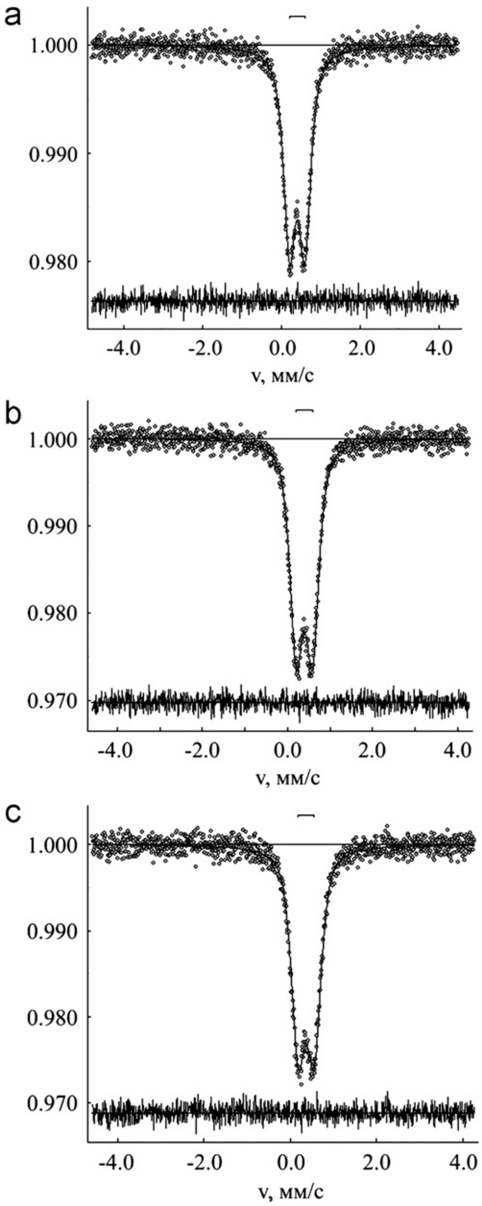

Fig. 7. Mössbauer spectra from the ceramic PFN sample obtained at 300 K (a), 353 K (b) and 393 K (c).

Table 1
Parameters of the Mössbauer spectrum for the ceramic PbFe$_{1/2}$Nb$_{1/2}$O$_3$ sample.

T (K)	δ* (mm/s)	ΔE_Q^{**} (mm/s)	G*** (mm/s)
300	0.40(7)	0.38(9)	0.36(1)
353	0.39(9)	0.38(1)	0.36(7)
393	0.37(1)	0.37(3)	0.38(7)

δ* is the magnitude of the isomeric chemical shift, ΔE_Q^{**} is the magnitude of the quadrupole splitting, and G*** is the width of spectrum lines.

This is also indicated by the results of studying the Mössbauer effect presented in Fig. 7 and in Table 1. It is seen that on the Mössbauer spectra measured in both the FE (Fig. 7a and b) and paraelectric (PE) (Fig. 7c) phases one can observe a paramagnetic doublet.

The doublet parameters (see Table 1) correspond to the high-spin Fe^{3+} ions in the octahedral environment. The presence of quadrupole splitting is typical of the given class of compounds and is due to the distortion of oxygen polyhedra. The broadening of Mössbauer spectra lines is related to the random distribution of Fe^{3+} and Nb^{5+} ions.

It should be noted that a precision of determination of the Fe valent state under the procedure described above is ≈0.5–1.0%, but, as is known, in such ceramics even hundredth fractions of the impurity percentage (in our case, Fe^{2+}) can have a substantial influence on their properties [19]. Our qualitative chemical analysis for the presence of Fe^{2+} and Fe^{3+} ions in lead ferroniobate has shown that, together with Fe^{3+}, in the sample under study Fe^{2+} is also present in the amount sufficient for its qualitative determination by the methods of analytical chemistry.

4. Conclusions

It has been established that in the PFN ceramics:

- the Curie temperature, T_C, is equal to 369 ± 1 K and, in the range of temperatures exceeding T_C, the additional relaxing maximum appears on the dependences $\varepsilon'/\varepsilon_0(T)$ in the range of 400–700 K;
- at $f < 1$ Hz, on the dependences $\varepsilon'(T)$ there takes place a formation of only one, highly diffuse maximum, which indicates a prevailing role of the mechanism(s) responsible for the formation of a highly relaxing process at these frequencies at $T > T_C$;
- in the vicinity of T_C, one can identify the following sequence of phase transitions: Rh($T < 368$ K)$\rightarrow$Psc(368 K $< T <$ 387 K)$\rightarrow$C($T > 387$ K);
- from the results of x-ray electron and Mössbauer spectroscopy it follows that in both the FE and PE phases the Fe ions are, mainly, in the high-spin valent state Fe^{3+} in the octahedral environment;
- a qualitative chemical analysis for the presence of Fe^{2+} and Fe^{3+} in lead ferroniobate has shown that, together

with Fe^{3+}, in the sample under study Fe^{2+} is also present.

From what was said above it may be concluded that the results obtained in the process of our investigations evidence the existence of the defect situation in lead ferroniobate ceramics substantially affecting their dielectric properties.

The results obtained in the course of these studies should be considered in the development and research of materials based on lead ferroniobate.

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