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Synthesis, Structure and Properties of the Magnetic Relaxor Ferroelectric $Pb(Fe_{2/3}W_{1/3})O_3$ [PFW]

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Single crystals of $Pb(Fe_{2/3}W_{1/3})O_3$ [PFW] have been grown from high temperature solution using (PbO-B_2O_3) flux. The crystal structure of PFW shows a B-site Fe/W disorder and a positional disorder due to atomic shifts. The dielectric properties indicate relaxor ferroelectric behavior with a dispersive maximum of permittivity at T_m (from 178 K at 1 kHz to 190 K at 1 MHz). A macropolar phase can be induced by application of an electric field, leading to the induced ferroelectricity. The temperature dependence of the magnetization reveals two magnetic phase transitions at $T_{N1} = 350$ K and $T_{N2} = 20$ K, resulting from the microstructural features of the complex perovskite, characterized by B-site disordered and ordered clusters.

I. INTRODUCTION

Complex perovskites showing relaxor ferroelectric properties have been extensively studied for years, both for the fundamental understanding of the microstructure-property relations and for the exploiting of their exceptional electric and electro-mechanical properties [1–3]. Lead iron-tungstate $Pb(Fe_{2/3}W_{1/3})O_3$ [PFW] was one of the first complex compounds synthesized which show a "diffuse ferroelectric phase transition" [4,5]. Contrary to most of the relaxor ferroelectrics like $Pb(Mg_{1/3}Nb_{2/3})O_3$ or $Pb(Sc_{1/2}Ta_{1/2})O_3$, which are diamagnetic, PFW contains paramagnetic Fe^{3+} ($3d^5$) ion on the oxyoctahedral B-site with an occupancy of 66.7%. The magnetic interaction and ordering in this relaxor give rise to some peculiar properties. It is expected that the study of the magnetically ordered relaxor ferroelectrics may provide useful information for the understanding of the microstructure, dielectric relaxation and magnetoelectric coupling effects, since both the dielectric and magnetic interactions are related to the local structure, especially the chemical order/disorder on the nanoscale. So far there has been a great paucity of single crystal data of PFW due to the difficulties arising in the synthesis of pure perovskite crystals. This paper reports on the crystal growth, structure determination, dielectric and magnetic properties of the PFW single crystals.

II. GROWTH OF CRYSTALS

Single crystals of $Pb(Fe_{2/3}W_{1/3})O_3$ were grown from high temperature solution using PbO or (PbO-B_2O_3) as flux by a slow cooling from 1030 to 850 °C at 1 - 5 °C/h [6,7]. A pseudo-binary phase diagram established between PFW and PbO shows a eutectic point at 690 °C and a eutectic composition (0.48PFW + 0.52PbO). The melting point of pure PFW at 930 °C indicates some peritectic character. The growth results depend closely on the flux composition. The PbO flux (25 - 30 wt%) results in PFW crystals with rough facets, intergrown form and distorted morphology. Inclusions of a parasitic magnetoplumbite phase were revealed by X-ray and optical microscopy, leading to a ferromagnetic appearance. The addition of small amounts of B_2O_3 (up to 1 wt%) to the PbO flux gives rise to single crystals of pure PFW showing clean facets with {100} growth steps and a good optical isotropy without inclusions or internal stress, hence suitable for the subsequent physical characterization. The presence of B_2O_3 not only increases the dissolving power of the melt, but also gives an optimum degree of complex formation and viscosity [8].

III. CRYSTAL STRUCTURE

The crystal structure of $Pb(Fe_{2/3}W_{1/3})O_3$ was refined by Rietveld method [9] with a DBW32.S program [10] from X-ray diffractogram obtained on crushed crystals. It belongs to the ABO_3-type structure of space group $Pm\bar{3}m$ with random distribution of Fe and W on the B-site. Refinement with atoms at the ideal positions of the perovskite phase and normal isotropic temperature factors B resulted in a reliability factor $R_B = 26\%$. Refining the temperature factors can decrease R_B to 9.5% but with abnormally high B values for Pb, Fe/W and O

Table 1. Refinement results and crystallographic data of $Pb(Fe_{2/3}W_{1/3})O_3$.

$Pm\bar{3}m$	a = 3.9776(1)	R_{wp} = 6.46%	R_F = 3.66%	T = 300 K
Atom	x	y	z	B(Å^2)
Pb	0.02850(5)	0.02850(5)	0.07063(4)	0.77(6)
Fe/W	0.52403(3)	0.50000	0.50000	1.06(5)
O	0.54111(2)	0.50000	0.00000	2.43(4)

atoms. This indicates a positional disorder due to shifts of atoms form their ideal positions. A disorder structure model was proposed, in which Pb atom on the A-site is in reality located on a 24*m* (x, x, z) site with 24 disordered positions (x = 0.02850 (5) and z = 0.07063 (4) Å); Fe/W atoms shift from 1*b* site along [100] with a displacement of 0.02403 (3) Å to take a 6*f* site; O atom also shows a preferential shift along [100] in the faces of the cube on a 12*f* site (x, 1/2, 1/2). This model leads to quite satisfactory reliability factors and reasonable temperature factors. The results of refinement and the crystallographic data are given in Table 1. Note that this structure model is very close to that of $Pb(Mg_{1/3}Nb_{2/3})O_3$ refined from single crystal diffraction [11] and that the positional disorder is a common structural feature for perovskites [12–16].

IV. DIELECTRIC CHARACTERIZATION

The temperature and frequency dependence of the dielectric constant (ε'_r) and the dissipation factor (tan δ) measured on (100), (110) and (111) cuts of PFW crystals show a broad maximum with strong frequency dispersion, typical of relaxor ferroelectric behavior. The temperature of the maximum ε'_r varies from 178 K at 1 kHz to 195 K at 1 MHz. Application of an electric field can substantially attenuate the dielectric relaxation and induced an macroscopically polar phase (Fig. 1). The reversal of the induced polarization in an AC field gives rise to dielectric hysteresis loop of ferroelectric appearance (Fig. 2). The coercive field strength for the establishment of the polarization increases sharply with decreasing temperature. As in the case of relaxor $Pb(Mg_{1/3}Nb_{2/3})O_3$ [17], the ferroelectricity in PFW is shown to be induced by an electric field which "triggers" a macroscopic symmetry breaking [18].

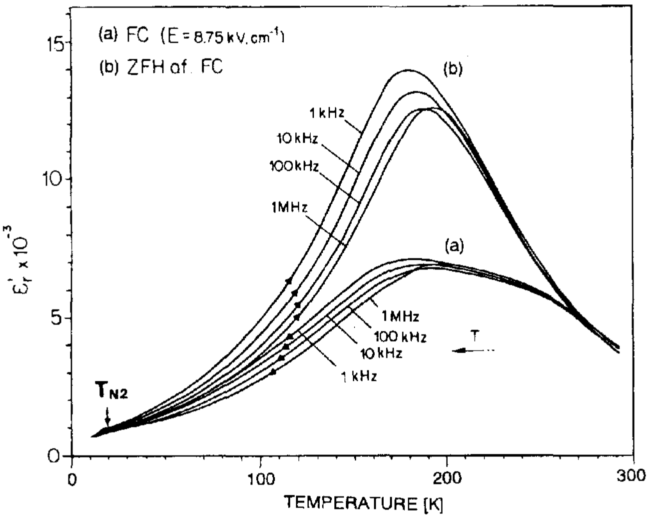

Fig. 1. Dielectric properties of a PFW $(111)_{cub}$ platelet (thickness = 40 μm) upon (a) field cooling (FC) and (b) zero field heating after field cooling (ZFH af. FC).

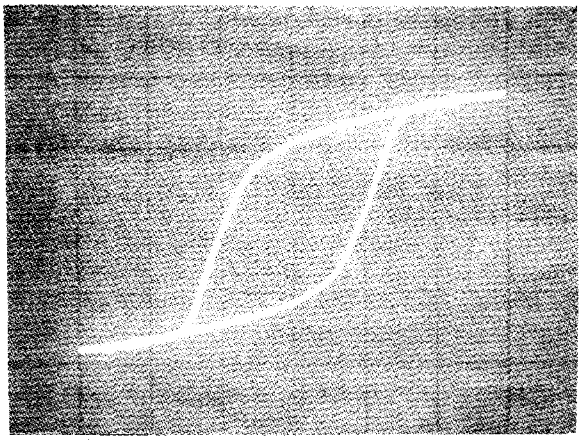

Fig. 2. Dielectric hysteresis loop displayed on a PFW $(100)_{cub}$-platelet (thickness = 40 μm) at 70 K (Scale: E = 8.33 (kV/cm)/div., P = 14.3 (μC/cm^2)/div., f = 3 Hz).

V. MAGNETIC PROPERTIES

The magnetic properties of PFW crystals were studied by means of a SQUID magnetometer. The temperature dependence of the magnetic susceptibility χ indicates two anomalies, corresponding to antiferromagnetic orderings at T_{N1} = 350 K and T_{N2} = 20 K, respectively (Fig. 3). The field dependence of the magnetization shows a weak ferromagnetism below T_{N2}, with a remanent magnetization of 0.03 emu/g. In the temperature interval of dielectric relaxation around T_m = 175 K, a slight deviation of the magnetization from linearity was detected. The slowing down in the dynamics of the polar clusters, which was considered to be at the origin of the dispersive dielectric peaks in relaxor ferroelectrics [1–3], seems to affect the magnetic interaction. Anomalies both on the dielectric constant (see Fig. 1) and the dissipation factor were measured at the magnetic phase transition at T_{N2} = 20 K, resulting from the influence of the magnetic ordering on the dielectric properties via a magneto-structural interaction, probably of magnetostrictive type.

The magnetic orderings in PFW can be related to the microstructure features. Although the average structure show a B-site disorder, the relaxor ferroelectric behavior implies the presence of partially ordered nanodomains between the off-valence cations on the B-site [19]. Two types of magnetic interaction may therefore take place in PFW. One results from a superexchange in the Fe/W disordered regions through - Fe^{3+} - O - Fe^{3+} - pathway; the other from a superexchange of - Fe^{3+} - O - W - O - Fe^{3+} - type in the Fe/W ordered nanodomains. The

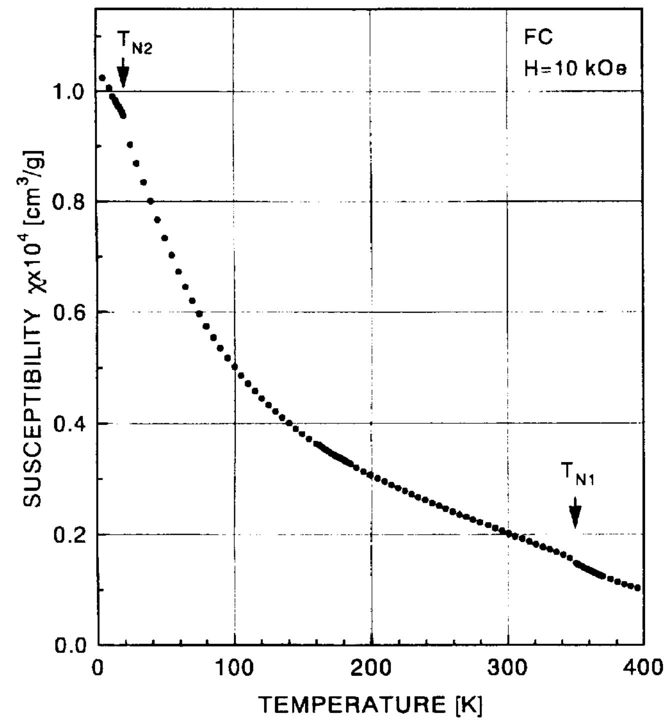

Fig. 3. Temperature dependence of the magnetic susceptibility (χ) of an as grown PFW single crystal (7.5 g) measured by SQUID at H = 10 kOe ($//< 100 >_{cub}$) after field cooling.

former with shorter Fe - Fe distance (about 4 Å) and stronger interaction would be responsible for the magnetic ordering at T_{N1} = 350 K, while the latter with longer distance (about 8 Å) and weaker interaction would give rise to the magnetic ordering at T_{N2} = 20 K. This picture of magnetic interaction can also explain the magnetic properties of some other complex perovskites. The completely order compounds with elpasolite structure such as $Pb(Co_{1/2}W_{1/2})O_3$ shows a single magnetic ordering at 8 K [20], while $Pb(Fe_{1/2}Nb_{1/2})O_3$ [21–23] and $Pb(Fe_{1/2}Ta_{1/2})O_3$ [21,24,25] present two magnetic phase transitions at T_{N1} = 161 K and 143 K, and T_{N2} = 9 K, respectively, suggesting the presence of disordered and ordered nanostructure. Figure 4 shows that the Néel temperature T_N increases with the concentration of Fe^{3+} ion on the B-site. More detailed results and discussion on the magnetic properties and magneto-electric interactions in PFW will be given in a forthcoming paper.

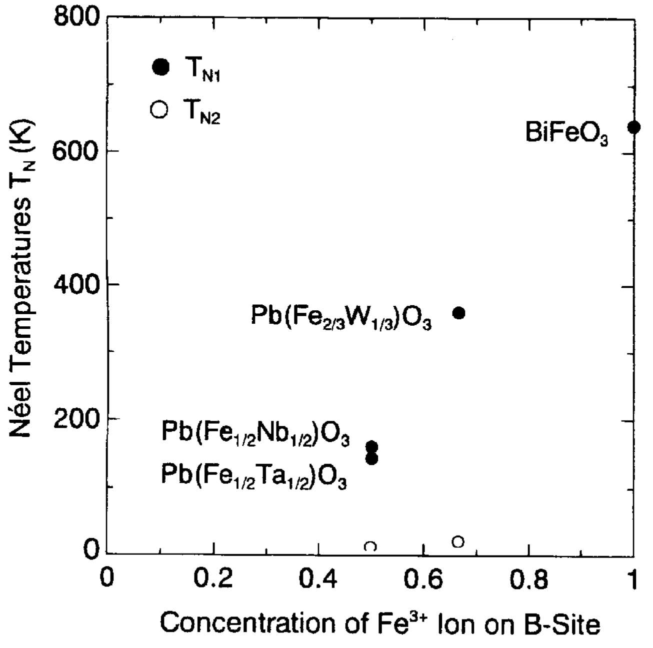

Fig. 4. Antiferromagnetic ordering temperatures T_N for some perovskite compounds with different Fe^{3+}-concentrations on the B-site.

VI. CONCLUSIONS

1. Single crystals of $Pb(Fe_{2/3}W_{1/3})O_3$ have been successfully grown from high temperature solution with (PbO - B_2O_3) flux. B_2O_3 was shown to play an important role in the formation of high quality PFW crystals without inclusions.
2. The long-range structure of PFW at 300 K is of cubic space group $Pm\bar{3}m$ with a disorder on the B-site. All atoms show a positional disorder, shifting from their idea positions in the perovskite structure.
3. The dielectric properties of PFW crystals indicate typical relaxor ferroelectric behavior. The ferroelectricity displayed by dielectric hysteresis loop results from the induction of a macro polarization by an external field.
4. The magnetic properties of PFW reveal two types of magnetic interaction via - Fe^{3+} - O - Fe^{3+} - and - Fe^{3+} - O - W - O - Fe^{3+} - O - pathways, which have been attributed to the disordered and partially ordered local structures.
5. The study of the magnetic properties and magneto-electric interactions in the magnetically ordered relaxor ferroelectrics like PFW provide useful information for the understanding of microstructure and dielectric relaxation.

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