

## EVOLUTION OF THE NANOPOLAR ORDER IN $(1-x)\text{PbFe}_{2/3}\text{W}_{1/3}\text{O}_3-x\text{PbTiO}_3$ RELAXOR INVESTIGATED BY RAMAN AND DIELECTRIC STUDY

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The multiferroic  $(1-x)\text{PbFe}_{2/3}\text{W}_{1/3}\text{O}_3-x\text{PbTiO}_3$  solid solution with various compositions in the range  $x \in (0, 1)$  was investigated. The dielectric data analysed using a Landau-type model allow to obtain the temperature dependence of the local order parameter and show that for high  $x$ , the extension of the Curie region and the degree of diffuseness of the phase transition is diminished. This indicates a transition from nanopolar order (relaxor) to long range order (ferroelectric) in this system. The evolution of the infrared and Raman spectra describes the changes of the nanopolar order degree with composition and temperature. Anomalies of the intensity, peak position and bandwidth were found in the Curie range of each composition, proving the changes in the nanopolar order associated with the macroscopic shift of the Curie temperatures determined by dielectric data study.

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### 1. Introduction

Lead iron-tungstate  $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$  (PFW) is a Pb-based ferroelectric relaxor with perovskite  $\text{ABO}_3$  disordered structure, in which  $\text{Fe}^{3+}$  and  $\text{W}^{6+}$  ions randomly occupy the B-sites of the  $\text{BO}_6$  octahedral positions. Typical relaxor properties with a broad maximum of the low-field permittivity at  $T=180\text{K}$  and a frequency dispersion at low frequencies were reported [1-2]. X-ray diffraction (XRD) experiments showed that the material remains in a pseudocubic phase down to 10K, like  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PMN) and other Pb-based relaxor materials [1-3]. The relaxors do not possess a non-zero macroscopic polarization, but local polarized nanoregions (with short range ordering - SRO) [3]. The nanoregions tend to grow and join by decreasing the temperature. However, as they are inhibited by the quenched compositional fluctuations and by the induced random fields, they will not establish adequate interaction to result in a long range ordering (LRO) as in normal ferroelectric. The system can be shifted from short range order (SRO) relaxor to a LRO ferroelectric state by applying an external field or by forming a perovskite relaxor-ferroelectric solid solution [4]. In order to understand the macroscopic behaviour of the present system, it is interesting to analyse the change of the order degree in  $(1-x)\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3-x\text{PbTiO}_3$  (PFW-PT) with the PT addition ( $x$ ) at various temperatures. Vibrational spectroscopy is a technique very sensitive to detect SRO modifications related to changes in the chemical bond characteristics and to the local crystalline symmetry. In the present study, dielectric and Raman analysis were performed in order to highlight the compositional-induced phase transition from SRO relaxor to LRO ferroelectric and the temperature-induced phase transition from relaxor to paraelectric state in  $(1-x)\text{PFW}-x\text{PT}$  solid solutions.

### 2. Experiment

The ceramics  $(1-x)\text{PFW}-x\text{PT}$  with the compositions  $x=0, 0.2, 0.3, 0.4, 0.5$  and 1.0 were

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prepared using a conventional solid state reaction route [5-6]. The phase symmetry was checked by XRD with Rietveld method [5]. At a fixed temperature, a transition from pseudocubic (in fact, rhombohedral with a distortion angle of less than 0.01) to tetragonal phase takes place with increasing  $x$ . In a large range of compositions both phases coexist (Morphotropic Phase Boundary - MPB), as shown in Fig. 1. The dielectric susceptibility of sintered ceramic disks was measured at various frequencies  $f \in (1 \text{ kHz}, 1 \text{ MHz})$  and temperatures (10, 600) K under isothermal conditions, using an impedance/gain phase Analyser (Solartron Model 1260, Farnborough, U.K) with a chamber for low temperature range (Model Displex APD, Cryogenics, Allentown, PA). The FT-IR spectra was recorded at room temperature using a Nicolet-Magna 750 Fourier Transform instrument. The samples have been prepared by dispersion of the ceramic powders in KBr for the IR region ( $350\text{-}2000 \text{ cm}^{-1}$ ) and in polyethylene for FIR region ( $50\text{-}600 \text{ cm}^{-1}$ ) and then were pressed into thin disks. The unpolarized Raman spectra were recorded in back scattering geometry (RENISHAW RM 2000 micro-Raman spectrometer) using a laser beam of 785 nm or 633 nm focused to a spot of 1-2  $\mu\text{m}$  in diameter, with a depth of field of about  $10 \mu\text{m}$ , at various temperatures between (70, 800) K by using LINKAM thermal cells [6].

### 3. Results and discussion

According to the structural data, a transition from pseudo-cubic to tetragonal phase takes place with increasing the PT addition. Consequently, the dielectric response has to reflect the transition of system from SRO relaxor to LRO ferroelectric, with possible anomalies around MPB, as reported in other relaxor-ferroelectric solid solutions [1,2]. This was also observed in this study. With increasing the addition of ferroelectric PT ( $x$ ), the character of the phase transition is changing from diffuse, typical for relaxors, to a sharp one, characteristic of ferroelectrics (Fig. 2). The temperature corresponding to the maximum value of the dielectric constant is increasing from  $T_m=180\text{K}$  for PFW ( $x=0$ ) to  $T_m=382 \text{ K}$  for 0.6PFW-0.4PT compound. On the basis of the dielectric data, a careful analysis using the cluster Landau model for relaxors presented in detail in Refs. 7-8 allowed to compute the temperature evolution of the local order parameter. According to these results, in the relaxor state ( $x < 0.3$ ), the local polarizations do not experience suddenly their phase transition and a continuously decreasing of the local order parameter with increasing temperature was observed. The local order parameter has non-zero values for very high temperatures far away the temperature corresponding to the maximum of the dielectric constant. This behaviour has to be seen also from the thermo-Raman experiments.

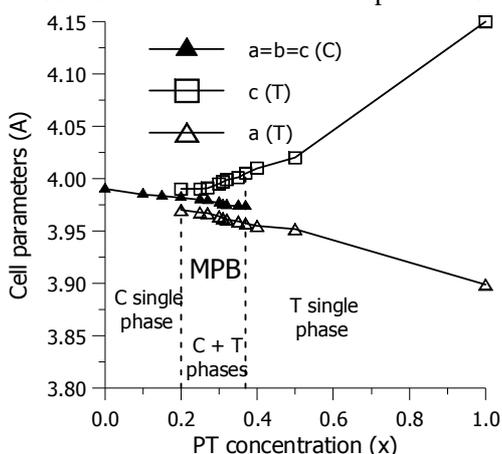


Fig. 1. Evolution of cell parameters and amount of phases in PFW-PT with  $x$ .

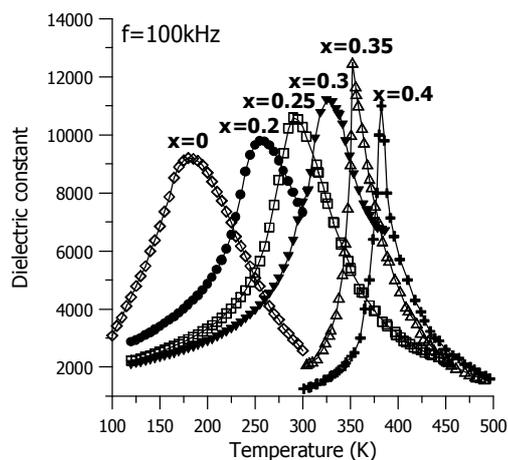


Fig. 2. Dielectric constant vs. temperature for various  $x$  in  $(1-x)\text{PFW}-x\text{PT}$  at  $f=100 \text{ kHz}$ .

The evolution of the system from SRO to a higher ordered state found by dielectric study is confirmed by the IR and Raman investigation. The Raman spectra at various temperatures and few compositions are shown in Fig. 3. All the spectra are stable and no visible thermal hysteresis was observed on cycles heating-cooling. The intensity of all the Raman modes decreases and the lines broaden on heating, for all the investigated compositions. Therefore, some low intensity peaks are

still present at temperatures few hundred degrees above  $T_c$ , where they should be forbidden in a  $\text{Pm}3\text{m}$  cubic symmetry. Since no first order Raman lines are allowed by the selection rules for such a cubic structure, the observed ones for  $x=0$  and  $x=0.1$  are due to the translational symmetry breaking caused by the existence of the nanopolar clusters in the relaxor state. The evolution of the Raman spectra with temperature showed in Fig. 3 confirms the stability of these nanoclusters in the present system at very high temperatures, far away from the Curie region [1-3]. It means that even the average ferroelectric LRO disappeared, there are still nanopolar islands (SRO) with a thermal stability far away the Curie temperature.

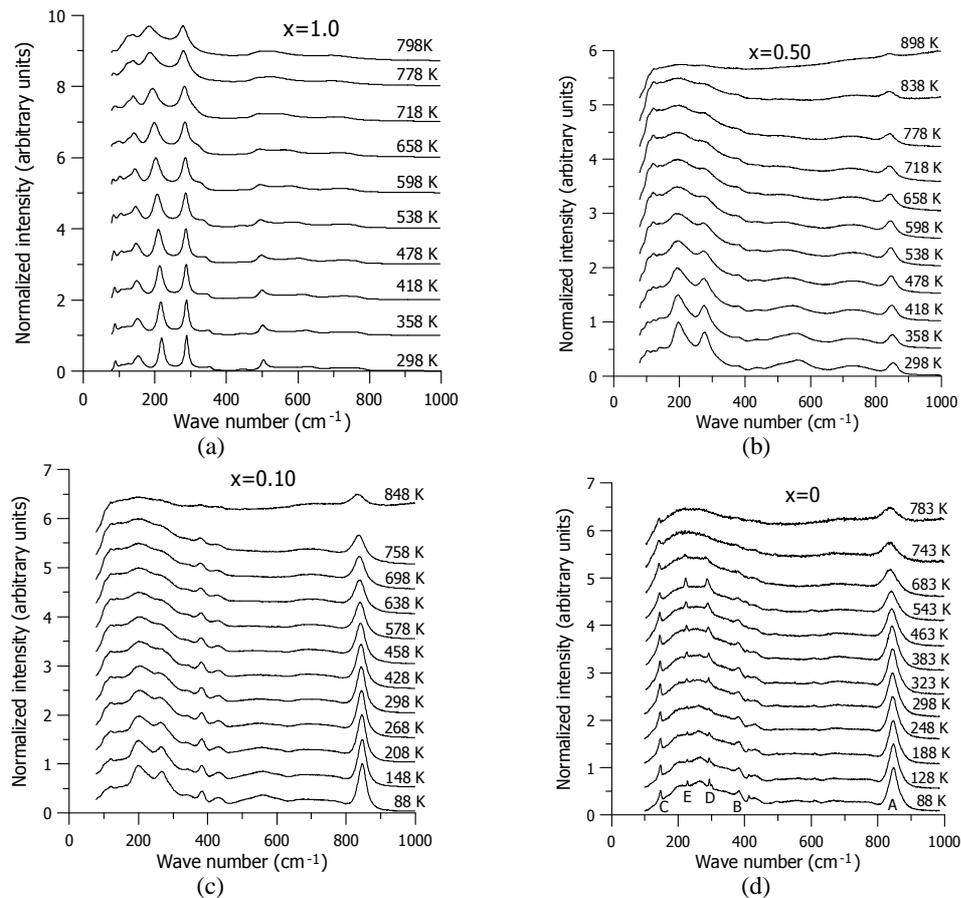


Fig. 3. The thermo-Raman spectra of  $(1-x)\text{PFW}-x\text{PT}$  with: (a)  $x=1$ , (b)  $x=0.5$ , (c)  $x=0.1$ , (d) 0.

The IR and Raman (Figs. 3-4) spectra show typical Metal-Oxygen bonds peaks in the range  $(200-800)\text{ cm}^{-1}$ . The aspect of both IR and FIR spectra at room temperature (Fig. 4) and the positions of maxims do not show a marked change with composition in the range of MPB. This indicates that a continuous change in symmetry (i.e. a transition from relaxor SRO to ferroelectric LRO) with metastable states of coexistence of phases with increasing of PT addition takes place. Therefore, a splitting and a relative increase in intensity of the pair of peaks around  $200\text{ cm}^{-1}$  and  $350\text{ cm}^{-1}$  that are overlapped in the case of pure PFW ( $x=0$ ), can be observed with increasing  $x$  (Fig. 4). Another maximum practically absent in the spectra of PFW relaxor appears in all the solid solutions around  $450\text{ cm}^{-1}$ . This can be related to the growth of ordering in the system with the increase of  $x$ . This maximum is also present in the Raman spectra of pure PT ceramics and vanishes in the case of solid solutions and in pure PFW spectra (Fig. 3). All the samples show a Raman low-frequency mode around  $85\text{ cm}^{-1}$  (Fig. 3), associated in literature to the movement of Pb atom in its coordination cuboctahedron [9]. Regarding the other Pb-based relaxors, the modes with frequencies in the range  $(200-300)\text{ cm}^{-1}$ , present both in the FIR and Raman spectra (Figs. 3-4) that are very sharp and well resolved in the pure PT spectra vanish in the pure PFW ones. They are related to the degree of B-site ordering in the perovskite cell  $\text{ABO}_3$  [10].

According to the present results and to the literature [1,3,10], the following peaks can be associated with ferroelectric LRO in the system: (a) the peaks around 200 and 265  $\text{cm}^{-1}$ , (b) the peaks around 510-540  $\text{cm}^{-1}$  which is very high for pure PT but broad for the PFW-PT compounds and its intensity diminishes with decreasing  $x$  and (c) the small peak at 85  $\text{cm}^{-1}$  which is high and sharp in pure PT and slightly diminishes with decreasing the PT addition. The peak position, integrated intensity and full width at half intensity of few peaks were found to show some anomalies in the range of temperatures corresponding to their ferroelectric-paraelectric phase transitions [6]. A clear increasing of the transition temperature with increasing the PT addition was also found by Raman investigation, in a perfect agreement with the results given by the dielectric study [7-8].

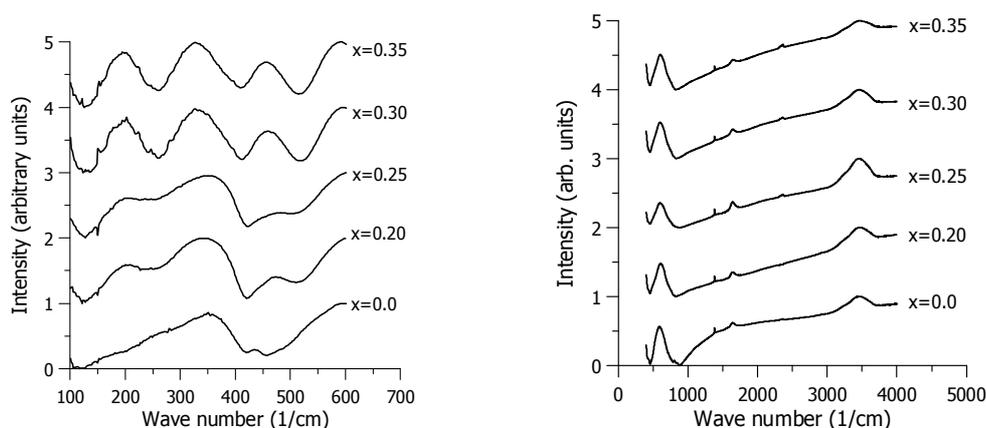


Fig. 4. FIR and IR transmission spectra of (1-x)PFW-xPT for various  $x$ .

#### 4. Conclusions

Structural, dielectric and vibrational spectroscopy (IR and Raman) investigations were performed on (1-x)PFW-xPT with various  $x$  at different temperatures. A change in the crystalline symmetry from pseudocubic to tetragonal with a large range of coexistence of phases (MPB) with increasing  $x$  was found. Together with the structural change, a transition from SRO relaxor to LRO ferroelectric state takes place, probed by the changes in the dielectric characteristics of the system. Infrared and Raman investigations also proved a transition in the local ordering of the system both with variation of temperature and composition.

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