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Superstructure ordering in lanthanum doped lead zinc niobate

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Abstract

Single crystals of pure and lanthanum doped lead zinc niobate, $Pb(Zn_{1/3}Nb_{2/3})O_3$, were studied by synchrotron radiation X-ray diffraction. Chemical ordering between the B-site ions of Zn and Nb results in superstructure peaks at the $(h + 1/2, k + 1/2, l + 1/2)$ positions. In comparison with earlier work on lead magnesium niobate, we find that the chemically ordered regions of PZN are much smaller. Doping with La greatly increased their size, while causing a decrease and broader transition in the measurement of dielectric constant versus temperature. Crystallographic analysis of the superstructure peaks in 10% La-PZN revealed a similar structure to 10% La-PMN, only with a larger oxygen displacement. This reflects the larger size difference that exists between Zn and Nb compared with Mg and Nb. The oxygen displacement within the ordered regions was 0.055(6) Å along a ⟨100⟩ direction towards the Nb ion. This result in 10% La-PZN is consistent with a "random layer" model of ordering between a B' site of $Zn_{2/3}Nb_{1/3}$ and a B'' site of Nb. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Relaxor ferroelectrics are characterized by a frequency dependent dielectric response which has a broad maximum as a function of temperature. The prototypical relaxor is lead magnesium niobate, or $Pb(Mg_{1/3}Nb_{2/3})O_3$, which was first synthesized by Smolenskii and Agranovskaya in the 1950s [1]. PMN has a very high dielectric constant (~30,000) over a wide temperature range near room temperature. Lead zinc niobate, or $Pb(Zn_{1/3}Nb_{2/3})O_3$, also has a very high dielectric constant, but with a Curie temperature of 140°C versus −7°C for PMN. PZN has excellent dielectric and piezoelectric properties, especially in solid solutions with lead titanate [2]. Whereas PMN remains cubic down to 5 K [3], PZN undergoes a symmetry change from cubic to rhombohedral at its Curie temperature and is able to sustain the growth of polar macrodomains [4]. Relaxor ferroelectrics represent a physically interesting and complex system whose behavior has been interpreted using models of super paraelectric clusters [5], an orientational glass [6], and a quenched random field [7].

Both PMN and PZN have the common ABO_3 cubic perovskite structure. There has been a growing interest in understanding the ordering that occurs at the B-sites. Initially [8], these compositional fluctuations within nanodomains were believed to create regions with a range of Curie temperatures, thus giving PMN its broad relaxor response. However, the situation appears more complicated as La-doped PMN retains its relaxor properties even when the chemically ordered domains grow to micron size [9] and experiments by Davies et al. have found relaxor behavior in highly ordered $Pb(Mg_{1/3}Ta_{2/3})O_3$ and similar systems [10]. Superstructure peaks were first observed in PMN in high-resolution transmission electron diffraction experiments [11]. Using a transmission electron microscope, superstructure spots were imaged at the $(h + 1/2, k + 1/2, l + 1/2)$ positions, and the ordered domain size was estimated at 20–50 Å. The observation of 1:1 B-site chemical ordering is somewhat unusual in PMN because the Mg:Nb composition ratio is 1:2. There are currently two models of chemical ordering concerning adjacent B-sites which are denoted B' and B''.

The "space charge" model has complete chemical ordering with Mg ions occupying the B' site and Nb ions on the B'' site. These non-stoichiometric domains would be

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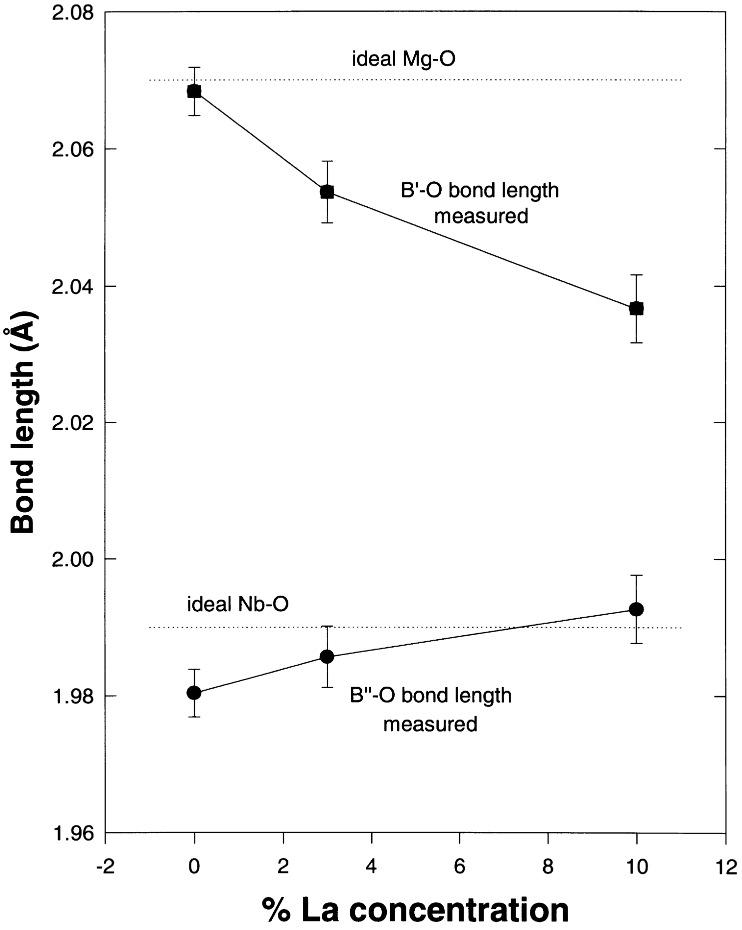

Fig. 1. Measured bond lengths of O–B$'$ and O–B$''$ as a function of La^{3+} doping in PMN. These are derived from accurate values of oxygen displacement and the lattice parameter. Oxygen displacements away from Mg^{2+} and towards Nb^{5+} give rise to the difference in bond lengths. The dotted lines indicate the 'expected' bond lengths of Mg–O and Nb–O using the ionic radii data (Ref. [18]).

embedded in a sea of Nb-rich domains. The ordered regions have a net negative charge which, it was proposed, restricts their size since these domains did not coarsen after annealing at 970°C for one week [12]. Chen et al. provided evidence for this model in their study [9]. By doping with La^{3+}, they showed that the size of the ordered domains can be increased dramatically. The La^{3+} ion contributes an extra positive charge compared with the Pb^{2+} thus lessening the charge restriction so the negatively charged ordered region can increase in size. The opposite effect was seen when doping with Na^{1+}.

In the "random layer" model, also suggested by Chen et al. [9], B$'$ contains a random occupation of Mg and Nb ions in a 2:1 ratio, while B$''$ contains only Nb. In this case, there would be no charge imbalance on average and the entire crystal volume could be composed of these ordered regions. The randomness on the B$'$ site within the 1:1 ordering may account for PMN's relaxor characteristics. Akbas and Davies [10] have found that the ordered regions in $Pb(Mg_{1/3}Ta_{2/3})O_3$ could be greatly increased by annealing at 1325°C. This is strong evidence for the random layer model because the excess electrostatic energy in such highly ordered systems would make the space charge model impossible. However, similar annealing experiments have so far failed to see coarsening in the ordered domains of PMN.

In a chemically ordered crystal, if the two B-site ions have effective atomic form factors f_{I} and f_{II}, then a simple derivation gives the form of the structure factors as a function of momentum transfer magnitude, $|q|$:

$$F_{hkl} \propto f_{\mathrm{I}} - f_{\mathrm{II}} \qquad \text{(when } h, k, l \text{ are all integers + 1/2).} \qquad (1)$$

We have found [13] that chemical ordering is the dominant cause of the superstructure peaks in PMN. However, our X-ray measurements cannot directly distinguish between the space charge and random layer models. In the space charge model, $F_{hkl} \propto (f_{\mathrm{Nb}} - f_{\mathrm{Mg}})$, while for the

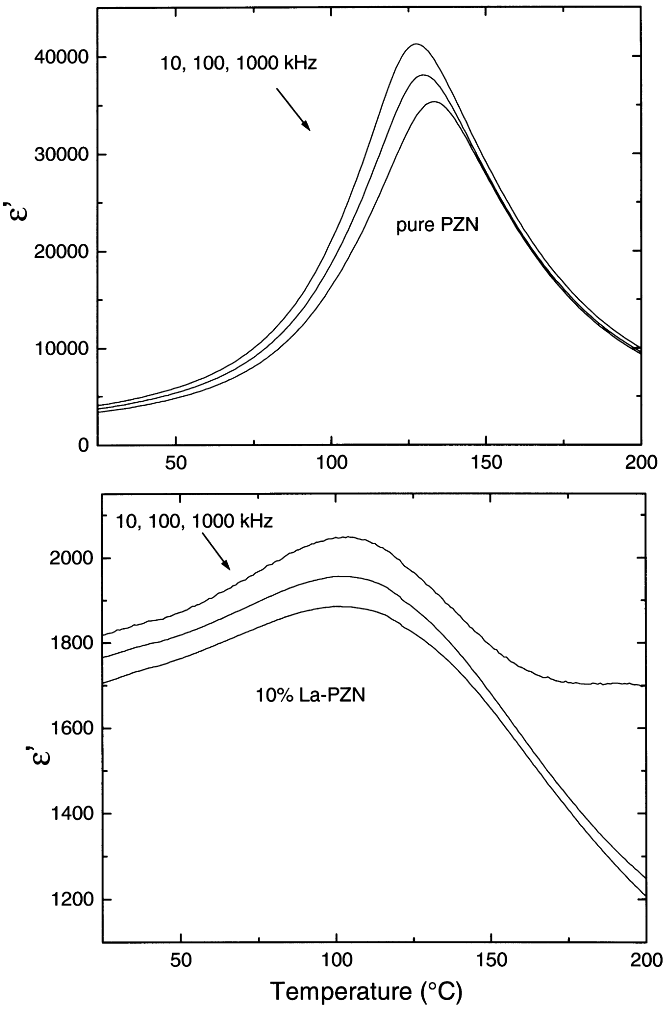

Fig. 2. Dielectric constant of PZN and 10% La-PZN single crystals as a function of temperature for three measurement frequencies.

random layer model, the result is:

$$F_{hkl} \propto f_{\mathrm{Nb}} - \left(\tfrac{2}{3}f_{\mathrm{Mg}} + \tfrac{1}{3}f_{\mathrm{Nb}}\right) = \tfrac{2}{3}(f_{\mathrm{Nb}} - f_{\mathrm{Mg}}) \qquad (2)$$

which makes the two chemically ordered models (or any linear combination of them) indistinguishable in their X-ray pattern, unless intensities are measured on an absolute scale and the volume fraction of ordered regions is known. Due to effects of extinction in almost perfect single crystals, we have not been able to compare quantitatively the bulk and superstructure reflections. Powder diffraction crystallographic studies of La-PMN [14], in which extinction should not be a problem, deduced that the random layer model is appropriate for $x \geq 10\%$ but were inconclusive for $x < 10\%$.

In a previous study [13], we measured a series of La-doped PMN crystals. Our half-order intensity data were fit to a model of the ordered domains including displacement of oxygen towards the Nb ion. Using the measured lattice constant and the oxygen displacement (model described below), the bond lengths B′–O and B″–O were found. We observed a shortening of the B′–O bond as La was added to PMN (Fig. 1). In pure PMN, the B′–O bond length was very close to the tabulated Mg–O bond length (dashed line in Fig. 1). In 10% La-PMN, the B′–O bond length was consistent with an ion that consisted of 60% Mg and 40% Nb on average. We interpreted this as a change in occupancy of the B′ site from mostly Mg to a combination of Mg and Nb, suggesting a change from a space charge model to a random layer one. We concluded that only the random layer model is possible in the highly ordered La-doped crystals, based on both ionic size and electrostatic energy constraints which is in agreement with the work of Viehland [15] and Davies [10]. However, in pure PMN, we could not rule out the space charge model, and ionic size considerations together

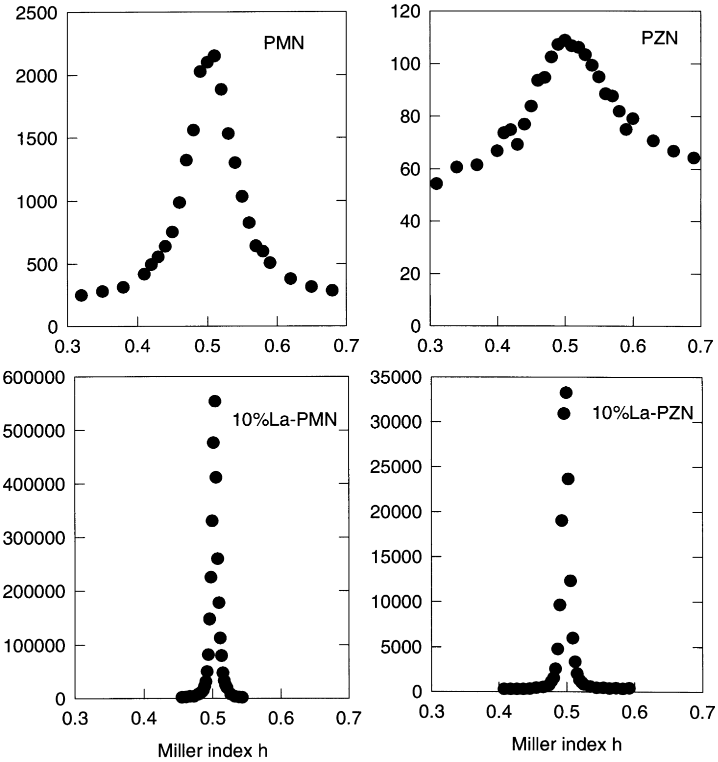

Fig. 3. Raw X-ray diffraction intensity measured in counts per second of the (0.5, 0.5, 2.5) superstructure peak scanned in the Miller index *h* showing the variation in peak width (and hence ordered domain size) as 10% La is added to PMN and PZN. Note the large intensity differences between the four crystals.

with the observed shrinking of the B′–O bond gave indirect evidence that the space charge model might be appropriate.

2. Crystal growth

Pure and lanthanum doped crystals of PZN were grown for this experiment using high temperature solution growth [16]. When doping with La^{3+} for Pb^{2+}, it is necessary to account for the charge imbalance by increasing the Zn:Nb ratio: $La_xPb_{1-x}(Zn_{(1+x)/3}Nb_{(2-x)/3})O_3$. Keeping the Zn:Nb ratio at 1:2 would force vacancies to be created. The mixed powders with purity >99.7% were ball milled and ground. The amount of PbO flux was one and a half times the weight of the powder. The powders were placed in a covered Pt crucible, which was placed in a larger, alumina filled crucible to prevent lead loss. A typical firing schedule involved rapid heating to 1300°C, soaking at 1250°C for 12 h, then slow cooling at 2° per hour to 800°C. The resulting crystals were on the order of 1–1.5 mm in size for both pure PZN and 10% La-PZN. Powder X-ray diffraction confirmed the perovskite phase. We also tried growing 5% La-PZN, but observed no change in lattice constant or ordered domain size, leading us to conclude that the La had separated out during firing. The irregularly shaped crystals were polished to a flat face for the X-ray and dielectric measurements.

3. Measurements

Dielectric data were measured for the PZN and 10% La-PZN crystals. The dielectric response was measured using a Hewlett–Packard (HP) 4284A inductance–capacitance–resistance (LCR) bridge, and the results are presented in Fig. 2. By doping with La, the $\varepsilon'(T)$ peak became broader and its maximum value decreased significantly. The La also caused the peak in the dielectric constant to move to lower temperatures. Typical of relaxors, as the measurement frequency increased, the peak decreased and shifted to higher temperatures. Similar results were found with La-PMN powders [9] and La-PMN crystals [13].

X-ray measurements were taken at Brookhaven National Laboratory's National Synchrotron Light Source on Beamline X16C. The incoming X-ray beam was tuned to 10.0 keV and focused onto a flat face of the crystal. We determined the crystal orientation and its lattice constant by first measuring several bulk Bragg reflections. The refined lattice parameters were 4.062(2) Å for pure PZN,

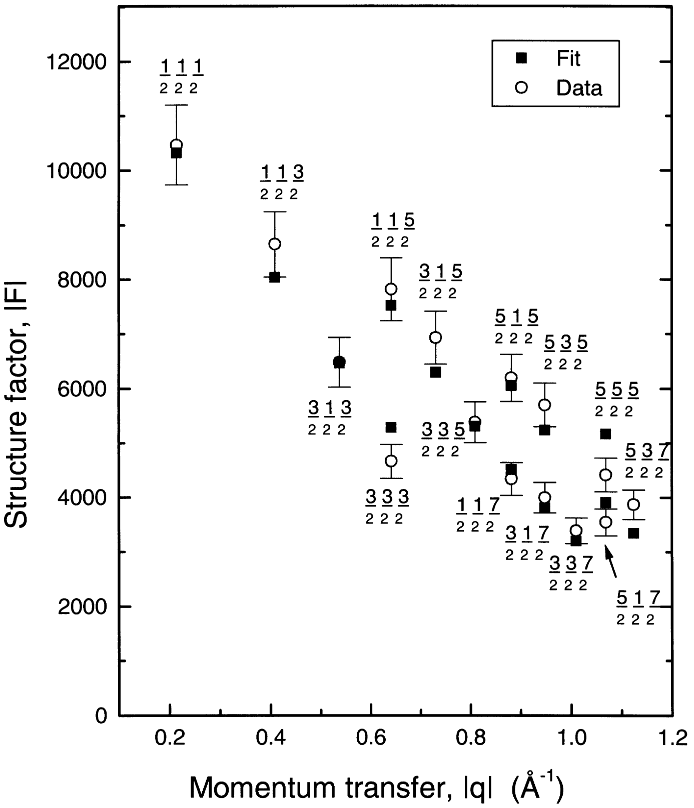

Fig. 4. Structure factor data of 10% La-PZN fit with the oxygen displacement model. The inclusion of the oxygen displacements makes it possible to explain the differences between structure factors of different index but the same $|q|$.

and 4.049(2) Å for 10% La-PZN. The decrease of a_0 with La doping is expected as the smaller La^{3+} ion substitutes for Pb^{2+} on the A-site.

We then measured integrated intensities of the $(h + 1/2, k + 1/2, l + 1/2)$ superstructure peaks using theta scans. For 10% La-PZN, 90 such reflections were measured which resulted in 15 crystallographically distinct reflections after averaging symmetrically equivalent peaks. We then derived their structure factors, $|F|$, by applying the necessary corrections. As with PMN, the observed drop off in structure factor with increasing momentum transfer indicates that chemical ordering is the dominant cause of the superstructure peaks in both PZN and 10% La-PZN. Since the structure factor of chemical ordering superstructure peaks is proportional to the atomic form factor difference (Eq. 1), these peaks are inherently seven times weaker in PZN compared to PMN.

The width of an X-ray peak is inversely proportional to the size of the domain that gives rise to it as given by the Scherrer formula:

$$L = 0.94\frac{2\pi}{\Delta q_{\mathrm{FWHM}}} \tag{3}$$

where L is the characteristic length of the ordered region and Δq_{FWHM} is the peak width measured in reciprocal space. We found a domain size of 25 Å in PZN and 50 Å in PMN. This eight times smaller volume, together with the smaller form factor difference, resulted in much weaker superstructure peaks for PZN compared to PMN. As a result, we do not yet have sufficient data to make a reliable fit. For the La-doped crystals, there were dramatic increases in ordered domain size for both systems (Fig. 3), so it was possible to fit the 10% La-PZN data. The average ordered domain size of 10% La-PZN was 1200 Å, slightly larger than the 900 Å found for 10% La-PMN.

4. Results

While chemical ordering is the dominant feature of the superstructure diffraction pattern, it does not explain the small variations that were observed in the data. Chemical ordering only fits the general shape of the data, but a perturbation to that model such as varying the position or shape of the oxygen octahedra can improve the fit. One such model, with R3m symmetry [17], fits the La-doped PZN data best, as seen in Fig. 4. It assumes complete 1:1 chemical ordering (space charge model), but would give the same results for the random layer model. The oxygen atoms "pinch" the smaller Nb^{5+} ions that they surround (and hence move away from the Mg^{2+} ions) by moving along the {100} axes. The Mg and Nb ions maintain their body center positions and are assigned a Debye–Waller factor. For 10% La-PZN, we found an oxygen displacement of 0.055(6) Å, considerably larger than the 0.022(3) Å that we measured for 10% La-PMN. This larger displacement is expected given that Zn has an ionic radius that is 0.03 Å larger than Mg [18]. The direction of the displacement is towards the smaller Nb ions, as expected. Note that since we fit only superstructure reflections, our model applies only to the ordered regions of the crystals.

5. Discussion

By considering atomic size [18], it is possible to lend insight to what might be driving the chemical ordering in PZN. For example, in pure PZN, subtracting two oxygen radii from the lattice constant leaves enough room for an average B-site ion with a radius of 0.681 Å. This is bigger than the Nb^{5+} ion but too small for the Zn^{2+} ion. By alternately displacing the oxygen atoms as in the $R\bar{3}m$ model, the two ions can be better accommodated. In PZN the B-site ion size difference is even greater than in PMN, but the ordered regions were only about half as large. In 10% La-PZN, however, we found that the chemically ordered regions were slightly larger than the 10% La-PMN crystals. As discussed above, only the random layer model is possible in the highly ordered La-doped crystals because of electrostatic considerations. In the random layer model for 10% La-PZN, the B' site of $Zn_{2/3}Nb_{1/3}$ has an average radius of 0.72 Å, and the B'' site (Nb) has an ionic radius of 0.64 Å. Our measured lattice constant and oxygen displacement result in an allowed B' site of 0.729 Å and an allowed B'' site of 0.620 Å. Thus, our measured oxygen displacement was within 0.01 Å of a "perfect fit." The slightly higher measured value may be due to a tilting of the oxygen octahedra, in addition to the displacement of the oxygen ions.

6. Conclusion

As we saw previously in PMN, La doping of PZN allows one to change several properties of these relaxor ferroelectrics. Perhaps most significant for applications, it is possible to adjust the dielectric constant maximum and make the temperature dependence less severe near room temperature. Lattice constants can also be tailored by substituting the appropriate amount of La for Pb on the A-site. Finally, the size of the chemically ordered regions is very sensitive to the amount of La dopant, providing a convenient method of adjusting the ordered domains so that their effect on dielectric properties and structure can be better understood. This is especially helpful in the PZN system, where the superstructure reflections in the undoped crystal are very weak. A better understanding of the interaction between the chemically ordered domains and the polar domains may lend insight to the relaxor behavior. This might be easier to study in the PZN system where macroscopic polar domains can form at room temperature.

Acknowledgements

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