



Magnetic and ferroelectric phase coexistence in multiferroic PFW-PT ceramics[#]

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Abstract

The multiferroic $(1-x)\text{PbFe}_{2/3}\text{W}_{1/3}\text{O}_3-x\text{PbTiO}_3$ solid solutions with various compositions $x = 0, 0.10, 0.20$ and 0.30 were investigated. The features of the relaxor-to-ferroelectric transition with increasing x were discussed based in connection with dielectric and ferroelectric properties. Different types of magnetic activity dependent on composition and temperature were found. The temperature of ferroelectric and antiferromagnetic phase coexistence was investigated in function of PT content, determining the temperature where each composition becomes multiferroic.

Keywords: $\text{PbFe}_{2/3}\text{W}_{1/3}\text{O}_3\text{-PbTiO}_3$, multiferroics, ferroelectric and magnetic properties, phase transitions

1. Introduction

A material is generally considered functional if it possesses a physical property that is usable in applications. In recent years, much attention has been paid to multiferroics - materials which simultaneously exhibit magnetic and ferroelectric ordering [1,2]. The interaction of the electric and magnetic subsystems can manifest itself as the magnetoelectric effect [3] and the effect of mutual influence of the polarization and magnetization [2].

In the past ferroelectric-magnets were much less studied due to their scarcity and indeed these properties seem to exclude each other. For magnetism one needs partially filled d shells of a transition metal, while practically all ferroelectric perovskites contain transition metal ions with an empty d shell. Ferroelectricity in these systems is caused by the off-center shifts of the transition metal ion, which forms strong covalent bonds with oxygen atoms, using their empty d states. On the other hand, the presence of magnetic transition metals'

electrons in d^n configurations suppresses this process, thus preventing ferroelectricity in magnetic perovskites [4,5]. One possible way around this problem is producing complex perovskites with d^0 and d^n ions, in B sites. In these materials, ferroelectricity and magnetism would have different sources and would appear independently of one another. Ferroelectricity typically appears at higher temperatures than magnetism [6]. Unfortunately, the coupling of magnetic and ferroelectric subsystems in mixed perovskites is rather weak. Additionally, a ferroelectric has to be a good insulator so that mobile charges do not neutralize ferroelectric polarization, but most ferromagnets are good conductors. As a consequence, the research on both new material systems and new coupling mechanisms are the principal conditions for a better understanding of magnetoelectric coupling mechanisms and its future development. A large number of Pb-based perovskites having the formula $\text{Pb}(\text{B}_1\text{B}_2)\text{O}_3$ with excellent dielectric, electromechanical and pyroelectric properties, make these and their solid solutions suitable for high performance materials with potential applications as sensors and actuators. But, unfortunately, the majority of relaxor perovskites have low ferroelectric transition temperatures.

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On the other hand, magnetic ordering temperature in Fe-based materials is proportional to Fe content, and generally, magnetic perovskites have low magnetic ordering temperatures.

An interesting peculiarity of $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ (PFW) system in comparison with other relaxors is caused by the presence of magnetic Fe^{3+} ions with an occupancy of 2/3 of the B-octahedral sites of the perovskite cells. This material has a disordered perovskite ABO_3 structure, where Fe^{3+} and W^{6+} ions are randomly distributed in B centers of the BO_6 octahedra. PFW is one of the classical relaxors with lower sintering temperature (about 1103 K). However, the lower Curie temperature T_C at 180 K is a disadvantage [6,7]. The lattice structure and the dielectric properties of the pure PFW can be easily changed by adding PbTiO_3 (PT). PTiO_3 is a typical ferroelectric with a sharp maximum of dielectric constant at 763 K. It is possible to move the Curie temperature close to room temperature and to modify the relaxation behaviour by choosing an appropriate amount of PT in the system. The magnetic activity of the $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ - PbTiO_3 (PFW-PT) single-crystal material can be defined with two phase transitions at $T_{N1} = 20$ K (weak ferromagnetism-to-antiferromagnetism) and $T_{N2} = 350$ K (antiferromagnetism-to-paramagnetism) [8]. Magnetic properties of the PFW-PT system have been studied on polycrystalline ceramic samples [9] and single crystals [8], but the results are contradictory.

The aim of the present work is to study the structural, dielectric, magnetic and ferroelectric changes of the PFW-PT system with composition and temperature, in order to detect the existence of a superposition of phases and the range of compositions that show multiferroic ordering.

II. Experimental

Fe_2O_3 and WO_3 powder were milled for 2 h, and then preheated at 1223 K for 3 h to form Fe_2WO_6 . Afterwards, PbO or a stoichiometric mixture of PbO and TiO_2 was mixed with Fe_2WO_6 to form $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ (PFW) and $(1-x)\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ - $x\text{PbTiO}_3$ with $x = 0.10$ (PFW-10PT), 0.20 (PFW-20PT) and 0.30 (PFW-30PT). The mixture was calcined at 1073 K for 3 h, ground and pressed in pellets and sintered at 1093–1153 K for 1–5 h. The heating rates were kept at 5 K/min for heating and 2 K/min for cooling.

PFW and PFW-PT were formed according to the following solid state reactions:



This two-step procedure suppresses the formation of pyrochlore phase [10].

Relative densities of the sintered samples were determined by the Archimedes method, while their micro-

structural features were analyzed using a JEOL/5800LV SEM. Structural characterization was done by X-ray powder diffraction at room temperature. Dielectric properties were measured at various frequencies between 100 Hz and 10 MHz in the temperature range of 10 K to 750 K, using an Impedance Analyzer HP 4194A, at a constant cooling rate of 2 K/min. Magnetic moments of samples were measured using a commercial superconducting quantum interferometric device - SQUID and in a Quantum design Physical Property Measurement System - PPMS in the temperature range of 4–400 K. The samples were cooled in the absence of a magnetic field (zero-field cooling - ZFC). A magnetic field was subsequently applied (200 Oe for DC measurements and 10 Oe for AC, at a frequency of 1 kHz) while heating (field heating, FH) for the measurement of the temperature dependence of the magnetization $M(T)$ and magnetic moment $m(T)$.

III. Results and discussion

The degree of PbO volatilization during the sintering of PFW was quite low, due to the low sintering temperatures. Relative densities of about 93–99 TD% could be achieved by this route. The densities increased, while the cell volume decreased as the PT content increased. XRD patterns of the PFW-PT ceramics indicate formation of a major phase with a cubic perovskite-type of structure (space group $pm\bar{3}m$) and a minor tetragonal pyrochlore-type phase (PbWO_4) (Fig. 1). The relative concentrations of perovskite and pyrochlore phases present in each sintered sample were calculated from the intensities of the major X-ray reflections from the respective phases and are presented in Table I. The complete structural phase diagram of PFW-PT solid solution was independently published by Feng and Ye [11] and by Mitoseriu *et al.* [12,13]. A morphotropic phase boundary (MPB) in crystals depends on x and is located within the composition interval of $0.25 < x < 0.35$ [12]. However, in ceramics, the MPB was not clearly resolved from structural studies and a coexistence of both pseudocubic and tetragonal phases for compositions from $x = 0.2$ to 0.37 was observed.

High degrees of densification could also be inferred by the scanning electron microscopy (SEM) observation of the polished surfaces. The microstructure of the

Table 1. Percentage of perovskite phase, resistivity and activation energies for electrical conductivity for PFW ceramics with various PT content

Sample	Perovskite [%]	E_a [eV]	ρ [$\Omega\cdot\text{m}$]
PFW	99.4	0.58	11391
PFW-10PT	99.0	0.49	7.25×10^7
PFW-20PT	98.5	0.50	1.56×10^8
PFW-30PT	98.5	0.47	7.28×10^7

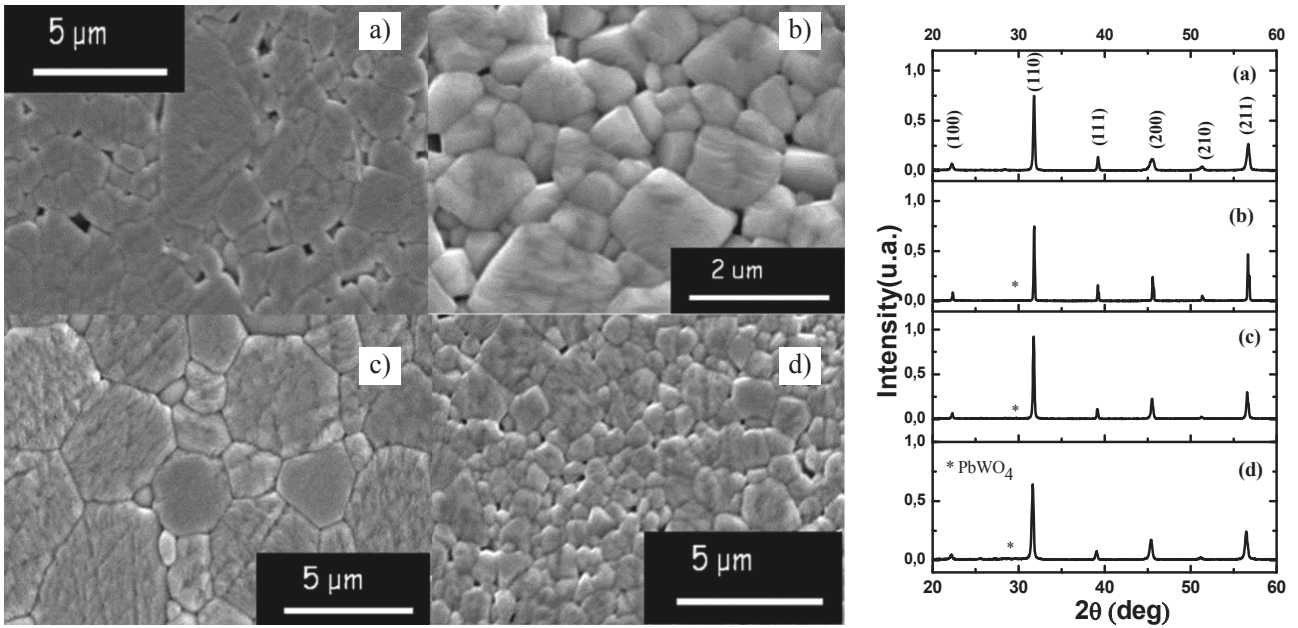


Figure 1. SEM microstructure and XRD of: a) PFW b) PFW-10PT, c) PFW-20PT and d) PFW-30PT ceramic

samples is shown in Fig. 1. The average grain size was around 5 μm for all samples and no systematic variation of grain size with change x .

In Table 1 the room temperature DC resistivity of PFW-PT ceramics are listed. All compositions with PT showed relatively high resistivity from 10^7 to $10^8 \Omega\cdot\text{m}$. As can be seen, the addition of PT increases the room temperature electrical resistivity of the PFW samples.

Dielectric permittivity curves as a function of the temperature for the pure PFW ceramic (Fig. 2a) are representative and similar to those measured in the other samples containing PT (Figs. 2b-d). In the temperature range of 150–700 K real and imaginary components show strong dependence on frequency and at least two peaks can be distinguished. The first peak, around 180 K, which can be attributed to the ferroelectric-paraelec-

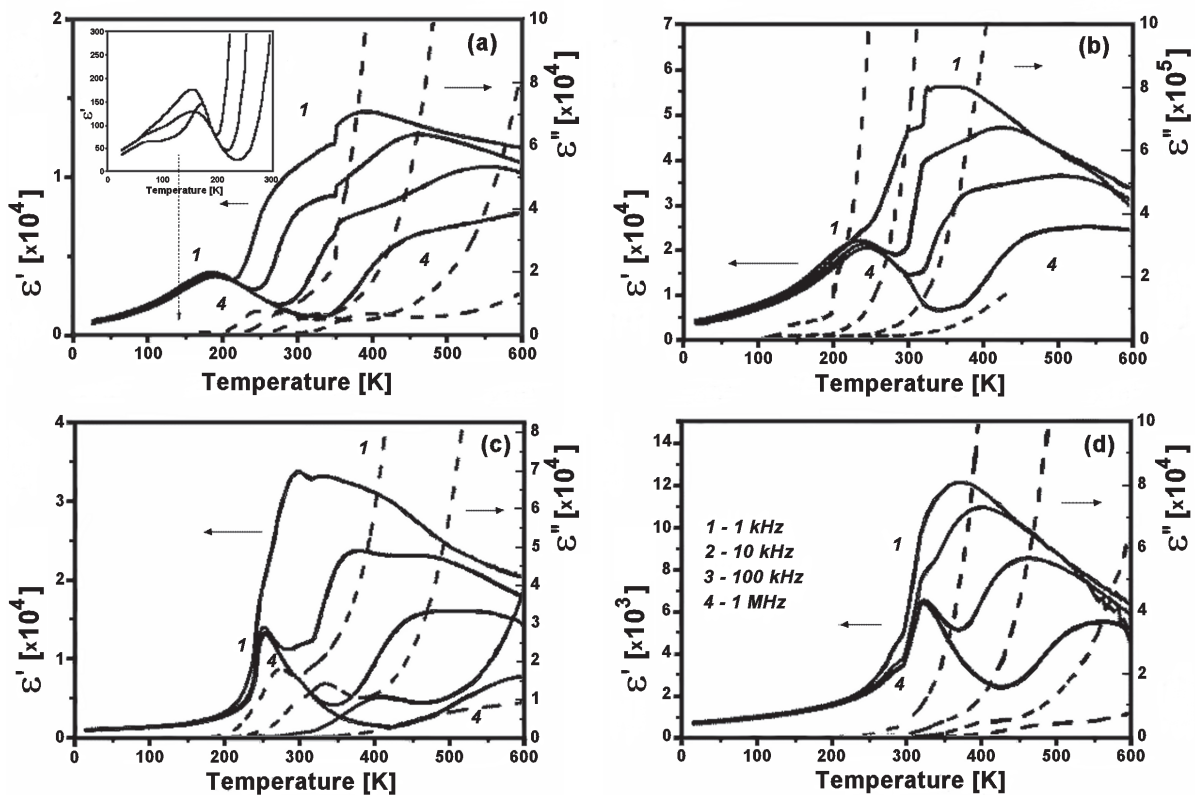


Figure 2. Relative dielectric permittivity at various frequencies as a function of the temperature for: a) PFW b) PFW-10PT, c) PFW-20PT and d) PFW-30PT ceramic

tric (FE) phase transition, shows relaxor behaviour and the temperature of maximum increases with the measuring frequency (Fig. 2a). As the PT content in the PFW-PT solid solutions increases, the maximum dielectric permittivity, corresponding to the FE transition increases (Fig. 2). Thus, the transition temperature corresponding to the maximum value of the dielectric constant increases from $T = 180$ K for $x = 0$ (PFW) to $T = 320$ K for $x = 0.3$ (PFW-30PT) compound, while the character of the phase transition changes from diffuse, typical for relaxors, to a sharp one, characteristic for “normal” ferroelectrics.

The dielectric relaxation of the $(1-x)$ PFW- x PT ceramics can be described by the Vogel-Fulcher (V-F) law:

$$f = f_o \exp[-E_a/k(T_m - T_f)],$$

where f is the measurement frequency, k the Boltzmann constant, T_m the temperature of the dielectric maximum, f_o the constant, E_a the activation energy and T_f the temperature of the dynamic freezing of the dipoles. The frequency dependence of the temperature of dielectric maximum can be well fitted by the V-F law, indicating typical relaxor behaviour. The results of fitting are listed in Table 2. The decrease of the temperature difference between T_m and T_f with the PT content confirms that the relaxation behaviour of the system gradually decreases.

The peaks observed in the real and imaginary part in Fig. 2, at temperatures higher than those related to the FE transition (in the range 200–700 K), shift to-

wards higher temperatures with increasing frequency. The maximum permittivity values decreased for higher frequencies. This result suggests that relaxation process is thermally activated and also appears for the samples with PT, however the peaks have smaller intensity with regard to the peak corresponding to the ferroelectric transition. This can be attributed to the conductivity effects due to electronic charges. These charges arise from the Fe^{+3} ions (d^n), which are usually combined with Fe^{+2} ions forming charge defects. Electron hopping between Fe^{+3} and Fe^{+2} ions would result in the conductivity, which in turn will give rise to dielectric dispersion. A detailed impedance spectroscopic study is required to analyze the contributions of different electrically active parts.

The macroscopic polarization in PFW-PT ceramics, induced by application of an electric field has been measured at various temperatures (Fig. 3). Non-linear polarization and a slim hysteresis were obtained at temperatures above the maximum temperature, indicating a relaxor ferroelectric behaviour. Figure 3 shows P - E loops for the PFW-PT ceramics measured at different

Table 2. Freezing and maximum temperature obtained for the dielectric data

	PFW	PFW-10PT	PFW-20PT
T_m	186	231	256
T_f	105	173	238

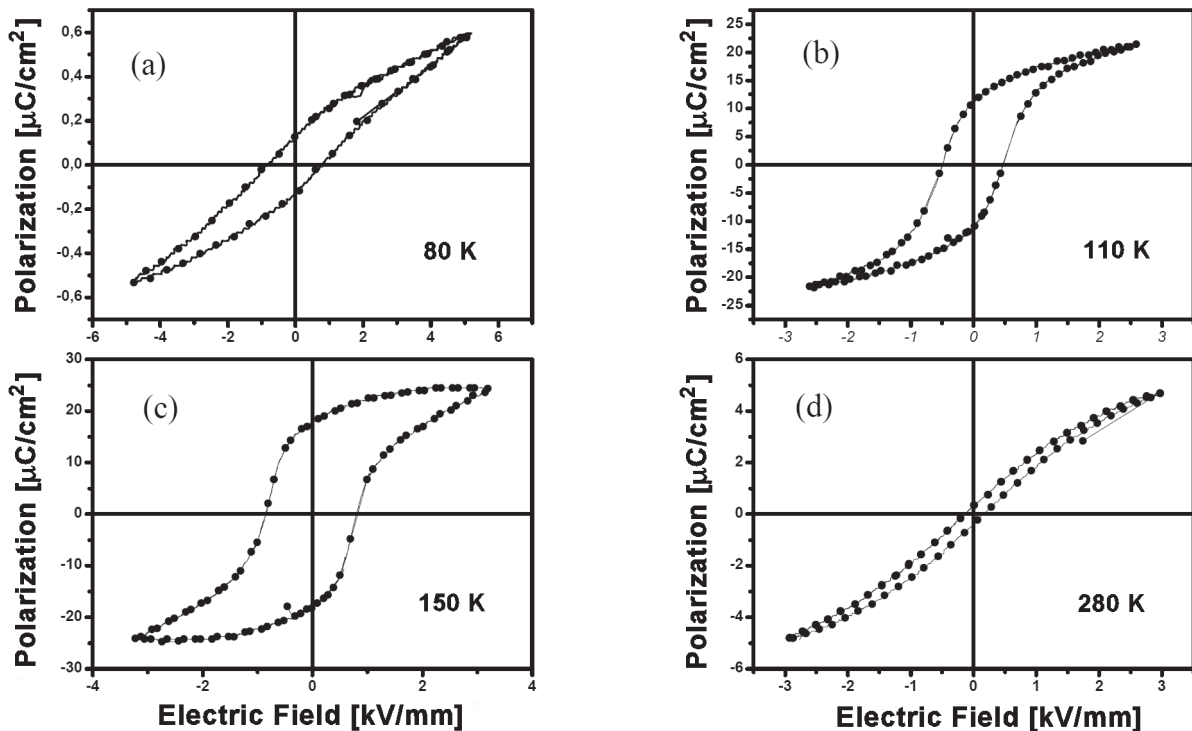


Figure 3. P - E hysteresis loops for a) PFW b) PFW-10PT, c) PFW-20PT and d) PFW-30PT ceramic

temperatures, selected below the freezing temperature. The remanent polarization (P_r) and coercive field (E_c) of (1-x)PFW-xPT ceramics, determined from the saturated hysteresis loops, for $x = 0, 0.10, 0.20$ and 0.30 are $0.12 \mu\text{C}/\text{cm}^2$ and $0.8 \text{ kV}/\text{mm}$, $13 \mu\text{C}/\text{cm}^2$ and $0.4 \text{ kV}/\text{mm}$, $18 \mu\text{C}/\text{cm}^2$ and $0.4 \text{ kV}/\text{mm}$, and $0.5 \mu\text{C}/\text{cm}^2$ and $0.2 \text{ kV}/\text{mm}$, respectively. The larger ferroelectric hysteresis is attributed to the enhancement of the ferroelectric order due to the addition of ferroelectric ion Ti^{4+} into the system.

It is difficult to analyze the remanent polarization (P_r) dependence on the PT content, since there are not only changes in the composition, but also in the measurement temperature. In spite of this, up to $x = 0.20$ P_r showed the tendency to increase with increasing PT content. The analysis is even more complicated as the sample PFW-30PT, at the same measuring criteria used for the other samples (30 K below T_f), has a tetragonal symmetry, while in all other compositions this symmetry is rhombohedral (pseudocubic) [13]. On the other hand, coercitive field decreases with increasing PT content.

The magnetic properties in the (1-x)PFW-xPT ceramic system, with $x = 0, 0.10, 0.20, 0.30$ were investigated by measuring the magnetization as a function of temperature and magnetic field. Figures 4a and 4b show the magnetic hysteresis loops $M(H)$ for the

PFW-PT ceramics at 10 K and 300 K, respectively, demonstrating the existence of weak ferromagnetism at low temperatures for all samples. The PFW sample shows the ferromagnetism at 300 K as well. From the XRD measurements there is no evidence of coexisting of iron or iron oxide-related phases with the perovskite phase. This suggests that the observed magnetic responses must be associated to the PFW pure phase. For the samples with PT, a quasi linear relationship of the magnetization vs. magnetic field was obtained, for 10 K and 300 K, i.e. in antiferromagnetic and paramagnetic phase.

As it was mentioned in our previous work [10], the weak ferromagnetic behaviour at room temperature in the PFW samples, in the antiferromagnetic phase, detected by the existence of remanent magnetization, arises because of the canting in antiferromagnetic interactions. The occurrence of Fe^{2+} and oxygen vacancies during the sintering and the significant difference in valence state and ionic size (radius) of Fe^{3+} and Fe^{2+} can produce a small distortion in the structure of PFW, in which the magnetic moment of two opposite sublattices are not aligned exactly antiparallel, leading to the weak magnetization. It is important to take into account that the PFW samples prepared under different conditions can have different degree of ion disorder, and, correspondingly, different magnetic behav-

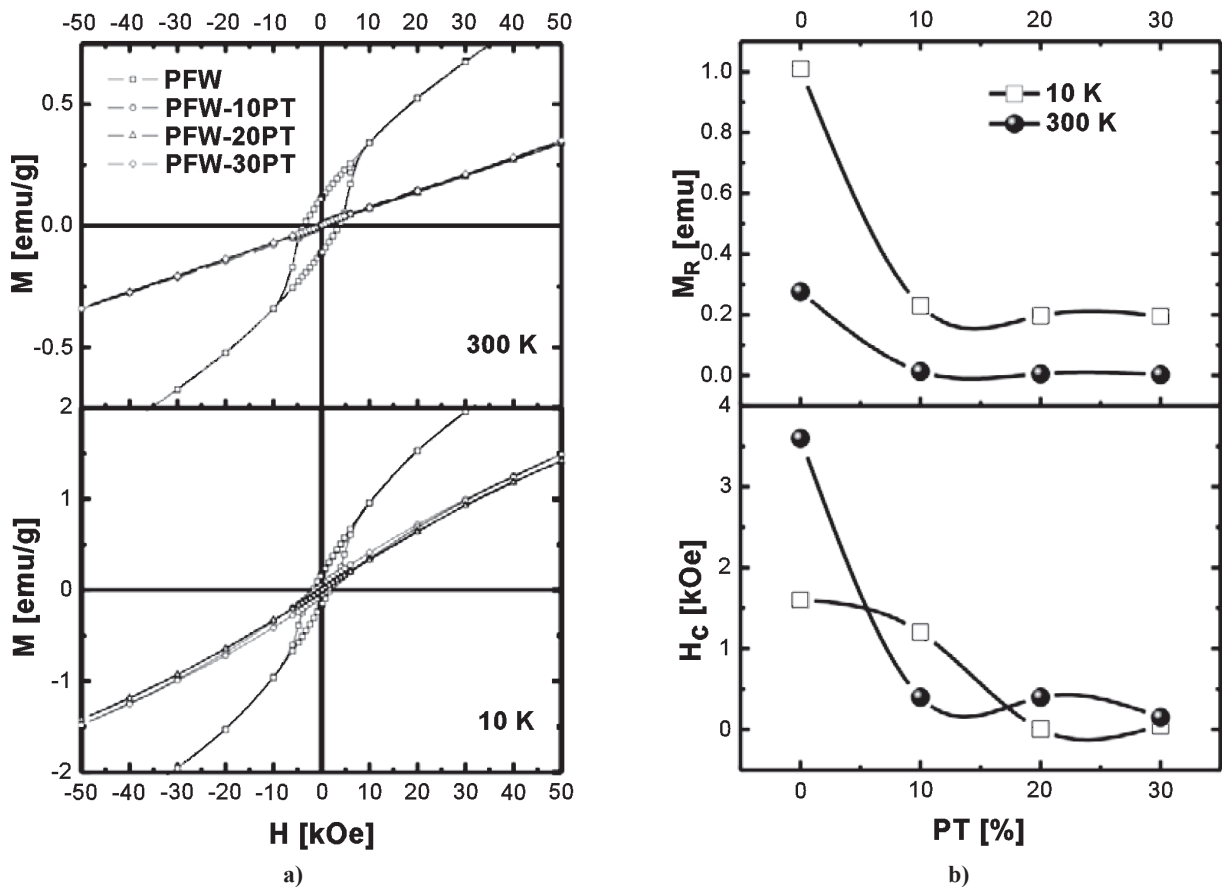


Figure 4. Magnetic hysteresis loops $M(H)$ for PFW-PT samples at 10 K and 300 K (a). Dependence of the coercive field (H_c) and remanent magnetization (M_r) with PT content and temperature for PFW-PT samples at 10 and 300 K

our [14]. The remanent magnetization (M_r) and the magnetic coercive field (H_c) of the PFW-PT samples are presented in Fig. 4b. The M_r of the PFW changes from 1.0 emu/g at 10 K to 0.26 emu/g at 300 K and from 0.19 emu/g at 10 K to 0.004 emu/g at 300 K for the PFW-30PT. Overall the remanent magnetization shows a tendency to decrease with increasing PT content at all temperatures. This tendency is opposite to that presented in the literature at 10 K for single crystals [8] where the remanent magnetization increased as the PT content increased from $x = 0$ to $x = 0.30$.

Two types of magnetic ordering have been observed from the temperature dependence of the magnetization (Fig. 5) which arises from different magnetic interactions [10]. The low temperature magnetic ordering corresponds to the weak ferromagnetic to antiferromagnetic transitions which occur at $T_{N2} = 10$ K to 17 K for $x = 0$ and $x = 0.30$, respectively. The high temperature ordering is attributed to antiferromagnetic to paramagnetic transition at $T_{N1} = 360$ K, 274 K, 161 K and 134 K for $x = 0, 0.10, 0.20, 0.30$, respectively. Information about antiferromagnetism of PFW were obtained by simulations [14,15], assuming different degrees of disorder of the Fe^{3+} and W^{6+} ions in the octahedral sites of the PFW lattice. The calculation assuming completely disordered Fe^{3+} and W^{6+} ions results in $T_N = 406$ K, while the experimental value for the PFW single crystal is $T_N = 363$ K. They concluded that if the ion-order degree is different, the properties (such as temperatures transitions and ferroelectric and magnetic proprieties) will be also different. The difference between the calculated and experimental values of T_{N2} and between the different ceramic samples prepared by different methods can be connected with a partial ion disordering in the PFW, which is an additional reason to consider a canted antiferromagnetic interaction.

There are two factors that affect the magnetic transition in the PFW-PT system [10]: i) the decrease of the concentration of the magnetic Fe^{3+} ions concentration by the addition of a non-magnetic PT component and, consequently, ii) the change in distances of the adjacent Fe^{3+} ions due to lattice changes. The magnetic interactions that give rise to the observed behaviour might be described as a weak superexchange of $-Fe^{3+}-O-W-O-Fe^{3+}$ type in the Fe/W ordered region of interaction which is responsible for the magnetic anomaly at low-temperature T_{N2} . However, in the Fe/W disordered regions, a stronger superexchange of pathway ($-Fe^{3+}-O-Fe^{3+}$) is responsible for the magnetic ordering at higher temperatures T_{N1} .

Nevertheless, different dependences of T_{N1} on PT concentration were observed in polycrystalline ceramics and single crystals and between ceramics prepared in different conditions. In results published by Mitoseriu *et al.* [9], the samples were also prepared by a mixed oxide route and T_{N1} rapidly decreases from 350

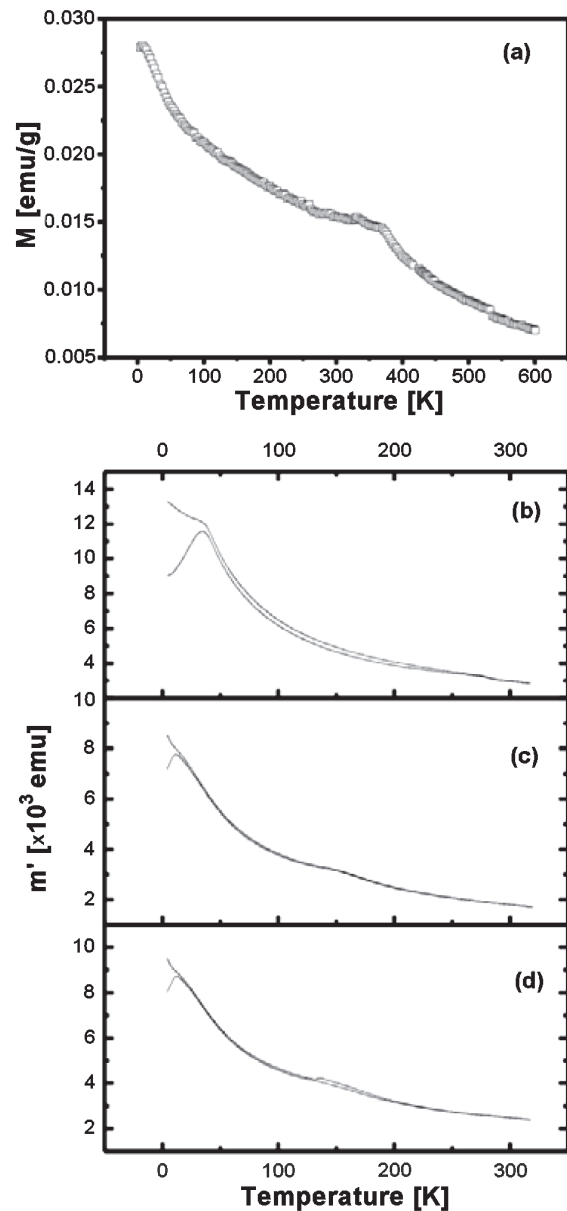


Figure 5. Temperature dependence of magnetization $M(T)$ (DC measurements) for PFW (a) and magnetic moment $m'(T)$ (AC measurements) for PFW-PT samples with $x = 0.10$ (b), 0.20 (c) and 0.30 (d)

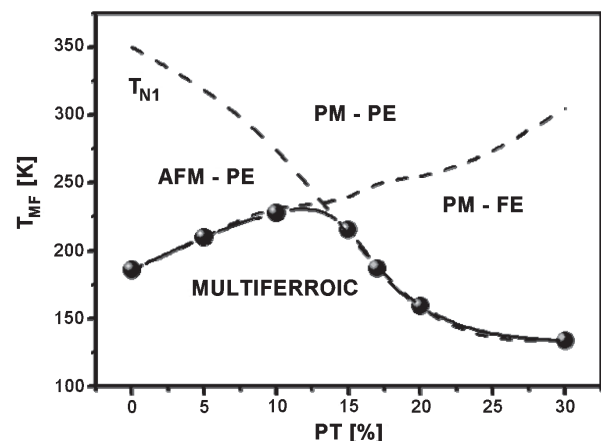


Figure 6. Partial phase transitions diagram of PFW-PT system

K for the sample with $x = 0$ to 170 K for the sample with $x = 0.20$, and above $x = 0.25$, no antiferromagnetic phase transition was observed. On the other hand, in single crystals, only a small decrease in T_{N2} with rising x was observed, and T_{NI} was detected even at higher PT content, $T_{NI} = 274$ K at $x = 0.27$ [8]. The unusual increase in T_{N2} with x was observed in the PFW-PT ceramics and was qualitatively confirmed in single crystals, but T_{N2} values are smaller in single crystals ($T_{N2} = 12.5$ K for $x = 0.27$) than in polycrystalline ceramics ($T_{N2} = 25$ K for $x = 0.25$).

The principal results obtained from structural, electric, dielectric and magnetic measurements can be summarized as follows:

- (i) The perovskite structure gradually changes from a cubic to a tetragonal phase by increasing the PT amount.
- (ii) PT addition increases the room temperature electrical resistivity of the PFW samples.
- (iii) The temperature corresponding to the maximum value of the dielectric constant increases with PT content, while the character of the phase transition changes from diffuse, typical for relaxors, to a sharp one, characteristic of “normal” ferroelectrics.
- (iv) In the PT containing samples, macroscopic remanent polarization increased, demonstrating the enhanced ferroelectricity in PFW-PT system.
- (v) The high magnetic ordering temperature decreases rapidly with PT content while the low temperature magnetic transition increases.

Based on the above mentioned results, a partial phase diagram of the PFW-PT system is established, as shown in Fig. 6. It indicates the areas of paraelectric, ferroelectric, paramagnetic, ferromagnetic and antiferromagnetic phases as a function of temperature and composition.

For $x = 0.12$ – 0.13 the $(1-x)$ PFW– x PT ceramics would be ferromagnetic and ferroelectric below 237 K. In other words, it would be multiferroic below this temperature. This is a relatively high temperature, surpassed only for multiferroics like BiFeO_3 [16] and PFN, in which magnetic properties has recently been discovered at room temperature [15]. However, in materials with relaxor behaviour, diffuse phase transition extended in a large range of temperatures around the temperature T_m for which the dielectric constant assumes its maximum value and the polar nanoregions appeared at temperatures as high as T_m . So, for samples with $x > 0.14$, where the AFM transition is above the ferroelectric transition, despite the fact that ferroelectric order is not present, some type of magnetoelectric coupling exists. This was noticed from dielectric measurements in the microwave region where the evidence of magnetoelectric coupling at 340 K can be found [17].

IV. Conclusions

A two-stage solid-state reaction was used for the preparation of multiferroic $(1-x)\text{PbFe}_{2/3}\text{W}_{1/3}\text{O}_3$ – $x\text{PbTiO}_3$ (PFW-PT) solid solutions (where $x = 0, 0.10, 0.20$ and 0.30) with low percentage of spurious phase, high density, dielectric constant and electric resistivity. It was shown that dielectric properties can be tailored by adding PbTiO_3 in $\text{PbFe}_{2/3}\text{W}_{1/3}\text{O}_3$ system to form PFW-PT solid solution, bringing the ferroelectric transition up to the room temperature and transform the phase transition from diffuse, typical for relaxors, to a sharp one, characteristic of “normal” ferroelectrics.

Two types of magnetic superexchange interactions and a succession of magnetic transitions with Néel temperatures dependent on the composition were found in the solid solution. The evolution of the degree of polar order in PFW-PT system is influenced by the composition, i.e. a transition from relaxor to “normal” ferroelectric with increasing x gradually takes place, while the magnetic ordering at T_{NI} is expected to vanish. We believe that the observed weak room-temperature ferromagnetism in pure PFW is due to spin canting. For $x = 0.12$ – 0.13 the PFW-PT ceramics are multiferroic below 237 K.

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