

## MAGNETOELECTRIC COUPLING IN THE MULTIFERROIC PbFe<sub>2/3</sub>W<sub>1/3</sub>O<sub>3</sub>-PbTiO<sub>3</sub> SYSTEM

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The properties of the ferroic (1-x)PbFe<sub>2/3</sub>W<sub>1/3</sub>O<sub>3</sub>-xPbTiO<sub>3</sub> ceramics with various compositions in the range  $x \in (0, 0.50)$  were investigated. The Raman spectra of the compounds show temperature and composition-induced phase transitions relaxor-ferroelectric and ferroelectric-paraelectric. The magnetic properties of the system change with composition. A magnetodielectric coupling is shown by an anomaly of the magnetic hysteresis loop found in the Curie range of temperatures for the relaxor PbFe<sub>2/3</sub>W<sub>1/3</sub>O<sub>3</sub> ceramic. Two types of superexchange magnetic interactions and a succession of magnetic transitions with Néel temperatures dependent on the composition were found in the solid solution. The present results confirm the hypothesis of a relationship between the magnetic properties and the nanopolar ordering in the relaxor-ferroelectric system.

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### 1. Introduction

Various lead-based relaxor ferroelectric ceramics have been investigated in recent years, due to their superior properties such as: exceptionally high permittivity, high piezoelectric activity and large pyroelectric coefficients [1-3]. The relaxors are a special class of ferroelectric materials characterised by a few peculiar properties [1-8]: (a) diffuse phase transition (DPT) extended in a large range of temperatures; (b) a non-Debye dielectric dispersion in the polar phase and frequency-independent dielectric constant in the paraelectric state; (c) Curie-Weiss dependence of the permittivity far above the temperature corresponding to the maximum value  $T_m$  and strong deviations from this law for  $T \geq T_m$ ; (d) the majority of relaxors have at low temperatures a pseudo-cubic phase and the transition relaxor-paraelectric is not accompanied by detectable structural modifications; (e) the relaxors do not possess a macroscopic polarisation, but local non-zero polarisations  $P_i \neq 0$  associated with the nanopolar regions. All the mentioned characteristics, together with excellent dielectric, electromechanical and pyroelectric properties make the relaxors and their solid solutions suitable for high performance materials with potential applications as sensors and actuators, multilayer ceramic capacitors or pyroelectric detectors. Among these materials, a large number of Pb-based perovskites having the formula  $Pb(B_1B_2)O_3$  were investigated: Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> – PMN [2], [4], Pb(Sc<sub>1/2</sub>Ta<sub>1/2</sub>)O<sub>3</sub> – PST [5], Pb(Mg<sub>1/3</sub>Ta<sub>2/3</sub>)O<sub>3</sub> – PMT [6], Pb(Fe<sub>2/3</sub>W<sub>1/3</sub>)O<sub>3</sub> – PFW [7-8]. The properties of these systems were considered as being due to the presence of polar microregions with short range order (SRO), whose existence in relaxors was firstly postulated by Smolenskii [9] and later confirmed by various experiments [1], [10-11]. Within the superparaelectric model, Cross [1] considered that the polar nano-regions behave like ideal non-interacting dipoles that switch under the fluctuations of random local fields and temperature. When the temperature decreases, the coupling between the microregions controls the kinetics of the

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fluctuations and the relaxor is frozen into a polar-glassy state [12-13]. Even at low temperatures, the nanoregions will never reach such an interaction strength between the neighbours to shift the system into a long range order (LRO) ferroelectric [14]. Therefore, the relaxor can be turned from SRO to LRO ferroelectric state by applying an external field or by forming a perovskite relaxor-ferroelectric solid solution [15-16].

Lead-iron tungstate  $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$  (PFW) is a disordered relaxor with perovskite structure  $\text{ABO}_3$  in which  $\text{Fe}^{3+}$  and  $\text{W}^{6+}$  ions randomly occupy the B-centres of the  $\text{BO}_6$  octahedral positions. The low-field permittivity has a diffuse phase transition (DPT) with a maximum around  $T_m=180\text{K}$  and a frequency dispersion at low temperatures  $T < T_m$  [7-8], [17]. The relaxor-paraelectric phase transition is not accompanied by structural changes of the symmetry at the temperature  $T_m$ , the material being pseudo-cubic down to 10K [18]. The ferroelectric LRO is induced by the presence of  $\text{PbTiO}_3$  (PT) and a Morphotropic Phase Boundary – MPB (where both the pseudo-cubic and tetragonal phases coexist), was found for  $(1-x)\text{PFW}-x\text{PT}$  ceramic at  $T=300\text{K}$ , in the range of compositions  $x \in (0.20, 0.37)$  [8]. The characterisation of the diffuse phase transition in  $(1-x)\text{PFW}-x\text{PT}$ , the quantitative description of the transition from SRO relaxor to LRO ferroelectric by increasing  $x$  and the dielectric data analysed in terms of the Landau cluster theory were reported in previous works [19-20]. An interesting peculiarity of PFW system by comparison with other relaxors is caused by the presence of magnetic ions  $\text{Fe}^{3+}$  with an occupancy of 66.66% of the B-octahedral sites of the perovskite cells. A magnetic activity was reported in the single-crystal material [21] with a succession of transitions at  $T_{N1} = 20\text{K}$  (weak ferromagnetism-to-antiferromagnetism) and at  $T_{N2} = 350\text{K}$  (antiferromagnetism-to-paramagnetism). A multiferroic behaviour and a possible magnetoelectric coupling were proposed in this system [21]. The coupling between the ferroelectric and magnetic activity in multiferroics opens the possibility to manipulate the magnetic properties through electric fields and *vice versa*, giving to these materials large potentiality for applications in spintronics, multiple state memory elements or novel memory devices which might use electric and/or magnetic fields for read/write operations. Although highly exciting for potential applications and very interesting on the fundamental physics aspects, the magnetodielectric multiferroism is very rare, being restricted to only few materials as: ferroelectric-ferromagnetic  $\text{BiMnO}_3$ ,  $\text{YMnO}_3$  [22] and  $\text{Pb}_2(\text{CoW})\text{O}_6$  [23] and ferroelectric-antiferromagnetics  $\text{PbFe}_{2/3}\text{W}_{1/3}\text{O}_3$  [21]  $\text{PbNi}_{1/3}\text{Nb}_{2/3}\text{O}_3$  (PNN) [24] and  $\text{Pb}_2(\text{FeTa})\text{O}_6$  [23]. First-principles calculations proved that the magnetoelectric multiferroism is such a rare behaviour due to the role of the transition metal d electrons associated with the magnetic properties, which tend to reduce the off-centre ferroelectric distortion [24-25]. On the other hand, a possible connection between the magnetic properties and the degree of order was recently proposed [24]. Due to the fact that in  $(1-x)\text{PFW}-x\text{PT}$  system, the order degree and the dielectric properties can be modified through the composition  $x$  [19-20], if magnetoelectric coupling does exist in the ceramic form of the material, it turns out that the magnetic properties might be dependent on  $x$ , as well. In the present paper, the Raman and magnetic properties of the  $(1-x)\text{PFW} - x\text{PT}$  ceramics with  $x$  ranging from 0 to 0.50 are investigated and a magnetoelectric coupling is reported.

## 2. Sample preparation and experiments

The sintered ceramics  $(1-x)\text{PFW} - x\text{PT}$  with various  $x$  were prepared using a mixed-oxide route following a method described elsewhere [8]. The structural symmetry was studied by XRD (high resolution Philips X'Pert MPD diffractometer). The Raman spectra were recorded in back scattering geometry (RENISHAW RM2000 micro-Raman spectrometer with 785nm radiation, 2 $\mu\text{m}$  spot diameter and 10  $\mu\text{m}$  field depth) in the range (70, 800) K using LINKAM thermal cells. The magnetic moments of samples were measured using a SQUID magnetometer (MPMS, Quantum Design) in the range (5,400) K. The samples were cooled down to the measuring temperature in the absence of magnetic field (zero field cooling ZFC). The field was subsequently applied while heating (field heating FH) for the measurement of the temperature dependence of the magnetic moment  $m(T)$ .

### 3. Results and discussions

#### 3.1 Raman results

Fig. 1 shows the Raman spectra of PFW ceramics at various temperatures (normalized and shifted in the intensity scale). Since no first-order Raman lines are allowed in a cubic  $\text{Pm}\bar{3}\text{m}$  structure, the observed ones arise from the breaking of translation symmetry created by the nanopolar clusters of non-centrosymmetric symmetry. The Raman spectra at low temperatures show an intense band at  $848\text{ cm}^{-1}$  (mode A), ascribed to the stretching mode of the rigid  $\text{B}_1\text{-O-B}_2$  (Fe-O-W) bonds and a peak at  $147\text{ cm}^{-1}$  (mode B) that in other  $\text{Pb}(\text{B}_1\text{B}_2)\text{O}_3$  systems is considered to be related to the ferroelectric LRO [18]. As in case of other relaxors, no soft mode is present even at low temperature, contrasting to the normal ferroelectric behaviour. The bands below  $200\text{ cm}^{-1}$  in similar systems are usually ascribed to the motion of Pb ion in its coordination cuboctahedron, i.e. to Pb against  $\text{BO}_6$  octahedra vibration ( $\text{TO}_1$  mode) and B-ion against O stretching vibration inside the octahedral ( $\text{TO}_2$  mode). The peak B overlapped on a broad spectral feature was assigned to a mode involving Pb and O atoms [18]. Particularly interesting are the two sharp peaks at  $294\text{ cm}^{-1}$  and  $228\text{ cm}^{-1}$ , in a spectral range where bending modes are expected. They are sensitive to microstructural effects, involving the deformation of the angles between O atoms and cations. Their evolution with temperature shows that they can be associated to modes activated in small ordered domains with SRO.

The Raman spectra of the compounds change with composition (Fig. 2). Some peaks sensitive to the phase transition or local order were identified. The normalized Raman spectra of few compositions at  $T=300\text{ K}$ , indicate an evolution from SRO to LRO with increasing  $x$ . The relative intensity of the peaks of  $200\text{ cm}^{-1}$  and  $300\text{ cm}^{-1}$  respectively is inverted for  $x=0.10$ ,  $0.30$  and  $0.50$  by comparison with the spectra of PT ( $x=1.0$ ). Their relative intensity is connected with the degree of order on the B-site perovskite cell (the intensity ratio between the higher and the lower frequency peak is larger for ordered systems). The inversion of their relative intensities reflects the reduction of the order degree with decreasing  $x$  from a high ordered system (PT) to a fully disordered one (PFW).

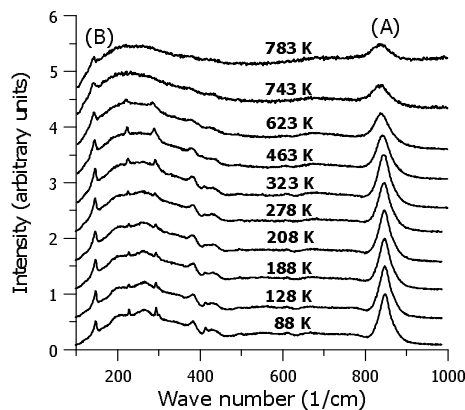


Fig. 1. Raman spectra of the PFW ceramic at various temperatures.

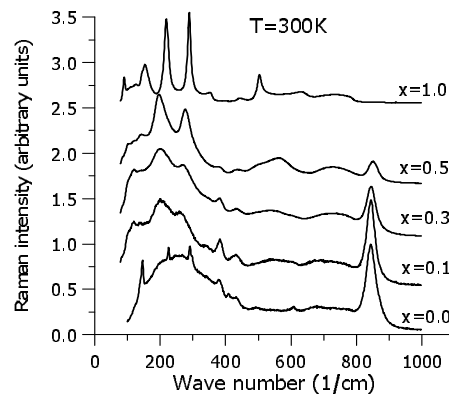


Fig. 2. Raman spectra of  $(1-x)\text{PFW-xPT}$  ceramics with different compositions at  $T=300\text{ K}$ .

#### 3.2 Magnetic properties

Fig. 3 shows the hysteresis loops  $m(H)$  obtained for PFW at few temperatures, proving a temperature dependent magnetic activity. The evolution with temperatures of the magnetic moment of  $(1-x)\text{PFW-xPT}$  ceramics is presented in Fig. 4.

In the PFW ceramic the transition antiferromagnetic-to-paramagnetic was found at  $T_{\text{N}2} = 340\text{ K}$  (Fig. 4), while the low temperature transition ferromagnetic-antiferromagnetic expected around  $T_{\text{N}1} = 20\text{ K}$  [21], was impossible to be put in evidence in our experiment. Therefore, by analysing the evolution with temperature of the  $m(H)$  loops and comparing with the data reported for

the single crystal [21], a succession of magnetic properties can be proposed for the present system at various temperatures:

(I) At low temperatures ( $T = 5$  K), a non-linearity of the  $m(H)$  dependence with a very slim hysteresis loop is observed (Fig. 3a). This behaviour can be attributed to a weak ferromagnetism which probably extends below a temperature around  $T_{N1} = 20$  K;

(II) In the range of temperatures  $T \in (5, 175)$  K, the non-linearity diminishes and a change of  $m(H)$  towards a triple hysteresis loop gradually takes place. In the Curie region for the transition relaxor-ferroelectric at around  $T_c = 175$  K, a triple hysteresis  $m(H)$  with a central loop at  $\pm 7$  kOe and two lateral loops at  $(\pm 7, \pm 45)$  kOe is observed (Fig. 3b). The temperature dependence of the magnetic moment  $m(T)$  shows no anomaly in this range of temperatures;

(III) By increasing the temperature to just below  $T_{N2} = 340$  K, the triple hysteresis loop changes into a normal small loop located at  $\pm 7$  kOe and a weak nonlinear shape (Fig. 3c). In the range of temperatures  $(T_{N1}, T_{N2})$ , the system behaves as an antiferromagnetic material;

(IV) For  $T > T_{N2}$ , a perfect linear dependence of  $m(H)$  and a hyperbolic variation of  $m(T)$  following the Curie-Weiss law show that the system is in a paramagnetic state (Fig. 3d).

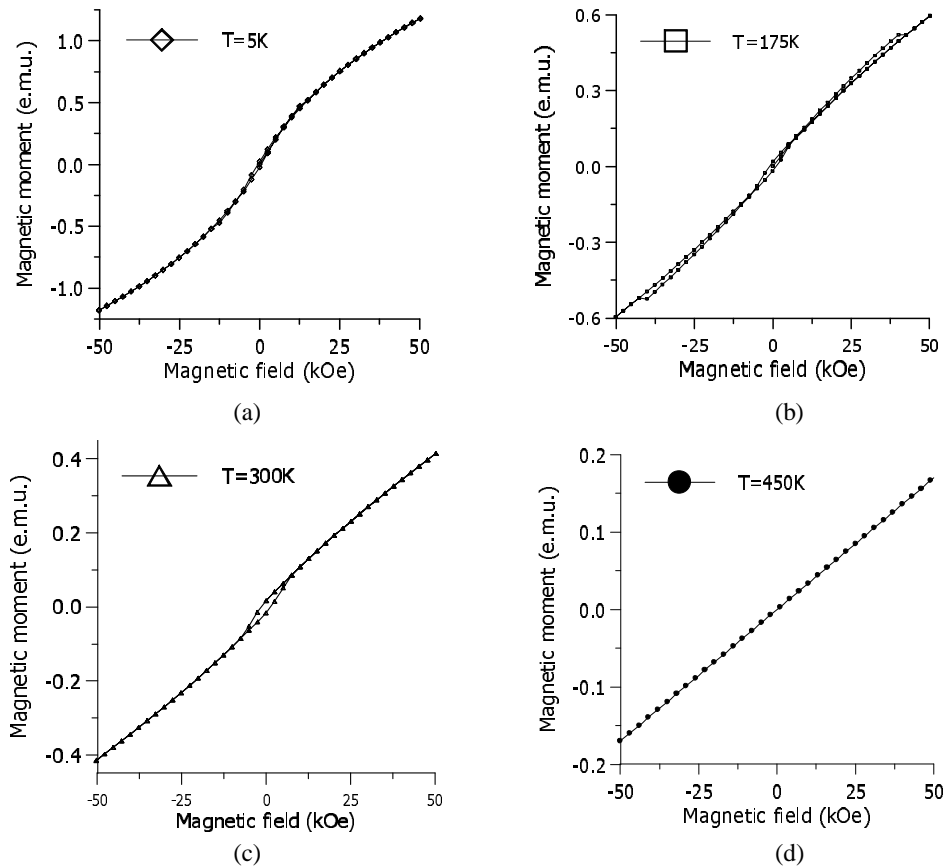


Fig. 3. Magnetic hysteresis loops obtained for PFW at few temperatures: (a)  $T = 5$  K (ferroelectric relaxor state), (b)  $T = 175$  K (phase transition ferroelectric relaxor-paraelectric), (c)  $T = 300$  K (paraelectric), (d)  $T = 450$  K (paraelectric).

According to the mentioned anomaly of the magnetic  $m(H)$  loop around  $T_c = 175$  K, a magnetoelectric coupling is probably present. The magnetic behaviour is affected by the slowing down in the dynamics of the polar clusters originating the dispersive dielectric peaks in relaxors [1], since the relaxor-to-paraelectric transition is not accompanied by structural changes [18] that might influence the magnetic properties *via* magnetostructural interaction. By increasing  $x$  in the solid solution, the evolution with temperature of the magnetic moments shows a shift of both Néel temperatures:  $T_{N1}$  towards high temperatures and  $T_{N2}$  towards lower temperatures (Fig. 4). The transition antiferroelectric-paraelectric at  $T_{N2}$  was accurately determined for compositions below

$x=0.25$  only. For the composition  $x=0.0$  and  $x=0.10$ ,  $T_{N1}$  was not determined, the anomaly of  $m(T)$  being under the limit of detectability of the experiments. The LRO ferroelectric composition  $x=0.5$  shows no longer magnetic anomaly and is in the paramagnetic phase in the whole range of temperatures. The present results confirm the mechanism of the magnetic interaction proposed by Ye *et al.* for PFW [21] and the magnetoelectric coupling is explained through microstructural characteristics of PFW-PT ceramics containing both disordered and partially ordered nanopolar clusters [27]. The magnetic interactions giving rise to the observed behaviour are summarized as: (a) in the Fe/W ordered nanoregions, a weak superexchange of  $-\text{Fe}^{3+}-\text{O}-\text{W}-\text{O}-\text{Fe}^{3+}$  type of interaction responsible for the magnetic anomaly at low temperature ( $T_{N1}$ ); (b) in the Fe/W disordered regions, a stronger superexchange of  $-\text{Fe}^{3+}-\text{O}-\text{Fe}^{3+}$  pathways interaction is responsible for the magnetic ordering at higher temperatures ( $T < T_{N2}$ ). The paramagnetic behaviour indicates the presence of magnetically isolated  $\text{Fe}^{3+}$  ions. In a perfect ordered system on the B-site of the perovskite cell, all of the magnetic  $\text{Fe}^{3+}$  ions are isolated. It results a direct relationship between the order degree and the magnetic behaviour. This picture was already applied to obtain information about the degree of order in the relaxor PNN, in connection with the concentration of magnetic ions  $\text{Ni}^{2+}$  [24]. The same approach explains the magnetic properties of some other complex perovskites, such as the ordered  $\text{Pb}(\text{Co}_{1/2}\text{W}_{1/2})\text{O}_3$  showing a magnetic ordering at a single temperature  $T_{N1} = 8$  K [27].

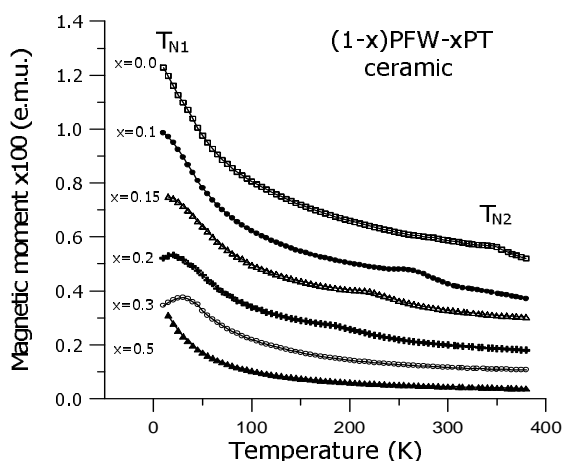


Fig. 4. Temperature dependence of the magnetic moment of  $(1-x)\text{PFW} - x\text{PT}$  ceramics with various compositions at  $H=5$  kOe.

In case of  $(1-x)\text{PbFe}_{2/3}\text{W}_{1/3}\text{O}_3 - x\text{PbTiO}_3$  solid solution, the small shift of  $T_{N1}$  towards higher temperatures shows a tendency for stabilization of the ferromagnetic phase with increasing  $x$ . Meanwhile, the “dilution” of magnetic ions  $\text{Fe}^{3+}$  concentration tends to destabilize the weak ferromagnetic interaction and finally causes the vanishing of the ferromagnetic phase. The other magnetic interaction with the critical temperature  $T_{N2}$  related to the disordered regions strongly shifts towards lower temperatures by increasing  $x$ . The evolution of the degree of polar order in PFW-PT system is influenced by the composition, *i.e.* a transition from SRO relaxor to LRO ferroelectric with increasing  $x$  gradually takes place, as proved in Refs. [19-20]. When the ferroelectric order is established (for high  $x$ ), the magnetic ordering by superexchange  $-\text{Fe}^{3+}-\text{O}-\text{Fe}^{3+}$  pathways interaction at  $T_{N2}$  is expected to vanish. For high enough concentration of PT ( $x = 0.5$ ), a stable state of the system with high ferroelectric order and zero magnetic interaction (*i.e.* magnetic spins mutually isolated, causing paramagnetism) is indeed obtained.

#### 4. Conclusions

The solid solution  $(1-x)\text{PFW} - x\text{PT}$  is a ferroic material with magneto-electric coupling, showing simultaneously ferroelectric and magnetoelectric polarization. The Raman activity in the

relaxor state shows bands related to the local polar order at nanoscale causing the breaking of the translational symmetry, as similar found in other  $\text{Pb}(\text{B}_1\text{B}_2)\text{O}_3$  systems. The evolution of the Raman activity with temperature proved that this local order is very stable even at few hundred degrees above the relaxor ferroelectric - to - paraelectric phase transition. The spectra found in the compounds with various  $x$  show temperature and composition-induced phase transitions from SRO relaxor to LRO ferroelectric and from LRO ferroelectric to paraelectric state. Both the ferroelectric and magnetic dipolar order are influenced by composition and are temperature dependent. By tuning the temperature and/or composition, a succession of transitions ferromagnetic-antiferromagnetic-paramagnetic and LRO ferroelectric-SRO relaxor-paraelectric can be induced.

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