Structural, dielectric, and Mossbauer studies of multiferroic (1-x)PbFe$_{0.5}$Nb$_{0.5}$O$_3$ - xPbCr$_{0.5}$Nb$_{0.5}$O$_3$ solid solution ceramics obtained by usual sintering and by high-pressure synthesis

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ABSTRACT

In the (1-x)PbFe$_{0.5}$Nb$_{0.5}$O$_3$ - xPbCr$_{0.5}$Nb$_{0.5}$O$_3$ (PFN-xPCN) ceramics fabricated by a usual solid state synthesis route the content of the pyrochlore phase increases dramatically with x, exceeding 50% for x = 0.3 composition. Synthesis under high (6 GPa) pressure enabled us to obtain perovskite PFN-xPCN ceramics, though for compositions with x ≥ 0.4 an admixture of the pyrochlore phase was still present. Both the pseudocubic lattice parameter and ferroelectric phase transition temperature decrease monotonically as x grows. The composition dependence of the antiferromagnetic phase transition temperature for PFN-xPCN is very similar to that in the PFN-PbMO$_3$ (M-Ti, Zr, Sn) solid solution systems implying the lack of magnetic exchange between Fe$^{3+}$ and Cr$^{3+}$ ions.

KEYWORDS

PbFe$_{0.5}$Nb$_{0.5}$O$_3$; PFN; PbCr$_{0.5}$Nb$_{0.5}$O$_3$; high-pressure synthesis; Mossbauer spectra

1. Introduction

Multiferroics are a class of substances possessing simultaneously several order parameters [1]. Multiferroics, which combine ferroelectric and magnetic properties, attract most attention nowadays, as they can be used to convert the magnetic signals to electric responses and vice versa [2]. Lead iron niobate PbFe$_{0.5}$Nb$_{0.5}$O$_3$ (PFN) based materials are among the promising multiferroics as they exhibit very high dielectric, pyroelectric, and piezoelectric responses [3–8] and can be sintered at relatively low temperature [7, 8]. Recently, PFN-based materials have attracted much attention, as PFN-Pb(Zr,Ti)O$_3$ (PZT) solid solutions were reported to exhibit room-temperature magnetic hysteresis loops [9]. Later, such loops were observed also in PFN-CaFe$_{0.5}$Nb$_{0.5}$O$_3$ solid solutions [10]. Both PPFN and its analog PbFe$_{0.5}$Ta$_{0.5}$O$_3$ (PFT) are antiferromagnets with Neel temperature $T_N$ ≈ 150 K [3, 11]. As the $T_N$ values of PFN and PFT solid solutions with PbTiO$_3$ (PT), PbZrO$_3$ (PZ), and CaFe$_{0.5}$Nb$_{0.5}$O$_3$ are well below the room temperature, a possible origin of these room-temperature magnetic properties was supposed to be the formation of super-paramagnetic clusters and/or...
Fe spin clustering [9]. However, though in the similar multiferroics, e.g. PFN-PT single crystals [13] and PbFeO$_{0.5}$Sb$_{0.5}$O$_3$ ceramics [15], the super-antiferromagnetic and/or super-paramagnetic clusters were observed up to rather high temperatures well above the $T_N$, magnetization loops were observed only below $\approx 30$–$50$ K. Another possible explanation of these room-temperature magnetic properties is the presence of a small (below the detection limit of X-ray diffraction and Mossbauer spectroscopy) admixture of the ferromagnetic or ferrimagnetic phase [10, 11, 16–18]. Small grains of ferrimagnetic PbFe$_{12}$O$_{19}$ were observed by scanning electron microscopy on the surface of PFN ceramics [17], while in Li-doped PFN ceramics small inclusions of another ferrimagnetic compound, LiFe$_5$O$_9$, were observed [18]. Thus, the origin of room-temperature ferromagnetic properties of PFN-PZT and PFN-CaFe$_{0.5}$Nb$_{0.5}$O$_3$ compositions remains a matter of debate and this uncertainty stimulates an interest for studying other PFN-based solid solutions.

The increase of $T_N$ values, preferably up to room temperatures, remains an important but yet unresolved problem for PFN-based materials. Though linear-quadratic paramagnetoelectric effect in PFN ceramics was observed at room temperature and up to the ferroelectric Curie temperature $T_C \approx 380$ K, the value of this effect is by several orders of magnitude lower than the one in the magnetic phase [19]. It was reported that $T_N$ values of both PFN and PFT powders could be increased by 50–70 K by means of a high-energy mechanical activation [17, 20]. Similar increase of $T_N$ by $\approx 50$ K was reported for epitaxial PFN film [21]. This enhancement of $T_N$ seems to be due to the increase of disorder of Fe$^{3+}$ and Nb$^{5+}$ cations in PFN, as both mechanical activation and compressive misfit strain promote such disordering [22, 23]. Disordering of Fe$^{3+}$ and Nb$^{5+}$ increases the number of the nearest magnetic neighbors for Fe$^{3+}$ ions. $T_N$ value is just proportional to this number [24]. One can suppose that doping of PFN by magnetic ions can slow down reduction of $T_N$, and perhaps even to increase $T_N$, in contrast to substitution of paramagnetic ions (e.g. Ti or Zr) for Fe. Multiferroics containing two different magnetic cations attract much attention nowadays, as in such systems one can expect the appearance of the ferromagnetic properties [25, 26]. The scope of the present work was to study how Cr substitution for Fe affects ferroelectric and magnetic phase transition temperatures of PFN.

2. Experimental

PbCr$_{0.5}$Nb$_{0.5}$O$_3$ (PCN) crystallizes at ambient pressure into pyrochlore structure [27]. Thus, for the present study PFN-xPCN ceramic samples were obtained by two methods. Compositions with $x = 0.05$, 0.10, 0.20, and 0.30 were prepared by solid state synthesis and usual sintering. Reagent grade PbO, Fe$_2$O$_3$, Nb$_2$O$_5$, and Cr$_2$O$_3$ oxides were batched in stoichiometric proportions and 1 wt% Li$_2$CO$_3$ was added to the batch. This addition promotes formation of the perovskite modification of PFN and its solid solutions and reduces their conductivity [7, 8]. To compensate Pb losses during sintering 2 mol.% of PbO was also added at this stage. Synthesis was carried out at 900°C for 2 hours and sintering was performed at 1050–1100°C for 2 hours in a closed alumina crucible. PbZrO$_3$ powder was placed in the crucible to reduce PbO losses at high temperatures. The density of ceramics obtained was about 92–95% of the theoretical one.

Compositions with $x = 0.2$, 0.4, 0.6, 0.8, and 1.0 were prepared by high-pressure synthesis [28]. First, we synthesized stoichiometric mixtures of PbO, Fe$_2$O$_3$, Nb$_2$O$_5$, and Cr$_2$O$_3$ corresponding to these compositions at $T = 900$°C for 4 hours. The resulting products possessed either pyrochlore
crystal structure or were the mixture of the pyrochlore and perovskite phases. The second stage of this synthesis has been performed under hydrostatic pressure 6 GPa and temperature 1200–1300°C for 1–2 min [28]. After the synthesis, the system was rapidly cooled to the room temperature under pressure and only then the high-pressure apparatus was unloaded. The product of the second high-pressure synthesis was dense coarse-grained (the grain size varied from 1 to 5 μm) ceramics. The samples obtained by a high-pressure synthesis usually possess an enhanced conductivity due to slightly reducing atmosphere in a high-pressure apparatus. As this conductivity is mainly due to oxygen vacancies, which are the most easily-formed intrinsic defects in the perovskite oxides [29], all the samples obtained by a high-pressure synthesis, were annealed in air at 600–700 K for 2 hours prior to measurements. Such annealing, indeed, have led to a decrease of conductivity by 1 or 2 orders of magnitude. The sintered samples were grinded and electroded by firing on the Ag paste at 500°C. X-ray phase analysis was performed using DRON-7 diffractometer and Cu-Kα radiation. The volume percent of pyrochlore phase was estimated from the ratio of relative intensities of the (222) pyrochlore peak and the (110) perovskite peak [30].

Dielectric studies were carried out in the course of both heating and cooling at a rate of 2–3 K/min with the aid of Wayne Kerr 6500B impedance analyzer. Mossbauer spectra were recorded with the aid of the MS-1104EM rapid spectrometer attached to helium refrigerator CCS-850 and analyzed using the original computer code UnivemMS [31, 32]. The isomer shifts were calculated with respect to the metallic α-Fe.

3. Results and discussion

As was already mentioned above, PCN crystallizes at ambient pressure in the pyrochlore structure. Accordingly, in the PFN-xPCN samples, fabricated by a usual solid state synthesis route, the content of the pyrochlore phase increased dramatically with x, exceeding 50% for x = 0.3 composition (Fig. 1, curve 1). Synthesis under high pressure enabled us to obtain perovskite PFN-xPCN ceramics in the whole range of concentrations, though for compositions with x ≥ 0.4 an admixture of the pyrochlore phase was still present (Fig. 1, curve 2). Pure PFN as well as PFN-xPCN compositions with x < 0.2, have a rhombohedral symmetry. However, the rhombohedral angle β

![Figure 1. Content of the pyrochlore phase in PFN-xPCN ceramics obtained by usual sintering (curve 1) and by high-pressure (6 GPa) synthesis (curve 2).](image)
decreases gradually as \( x \) grows (Fig. 2) and compositions with \( x \geq 0.2 \) are cubic at room temperature. It is worth noting that similar to other \( \text{PbM}_3 \text{C}_{0.5}\text{Nb}_{0.5}\text{O}_3 \) perovskites (\( \text{M}^3{+} = \text{In}, \text{Sc} \)), though being macroscopically cubic, PFN and its solid solutions are non-cubic on the nanoscale, as is evidenced e.g. by EXAFS and Raman spectroscopy [33, 34]. Pseudocubic lattice parameter \( a = V^{1/3} \), where \( V \) is the unit cell volume, decreases gradually as \( x \) grows (Fig. 2). However, the \( a(x) \) dependence deviates from a linearity predicted by an empirical Vegard’s law [35]. Such deviation is often observed for solid solutions with a large difference in the unit cell volume of terminal members, e.g. for \( \text{BaTiO}_3-\text{CaTiO}_3 \) [36] and \( \text{BiFeO}_3-\text{NaNbO}_3 \) [37] systems.

Fig. 3 shows temperature dependences of the real part of permittivity \( \varepsilon' \) for the compositions studied. One can see that \( \varepsilon'(T) \) maximum lowers, diffuses and its temperature \( T_{max} \) decreases gradually as \( x \) grows (Fig. 2) and compositions with \( x \geq 0.2 \) are cubic at room temperature. It is worth noting that similar to other \( \text{PbM}_3 \text{C}_{0.5}\text{Nb}_{0.5}\text{O}_3 \) perovskites (\( \text{M}^3{+} = \text{In}, \text{Sc} \)), though being macroscopically cubic, PFN and its solid solutions are non-cubic on the nanoscale, as is evidenced e.g. by EXAFS and Raman spectroscopy [33, 34]. Pseudocubic lattice parameter \( a = V^{1/3} \), where \( V \) is the unit cell volume, decreases gradually as \( x \) grows (Fig. 2). However, the \( a(x) \) dependence deviates from a linearity predicted by an empirical Vegard’s law [35]. Such deviation is often observed for solid solutions with a large difference in the unit cell volume of terminal members, e.g. for \( \text{BaTiO}_3-\text{CaTiO}_3 \) [36] and \( \text{BiFeO}_3-\text{NaNbO}_3 \) [37] systems.

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decreases as x grows. For x = 0.8 and 1.0 (pure PCN) compositions no \( \varepsilon(T) \) maximum is observed. Instead, the step appears in the \( \varepsilon(T) \) curve, which position depends strongly on frequency (Fig. 4). Such shape of the \( \varepsilon(T) \) dependence is often observed in non-ferroelectric oxides and is attributed to the Maxwell-Wagner-type relaxation due to the difference in the conductivity of the grain bulk and grain boundaries \([38, 39]\). Note that our data for PCN do not confirm the data of Ref. \([27]\), where a sharp \( \varepsilon(T) \) maximum at 260 K was reported for high-pressure synthesized perovskite modification of PCN. To estimate quantitatively diffusion of the \( \varepsilon(T) \) maximum for compositions with x \( \leq 0.4 \), we used the parameter \( W_{2/3M-L} \) defined as the difference between \( T_m \) and the temperature \( T_{m_{\Delta}} \), at which \( \varepsilon' \) reaches 2/3 of the maximum value from the low-temperature side of the peak. It is well documented for relaxors and ferroelectrics with a diffused phase transition having different composition and structure \([40–43]\) that \( W_{2/3M-L} \) values are very close to the diffusion parameter \( \delta \), calculated with the help of widely used quadratic formula \([44]\). Fig. 5 shows the concentration dependences of \( T_{m_{\Delta}} \) and \( W_{2/3-L} \) for PFN-xPCN compositions.

At room temperature, Mossbauer \(^{57}\)Fe spectra of all the compositions studied appeared to be doublets with quadrupole splitting of \( \approx 0.4 \) mm/s and isomer shift of \( \approx 0.4–0.5 \) mm/s, corresponding to the Fe\(^{3+}\) ions occupying the octahedral sites of the perovskite lattice. To determine the magnetic phase transition temperature \( T_M \), we used the change of Mossbauer spectrum at this transition \([3, 31]\). When cooling below \( T_M \), the Mossbauer spectrum transforms from doublet to sextet \([3, 12, 14, 17, 18, 20, 28, 31]\). This transformation is accompanied by a dramatic decrease of the magnitude \( \eta \) of Mossbauer spectra intensity within the 0–1.2 mm/s velocity range normalized to its value at 300 K (Fig. 6). As one can see from Fig. 6, the temperatures of the abrupt drop of the \( \eta(T) \) curves for PFN-xPCN compositions studied are very close to each other and are much lower than that for undoped PFN. \( T_M \) value of PFN-xPCN compositions at first decreases rapidly as x grows (i.e. the Fe\(^{3+}\) concentration decreases), but then it saturates at \( T_M \approx 40–50 \) K level (Fig. 7). Interestingly, very similar \( T_M(x) \) dependences were observed for PFN-xPbTiO\(_3\), PFN-xPbZrO\(_3\), and PFN-xPbSnO\(_3\) solid solution systems \([3, 12, 45]\). These
dependences are shown for comparison in Fig. 7. Thus, doping of PFN with magnetic Cr\(^{3+}\) ions gives the similar result as in the case of doping with non-magnetic Ti\(^{4+}\), Zr\(^{4+}\), and Sn\(^{4+}\) ions. In the case of both Ti and Zr doping it was established earlier that a sharp change in the slope of \(T_m(x)\) dependence roughly corresponded to the percolative phase transition from a long-range antiferromagnetic order to a short-range spin-glass one \cite{3, 12, 13}. The results obtained imply that there is no magnetic exchange between Fe\(^{3+}\) and Cr\(^{3+}\) ions. The reason of such behavior seems to be a difference in electronic configuration of Cr\(^{3+}\) and Fe\(^{3+}\) ions. Cr\(^{3+}\) has a \(t^3\_2g^1\_e^1\) electronic configuration, while Fe\(^{3+}\) ion has a \(t^3\_2g^2\_e^2\) one. Thus, the value of transfer integral for 180° cation-anion-cation superexchange between octahedron-site \(t^3\_2g^1\_e^1\) and \(t^3\_2g^2\_e^2\) cations is close or equal to zero \cite{46}.

Figure 5. Concentration dependences of the \(\varepsilon(T)\), maximum temperature \(T_m\) (measured at 1 MHz) and the W2/3-L parameter characterizing the diffusion of the \(\varepsilon(T)\) maximum (see text for details) for PFN-xPCN ceramic compositions.

Figure 6. Temperature dependences of Mossbauer spectrum intensity within the 0–1.2 mm/s velocity range, related to its value at 300 K, for several PFN-xPCN compositions. Numbers at the curves correspond to \(x\) values.

4. Conclusion

Using the high-pressure (6 GPa) synthesis, perovskite PFN-xPCN ceramic compositions have been obtained in the whole range of concentrations. Both the temperature $T_{\text{m}}$ and the height of the permittivity-temperature maximum corresponding to ferroelectric phase transition decrease monotonically with x. Magnetic phase transition temperature $T_M$ also diminishes as the Cr content increases and $T_M(x)$ dependence is very similar to that observed when PFN is diluted by paramagnetic ions (Ti$^{4+}$, Zr$^{4+}$, Sn$^{4+}$). This fact implies that there is no magnetic exchange between Fe$^{3+}$ and Cr$^{3+}$ ions. The reason for the absence of such exchange seems to be the difference in electronic configurations of Cr$^{3+}$ and Fe$^{3+}$ ions [46].

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