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Microstructure and dielectric relaxation of dipolar defects in Mn-doped $(1 - x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ single crystals

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The atomic-scale defect structures in Mn-doped $(1 - x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ (PMNT) single crystal have been investigated by using X-ray absorption fine structure analysis. Temperature-dependent diffusive dielectric loss peaks as a doping effect were found for Mn-doped PMNT. Combined with these experiments the structure of dipolar defects was confirmed. There is an oxygen vacancy around Mn^{2+} ions, and vacancy and ion interact strongly to form the charge-dipole $[(Mn_{Ti}^{2+})'' - V_{\ddot{O}}]$. The dipolar defects will pin the domain walls, thereby reducing the dielectric loss of the crystals.

Keywords: X-ray absorption fine structure; Ferroelectric; Single crystals: dielectric loss relaxation spectrum; Dipolar defects

Relaxor-based ferroelectric crystals $(1 - x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ (PMNT) have outstanding piezoelectric [1–3], pyroelectric [3,4] and electro-optical [5,6] performances, and it is well known that atomic substitutions strongly influence these properties. For example, Mn doping increases the coercive electric field from 250 to 420 V mm^{-1}, and the mechanical quality factor from 40 to 300 V mm^{-1}, while the piezoelectric constant decreases from 2000 pC/N to 1200 pC/N, and the dielectric loss from 1% to 0.05% [4,7]. The substantial depression of dielectric loss, in particular, is crucial for practical infrared device applications. Therefore, for Mn doping in PMNT, the structure and dynamic mechanism of the defects are significant both for practical use and for understanding the science of ferroelectric materials.

These modifications of properties indicate that the ferroelectricity became "harder", an effect caused by the substitution of a cation inducing an oxygen vacancy around it, and these ions and vacancies then forming "dipolar defects". There are two common characteristics of these dipolar defects based on classical mechanics, namely thermal activation and dielectric relaxations due to ion hopping. Therefore, dipolar defects can depress the motion of domain walls and thereby reduce the dielectric loss of ferroelectrics. However, the structure of these defects has never been observed directly.

X-ray absorption near-edge structure and extended X-ray absorption fine structure (EXAFS) provides a effective way to determined the local coordination and dynamics for a selected atomic species in condensed matter [8]. XAFS is sensitive to the arrangement of atomics in short-range rather than long-range order [9–11]. However, for certain solid solutions, especially relaxor-based perovskite ferroelectric crystals of ABO_3 type, the A or B sites maybe occupied in a disordered fashion [12]. Fortunately, most ferroelectric properties are believed to derive from the atomic off-center displacement of the B-site from the center of the oxygen octahedra [13–17], and hence we can focus on the oxygen atoms around the B-site, which is considered to be approximately short-range order. For defect structure studies in PMNT, there are three questions that need to be answered to describe the local atomic environment of Mn clearly: (i) the valence state of Mn when it is doped in PMNT crystals; (ii) the occupancy site of substituted Mn in the ABO_3-type perovskite crystal; (iii) the coordination number of Mn.

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The dielectric loss relaxation spectrum is an effective way to investigate the dynamic properties of dipoles [18]. It has been applied to investigate the defect structure such as the dipole complexes in $PbWO_4$:La^{3+} single crystals. Dipole complexes $[2(La_{Pb}^{3+})^{\cdot} - V_{Pb}'']$ have been shown in $PbWO_4$ single crystals [19]. The low-frequency dielectric relaxation of oxygen vacancies of Bi:$SrTiO_3$ has also been studied. Three sets of dielectric peaks are considered to be related to oxygen vacancy [20]. These are instructive for studying defects study in ferroelectrics.

In the present work, we report the valence, the Mn occupancy site and a detailed analysis of the local structure of Mn-doped PMNT by XAFS. A typical dielectric relaxation phenomenon in Mn-doped PMNT crystals has been observed. Microstructure study by XAFS and an investigation of the dynamic properties based on the dielectric relaxation spectrum were combined to study the defect properties.

It is well known that Mn ions tend to exist at +2, +3 or +4 valence states in perovskite oxides. Three samples with different valence states of Mn were prepared, including MnO_2 powder, $Pb(Mn_{1/2}Nb_{1/2})O_3$ powder and powder of as-grown Mn-doped PMNT crystal. The samples were ground and sieved through a 400 mesh (30 μm opening), and were then rubbed onto adhesive tape. The tape samples were folded four times to obtain $\Delta\mu t \approx 0.4 - 1$ ($\Delta\mu$ is the shift of absorption coefficient μ below and above the Mn absorption edge, and t is the thickness of the sample). The K edge ($E_0 \approx 6539$ eV) of Mn in XAFS spectra was measured at room temperature. All the measurements were performed in fluorescence detection mode at BL14M1, Shanghai Synchrotron Radiation Facility (SSRF). In all experiments a Si(1 1 1) double-crystal monochromator in non-dispersive mode was used. The monochromator was detuned to 75% of the maximum intensity for harmonic rejection. Care was taken at every stage of the experiment to avoid systematic distortions of the data. Gases were chosen to obtain a linear response in all detection chambers.

The XAFS oscillations of $\chi(k) = (\mu - \mu_0)/\mu_0$ were obtained from absorption coefficient data. The Fourier transforms of χ were made in k and r spaces, and were fitte using IFEFFIT software. The fits are based on the lattice structure of cubic PMN crystal and rhombohedral PMN-0.30PT crystal obtained from the X-ray diffraction measurements. For a certain r-range, for the $\chi(r)$ corresponding some particular short-range structures, inverse Fourier transforms were carried out to investigate the details of the corresponding structure.

Prior to dielectric loss measurements, the Mn-doped PMNT crystals were cut into wafers along the ⟨001⟩ direction determined by an X-ray diffractometer and fired silver electrodes were formed on both sides of these samples at 750 °C. An HP4192A impedance analyzer was used to measure the dielectric loss as a function of frequency from 300 Hz to 1 MHz within the temperature range 433–653 K.

The XAFS spectra of Mn^{2+} in $(Sr_{0.97}Mn_{0.03})TiO_3$, Mn^{4+} in $Sr(Ti_{0.97}Mn_{0.03})O_3$ [15], Mn^{3+} in $Pb(Mn_{1/2}Nb_{1/2})O_3$ and Mn in as-grown Mn-doped PMNT crystal are shown in Figure 1. It can be seen that the higher the element valence state, the higher the absorption edge energy because the lower number of extranuclear electrons makes the inner electron electronic transition more difficult. The comparison shows that the valence state of Mn in $Pb(Mn_{1/2}Nb_{1/2})O_3$ is higher than 2+ but lower than 4+. This is consistent with its structure as the Mn in $Pb(Mn_{1/2}Nb_{1/2})O_3$ is of valence state of +3. The absorption edge energies are the same in Mn-doped PMNT and in $(Sr_{0.97}Mn_{0.03})TiO_3$, indicating that the Mn has the same valence state of +2 in both Mn-doped PMNT and $(Sr_{0.97}Mn_{0.03})TiO_3$. It should be noted that the average charge of the cation in ABO_3-type perovskite crystal is 2+ in the A site and 4+ in the B site. However, the Mn in Mn-doped PMNT could not be assumed to occupy the A site even though the valence state of the Mn is 2+.

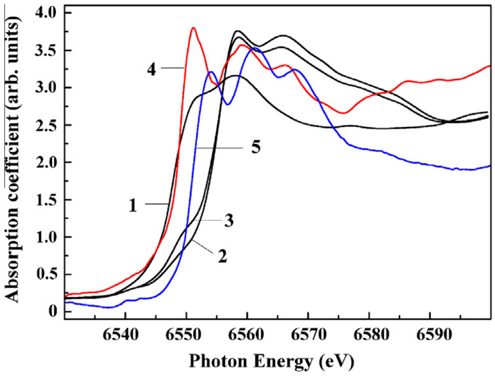

Figure 1. The absorption efficient as a function of photon energy near the K-edge of Mn in different samples: (1) $(Sr_{0.97}Mn_{0.03})TiO_3$ [17]; (2,3) $Sr(Ti_{0.97}Mn_{0.03})O_3$ [17]; (4) Mn-doped PMNT; (5) $Pb(Mn_{1/2}Nb_{1/2})O_3$.

The general chemical formula of the relaxor-based ferroelectric crystal is written $A(B'B'')O_3$–$PbTiO_3$, where, in PMNT, the A-site is usually occupied by Pb, the B′-site is occupied by Mg^{2+} and the B″-site is occupied by Nb^{5+}. The lattice structure is shown in Figure 2. As the structure of PMNT is a pseudocubic lattice, the k-edge XAFS spectra of Mn were preliminarily fitted using IFEFFIT software for the oxygen shell in the cubic phase. First, Mn were assumed occupy the Pb site in the perovskite lattice, and hence the coordination number of Mn is 12 for the perfect lattice. In this case, the experimental XAFS spectra cannot be fitted well when the Mn is supposed to substitute the Pb site irrespective

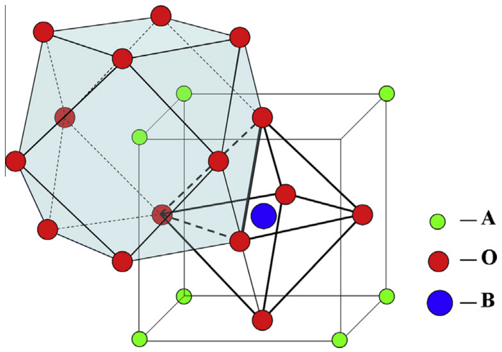

Figure 2. The crystal cell of ABO_3-type perovskite ferroelectrics.