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## Effects of B-site ordering/disordering in lead scandium niobate

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**Abstract.** Effects of disordering of  $\text{Sc}^{3+}$  and  $\text{Nb}^{5+}$  in the relaxor ferroelectrics  $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$  (PSN) were investigated by means of measurements of x-ray scattering and dielectricity.

Results on the diffuse scattering from ordered PSN indicate lattice instabilities at the  $\Gamma$  and M points near 353 K, and these were expected to cause the formation of ferroelectric (FE) and antiferroelectric (AF) phases. The freezing behaviours are slightly diffuse because of the partitioning of the thermal energy to the two modes, but yet of the type characteristic of normal soft-phonon modes. The results of the dielectric constant measurement under an alternating-current field indicated a highly polydispersive dispersion and a significant temperature dependence of the relaxation frequency. These unusual results imply a competing interaction between the two lattice instabilities.

The x-ray work on disordered PSN shows ‘diffuse’ transition behaviours at the two points. It is suggested that this feature originates from lattice relaxation through the softening of the two modes. The distortions are self-accommodated in atomic displacements at the M point, and analysis of the intensities suggests that the displacement pattern has the form of an AF distortion. During the FE freezing, the coexisting FE and AF regions may give rise to a dipole-glass state, and this is thought to cause relaxor behaviours through frustration between the two states.

### 1. Introduction

A relaxor is a type of simple perovskite ferroelectric [1, 2], and is known to exhibit a diffuse transition and significant polydispersive dielectric dispersion. The mechanism is explained by either of the following two models: (1) frustration of polarizations among microscopic ferroelectric domains by local random fields [3]; and (2) glassy interactions between electric dipoles [4]. However, as described below, a recent x-ray scattering study on  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PMN) [5], the representative system, has proposed a model which is different from the above two.

Two cations in PMN,  $\text{Mg}^{2+}$  and  $\text{Nb}^{5+}$ , called *B-site ions* because of their locations,  $B_1$  and  $B_2$  in  $A(B_1B_2)O_3$  frames, are known to give rise to 1:1 short-range ordering along  $\langle 111 \rangle$  [2]. Because of this ordering nature, one extra electron is stored by two unit cells, and the system is not neutral on a microscopic or mesoscopic scale. The x-ray scattering work on PMN

[5] indicated that those extra electrons produce lattice distortions electrostatically—this may be called the Coulombic *Jahn–Teller effect*—causing competing interactions with transverse optic (TO) phonons along the dispersion curve. A consequence of this effect is the obvious dependence of the phonon wavevector on the freezing temperature, which could provide an explanation for the mechanism of the relaxor behaviours. This model is the only one directly based upon the experimental evidence.

On the other hand, there is another type of relaxor,  $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ , called PSN [6, 7]. This system undergoes an order–disorder transition based on the 1:1 ordering of  $\text{Sc}^{3+}$  and  $\text{Nb}^{5+}$  near 1000 K, and the thermal history below that temperature controls the degree of long-range order (LRO). The dielectricity of this system is quite dependent on the LRO parameter, and its reduction leads to a ferroelectric-to-relaxor transition (we use the term ‘disorder’ in any case where the parameter value is less than one). Unlike the case for PMN, the 1:1 arrangements of  $\text{Sc}^{3+}$  and  $\text{Nb}^{5+}$  in PSN realize an electric neutrality of the system in two unit cells, and no electrostatic lattice distortion is generated. However, since the ionic radii of  $\text{Sc}^{3+}$  and  $\text{Nb}^{5+}$ ,  $\sim 0.75$  and  $\sim 0.65$  Å [8], have a size difference corresponding to  $\sim 2.5\%$  of the lattice parameter ( $a \sim 4.08$  Å), lattice distortion appears as the LRO parameter goes to zero (we define this effect as an ionic-size effect, but simply call it a *size effect* in this paper). Therefore, in the relaxor state, where the parameter value is much less than 1, the distortion is expected to be significant. This effect also occurs for PMN, but, as mentioned in the previous paragraph, distortion arises because of local charge imbalance as well. So, in PSN, only the size effect will cause distortion.

In this study, measurements of the x-ray scattering and dielectric constants were performed on ordered and disordered PSN [9–11]. A purpose of making the measurements is to observe the properties of the lattice and the dynamic response of the dipoles. Through comparison of the results obtained for the two systems, the size effect on the transition behaviour was investigated.

## 2. Experimental procedure

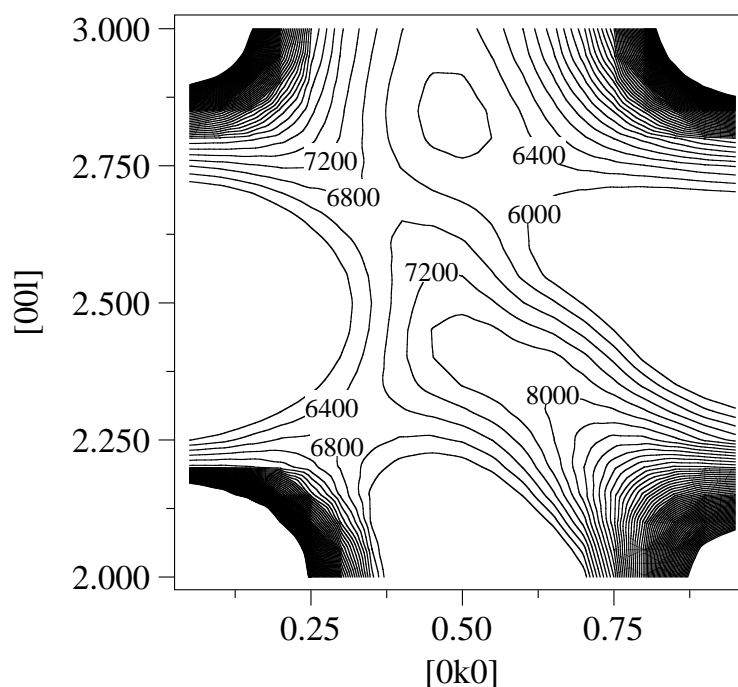
Two single crystals of PSN (provided by Toshiba Company, Limited) were prepared; the B-site ions are highly ordered in one system, and disordered in the other. On the basis of preliminary x-ray diffraction analysis, by integrating the intensities of  $(1/2)(hkl)$  reflections ( $h, k, l$  are all odd integers when using the doubled unit cell) which are an indication of the 1:1 ordering of  $\text{Sc}^{3+}$  and  $\text{Nb}^{5+}$ , the values of their LRO parameters were found to be about 1.0 and 0.4.

X-ray scattering experiments were performed at temperatures above 50 K up to 573 K by using NSLS (a wavelength of 1.2399 Å used) at Brookhaven National Laboratory. The sizes of the crystals were about  $4 \times 3 \times 2$  and  $5 \times 4 \times 2$  mm<sup>3</sup> with the surface normal oriented in the [001] direction. A conventional four-circle diffractometer was used for the measurement, and a KEVEX solid-state detector was employed to reject any contaminating radiation including the higher harmonics. The measurements were carried out only around the  $\Gamma$  and M points where the anomalies caused by freezing appear [9, 10]. Any difference in the temperature dependence of the intensities from that of normal soft modes was thought to give some idea of the size effect.

Complex dielectric constants were measured by an impedance analyser (Solartron SI-1260) in an AC-field frequency range between 10 and  $10^7$  Hz. The measurements were carried out from 573 K down to room temperature. The field was applied along [001]. The strength of the field was kept as low as  $10 \text{ mV } \mu\text{m}^{-1}$  to avoid any nonlinearity of the dielectric constant.

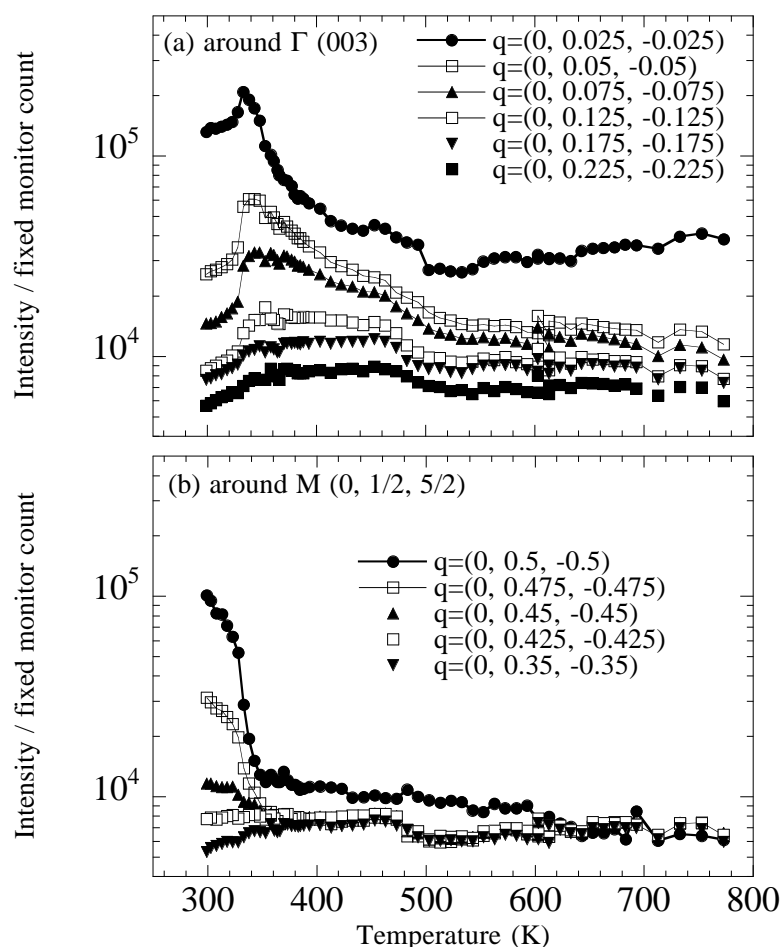
### 3. Results and discussion

Figure 1 shows the intensity distribution of the x-ray diffuse scattering in the (100) reciprocal-lattice plane. The measurement was done on ordered PSN at 473 K. Diffuse streaks along the  $[011]$  and  $[0\bar{1}\bar{1}]$  directions are clearly seen, as previously observed by a precession camera method [12] (the same distribution was previously observed for PMN [5], and the origin was also found to be the soft TO mode in that case). By inspecting the dependencies of the diffraction vector and temperature on the intensity, the distribution was attributed as originating from the soft TO mode [9]. The  $[0\bar{1}\bar{1}]$  phonons are found to have their displacement eigenvectors along  $[011]$ , and their presence is manifested as the stripe along  $[0\bar{1}\bar{1}]$  in the figure. The other stripe, along  $[011]$ , is caused by the equivalent  $[011]$  phonons with the  $[0\bar{1}\bar{1}]$  eigenvectors.



**Figure 1.** An intensity contour map of the x-ray diffuse scattering on the (100) plane. The data were taken for ordered PSN at 473 K. The contour interval is 400.

Figures 2(a) and 2(b) represent the temperature dependence of the intensities along one of the streaks at several wavevectors near the  $\Gamma$  and M points whose locations are  $(003)$  and  $(1/2)(015)$ , respectively. Figure 2(a) shows a significant increase of the intensities below 473 K which indicates an increase in the ferroelectric (FE) fluctuations toward the transition. The freezing is seen around 333 K as cusps of the profile curves (above this temperature, the system is paraelectric). Figure 2(b) also shows a noticeable increase of the intensities below 353 K, which indicates an increase of the antiferroelectric (AF) fluctuations, and the freezing temperature is approximately 343 K. A transition to the FE phase is already known to occur [6, 7], but the AF transition is seen for the first time in this study [9, 10]. Previously, this discovery was made indirectly, as a butterfly-like loop was observed in earlier measurements of electric hysteresis [6]. However, since no direct observation of AF freezing had been made

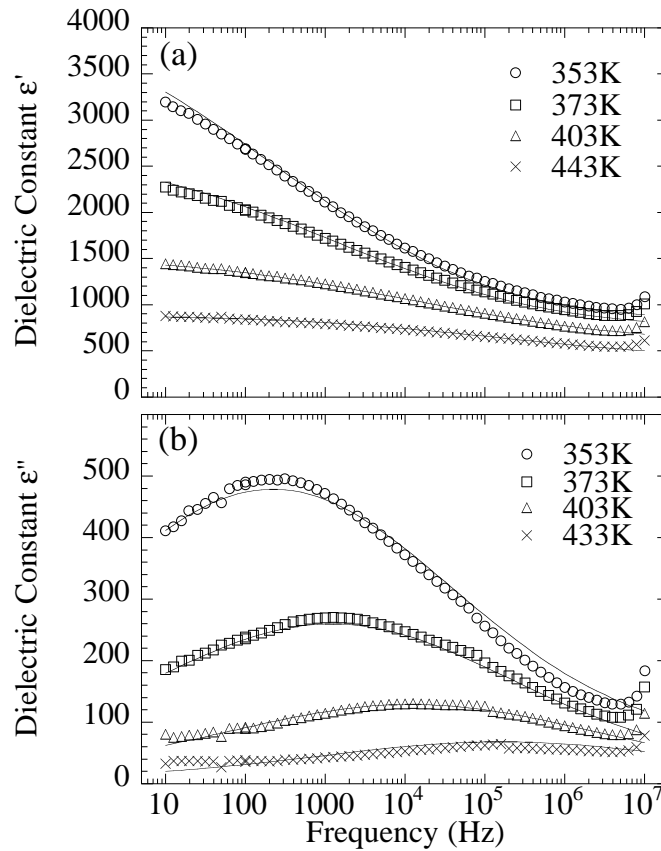


**Figure 2.** The temperature dependences of the diffuse scattering intensities at several wavevectors along  $[01\bar{1}]$  near (a) the  $\Gamma$  point (003) and (b) the M point  $(1/2)(015)$ . The data were taken for ordered PSN. The wavevectors of the atomic displacements are given as  $q$  in the figures.

then, the result suggested that the appearance of the loop might be caused by the coexistence of polar and nonpolar phases. But the occurrence of AF freezing observed in the current investigation supports the idea that the loop appears because of the AF response. The loop was also reproduced by our hysteresis measurement [11] around 340 K, slightly below the freezing point. However, since the FE phase also propagates on further cooling, the AF loop loses its profile immediately.

A comparison of figures 2(a) and 2(b) indicates simultaneous occurrence of the FE and AF fluctuations below 353 K. This can be recognized as a coexistence of these two interactions in the pre-transitional state. Since the thermal energy is partitioned to the two states, the freezing behaviours seen in the figures are slightly diffuse compared with those of the normal soft mode. The results lead to our expectation that competing interaction between the two states causes dielectric dispersion in the ordered system.

Figures 3(a) and 3(b) show the real and imaginary parts of the dielectric constants with respect to the AC-field frequency  $\nu$  at several temperatures. The data were taken for ordered



**Figure 3.** Complex dielectric constants of ordered PSN versus the AC-field frequency: (a) the real part; and (b) the imaginary part. The observed and calculated data are given by symbols and lines, respectively.

PSN. Dielectric dispersion is seen in the figures, and the dispersivity was analysed in terms of the following formula for the complex dielectric constant  $\epsilon(\omega)$  ( $\omega = \nu \times 2\pi$ ) based upon *Debye-type* relaxation:

$$\epsilon(\omega) = \epsilon_{\infty} + (\epsilon_s - \epsilon_{\infty}) \int g(\tau) d\tau / (1 + i\omega\tau) \quad (1a)$$

where  $\epsilon_s$  and  $\epsilon_{\infty}$  are the static and optical dielectric constants, and  $\tau$  is the relaxation time.  $g(\tau)$  has the form of a Gaussian time distribution and is written as

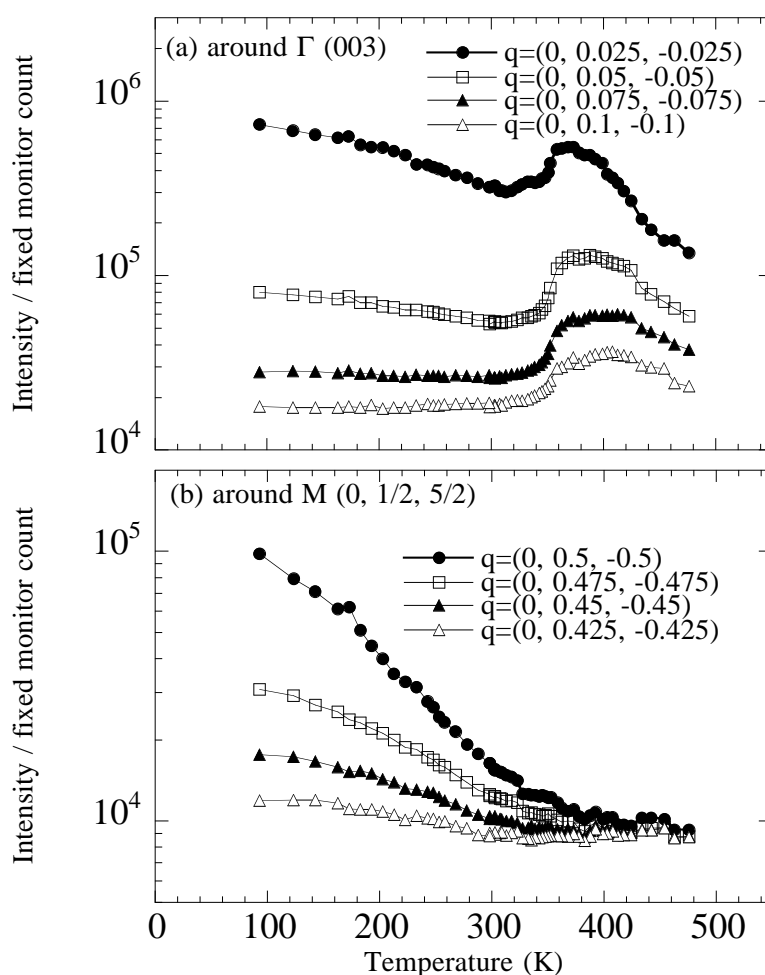
$$g(\tau) = \{1/[\Delta(\ln \tau')(\pi)^{1/2}]\} \exp[-(\ln \tau - \ln \tau')^2 / (\Delta(\ln \tau'))^2] \quad (1b)$$

where  $\ln \tau'$  and  $\Delta(\ln \tau')$  are the mean value of the relaxation time and its distribution width, respectively. If the width goes to zero, the relaxation becomes monodispersive (pure *Debye relaxation*).

As seen in figures 3(a) and 3(b), the observed and calculated profiles (given by symbols and lines, respectively) agree with each other. The distribution width is abnormally large,  $\Delta(\ln \tau') \sim 7.0$  (this value corresponds to a width of about 3 on a log scale), showing the large deviation from the monodispersive relaxation [11]. Although this value seems much smaller than those for relaxors (in the case of relaxors, the profiles of  $\epsilon'$  and  $\epsilon''$  become

significantly broadened; for example, on the scales of figure 3 the profiles look almost flat [13]). The relaxation time is remarkably temperature dependent, and the Arrhenius plot gives the activation energy  $\sim 990$  meV [11]. Compared with the value for  $\text{BaTiO}_3$ ,  $\sim 30$  meV [14], the value found for ordered PSN is larger by a factor of  $\sim 33$ . These unusual results suggest a complicated process of relaxation, which may be caused by coupling between the coexisting FE and AF interactions. However, ordered PSN is not a relaxor but a normal ferroelectric, as previously reported [6, 7], and our results also indicate the following differences from relaxors: (1)  $\ln \tau'(T)$  does not follow the Vogel–Fulcher relationship; and (2) the polydispersivity ( $\Delta(\ln \tau')$ ) is not sufficiently large. Therefore, not only is a competing interaction of the two instabilities an important factor as regards revealing the relaxor behaviour, but also the time distribution width is involved. The width is expected to increase with B-site disordering, as seen from a study of disordered PSN described below.

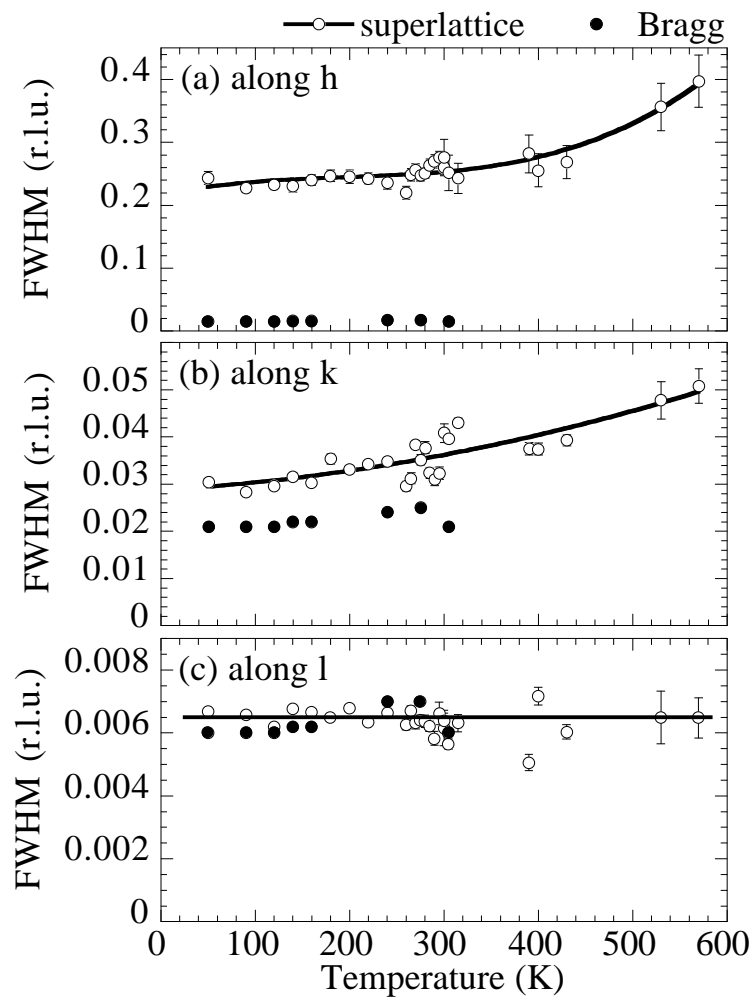
Figures 4(a) and 4(b) represent the temperature dependences of the diffuse scattering



**Figure 4.** Temperature dependences of the diffuse scattering intensities at several wavevectors along  $[01\bar{1}]$ . The data were taken for disordered PSN. Panels (a) and (b) correspond to those in figure 2.

intensities for disordered PSN. Panels (a) and (b) correspond to figures 2(a) and 2(b), respectively. Initiation of the FE transition is recognized at around 400 K from humps in the profiles in figure 4(a). Below this temperature, the FE diffuse freezing is recognized down to 330 K, and, in the freezing temperature region, the gradual AF transition is also seen as diffuse increases of the intensities in figure 4(b). The results are very similar to those for the ordered system, but the transition behaviour of the disordered system is more diffuse.

Figures 5(a), 5(b), and 5(c) show the temperature dependencies of the FWHMs of the M-point  $(0, 1/2, 5/2)$  intensity peak along three directions  $h$ ,  $k$ , and  $l$  in reciprocal-lattice space (the widths at the  $\Gamma$  point are thought to show no anomaly, since the correlation length of the fundamental structure does not vary through the transition(s); therefore, the observation was not carried out at many temperatures), and the results are for disordered PSN. The gradual



**Figure 5.** Temperature dependencies of FWHMs of the  $(0, 1/2, 5/2)$  peak along the  $h$ -,  $k$ -, and  $l$ -directions. The data for the  $(013)$  Bragg reflection which is near the superlattice peak are also given for comparison. The data were not taken at the  $(003)$  Bragg reflection which was used for figure 4, but there is no serious difference between the two Bragg reflections to indicate that only correlation lengths of the fundamental structure have an effect.



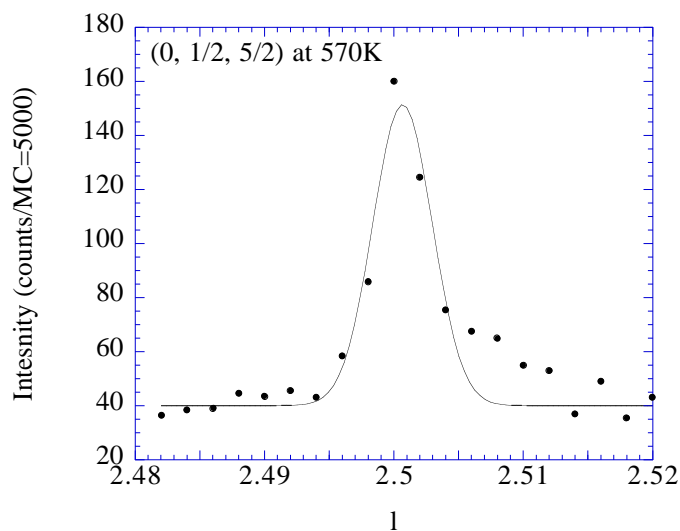
dependencies are seen in figures 5(a) and 5(b), and no dependence is recognized in figure 5(c). Comparison of the widths at the M point with those at the  $\Gamma$  point indicates quite anisotropic AF correlation lengths; in the unit-cell units, the lengths along  $h$  and  $k$  vary from 3 to 5 and 40 to 140 with changing temperature, and the long-range order along  $l$  is maintained. So the results indicate the existence of one-dimensionally correlated AF chains. This kind of anisotropic correlation of atomic displacements was also investigated for  $\text{KNbO}_3$  and  $\text{BaTiO}_3$  [15], but the anisotropy is seen around the  $\Gamma$  points because the two systems undergo ferroelectric transitions.

However, according to the symmetry of the cubic perovskite, the widths of the M-point peak observed along  $k$  and  $l$  for disordered PSN must be equivalent (that along  $h$  is not). However, this does not agree with the experimental result, which shows temperature-dependent behaviour of the width along  $k$  but not along  $l$ . The reason for this difference in the behaviour remains unknown. However, a scan along the  $k$ -direction, which is almost perpendicular to the diffraction vector  $(1/2)[015]$ , somehow causes rocking of the crystal, so the mosaicity increasing through the transition(s) may reveal the temperature dependence, and it is possible that the correlation is two dimensional rather than one dimensional.

The dimensionality of the AF correlation becomes less significant as the temperature is lowered, and the dependencies of the lengths are seen to saturate around the freezing temperature region. Down to that region, only a slight increase of the intensity is recognized, but below saturation, the intensity instead increases diffusely on cooling, as shown in figure 4(b). This substantial change in the intensity simply implies increase of the ionic shifts, indicating a crossover between increases of the correlation lengths and the displacements.

Figure 6 shows the result of a linear scan across the M point along the direction  $l$  at 570 K for the disordered system. This temperature is about 240 K higher than that of the transition region, and up to this temperature only a quite slight reduction of the intensity is seen. The result exhibits a distinct peak, and its existence can be explained by self-accommodation in the AF order of the lattice distortion caused by an ionic-size difference between  $\text{Sc}^{3+}$  and  $\text{Nb}^{5+}$ , which are in short-range-ordered arrangements.

As mentioned above, the size difference between  $\text{Sc}^{3+}$  and  $\text{Nb}^{5+}$  is  $\sim 2.5\%$  of the lattice



**Figure 6.** A linear scan profile of the  $(0, 1/2, 5/2)$  peak along the  $l$ -direction at 570 K.

parameter. Apparently, this difference will produce significant lattice distortion, i.e., elastic energy, in the short-range-ordered arrangements. However, the observed lattice instability of the soft TO mode at the M point [9] allows us to imagine a potential capability for relaxing the lattice by means of static atomic displacements of that mode, so the size difference may not appear as a disordered form of the distortion, but may select the formation of the M-point displacements which are considered to be energetically the most stable. So the peak observed above the AF transition temperature region is thought to be a result of self-accommodation of the distortion, but may not be related to any of the dynamic events such as heterophase fluctuations, critical fluctuations, or soft modes which reveal strong temperature dependence of the intensity (it seems that the peak exists even well above 570 K). From our x-ray investigation it is clear that pre-existence of the AF regions—representing a substantial difference from the case for ordered PSN—causes the relaxor behaviour. A similar phenomenon was observed for Li-doped  $\text{KNbO}_3$  [16, 17]. Dipoles are produced by the size difference between  $\text{K}^+$  and  $\text{Li}^+$ , and strong dielectric relaxation also appears, accompanied by ferroelectric order, near 50 K. However, above that temperature, the dipoles are disordered and there is no ionic displacement at any specific wavevector. Therefore, the size effect in this system does not involve coupling with a soft mode, and is different from the self-accommodation in disordered PSN.

In disordered PSN, the compensation of the elastic energy caused by the size effect at 570 K is thought to be insufficient, and the elastic energy is reduced by lattice softening as temperature is decreased. A first step in the energy relief on cooling from 570 K is carried out by enlargement of the AF regions as shown in figures 5(a) and 5(b). However, since a soft mode at the  $\Gamma$  point also exists, partitioning of the thermal energy of the two oscillator modes occurs; therefore, the softening at the M point becomes insignificant, unlike the case for pure soft modes, and a quite diffuse change of the peak widths is observed. Near the freezing temperature region, enlargement is prevented by the evolution of the FE regions which occurs simultaneously, and, below the freezing region, increase of the displacements, instead, takes over the energy relief as the second step. However, because of the two-mode partitioning, the softening at the  $\Gamma$  point is also gradual, so a diffuse increase of the intensity is observed, as shown in figure 4(b).

Also, regarding the instability of the  $\Gamma$  point [9], the distortion may be accommodated by the formation of displacements in the same sense. But in terms of x-ray diffraction, it is impossible to detect a size effect at that point, since the intensity contribution overlaps with the tremendous contribution from the paraelectric phase. However, our electric hysteresis study [11] on this sample indicated a quite weak ferroelectric response below 383 K in the paraelectric temperature region. This response may imply a size effect at the point, and the effect is expected to give rise to the formation of ferroelectric microdomains. Their existence was also suggested by a previous study of birefringence in a few relaxor systems including PSN [7]. That work simply indicated that compositional fluctuations of the B-site ions increase the population density of the microdomains, but did not explain what mechanism would give rise to the tendency.

The pre-existence of the AF regions found on disordered PSN is thought to cause glassy dipole arrangements, and a more complicated configuration of the minima of the potential energy is expected compared with the case for ordered PSN. Therefore, the width of the relaxation time distribution becomes larger, and a more polydispersive response appears. In this picture, dipoles may be frustrated by the applied field, and a process of multiple hopping among the potential dips will give rise to a deviation from the Arrhenius plot (we just guess that this leads to applicability of the Vogel–Fulcher relationship). Similar phenomena were found for dipole-glass systems [18–20] where FE and AF phases are mixed explicitly, e.g.,  $\text{RbH}_2\text{PO}_4$ – $\text{NH}_4\text{H}_2\text{PO}_4$  and  $\text{PbTiO}_3$ – $\text{PbZrO}_3$  systems. However, because of the

inhomogeneous distribution of each component in these mixtures, the frustration is expected as a matter of course. On the other hand, relaxors having the B-site mixed-perovskite structure, such as PSN and PMN, are not mixed systems, and frustration is not to be expected in view of the chemical formulae. Therefore, there must naturally be a chemical effect unique to simple perovskites which stabilizes both the FE and AF orders. The current results, to some extent, agree with the two proposed models [3, 4] on the following two points: (1) the existence of local polarizations caused by the FE fluctuations; and (2) frustration among the dipoles.

A search for the AF peak was also performed for ordered PSN at 470 K, but it shows that no peak exists, meaning that there is no distortion caused by the size effect; and the absence of the AF regions results in there being no relaxor behaviour. In addition to the transition behaviour being more distinct than that of the disordered system (see figures 2 and 4), the correlation lengths of the AF fluctuations are more sensitive to temperature, suggesting that the event is dynamic. In addition, the lengths and their temperature dependences are quite isotropic. These features may appear because there is no interaction between the distortion and the soft mode, and, unlike the case for the disordered system, glass states of dipoles cannot be produced.

X-ray scattering intensities at several M points were collected at 300 K. The following conventional formula for the x-ray diffuse scattering intensity caused by atomic displacements [21], given as  $I(\vec{q}_1)$  ( $\vec{q}_1$  is a diffraction vector) below, was employed:

$$I(\vec{q}_1) = \sum_{s\gamma} \sum_{s'\gamma'} f_{s\gamma} f_{s'\gamma'}^* \langle u_{s\gamma} \vec{q}_1 \rangle \langle u_{s'\gamma'} \vec{q}_1 \rangle^* \exp[i\vec{q}_1 \cdot (\vec{R}_{s\gamma} - \vec{R}_{s'\gamma'})] \quad (2a)$$

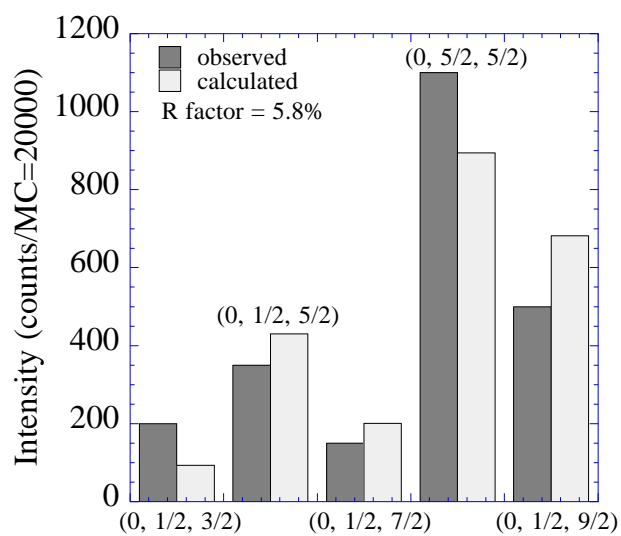
where  $s$  and  $\gamma$  are indices for unit cells and sublattices.  $f_{s\gamma}$  is the x-ray atomic scattering factor of atom  $\gamma$  at position  $\vec{R}_{s\gamma}$  in the crystal.  $u_{s\gamma}$  is an atomic displacement, and is written in the following form as a Fourier sum over all atomic displacement patterns,  $n$ , and all displacement wavevectors,  $\vec{q}$ , allowed in the first Brillouin zone:

$$u_{s\gamma} = \sum_n \sum_{\vec{q}} u_{n\gamma}(\vec{q}) \exp(i\vec{q} \cdot \vec{R}_s) \quad (2b)$$

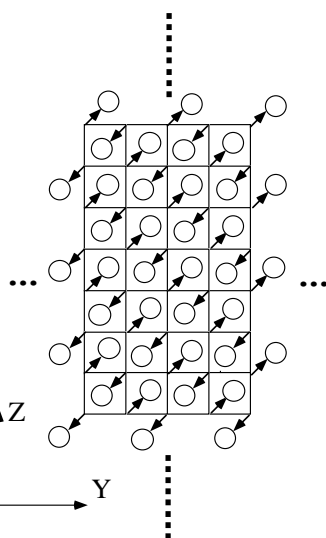
where  $u_{n\gamma}(\vec{q})$  is a displacement amplitude, and  $R_s$  is a unit-cell position.

The analysis was carried out for each of the possible atomic displacement patterns (each  $n$ ) at the M-point wavevector ( $(1/2)\langle 110 \rangle$ ). Figure 7 gives a comparison of the calculated intensities with those which were observed. The results indicate antiparallel shifts of Pb and Nb/Sc along  $\langle 011 \rangle$ , but no determination could be made for three oxygens since their contributions to the x-ray intensities are quite small. The ratio between the displacements of the two ions is found to be approximately 1:1, but the values of the shifts are unknown because there is no information on the absolute units of the intensity. The AF arrangements of the B-site dipoles at the (100) positions based upon the calculation are given in figure 8, and those of the A-site dipoles can be obtained by translating the figure by  $(1/2, 1/2, 1/2)$ , but the modulation becomes antiphase.

A similar perovskite crystal, CsPbCl<sub>3</sub>, also undergoes freezing at the M point [22]. A neutron scattering study found that the transition was instigated purely by a chlorine rotation mode, M<sub>3</sub> [22]. In this case, Pb and Cs ions do not participate in the correlation, and the system becomes a nonpolar phase. However, PSN exhibits a different situation from that for CsPbCl<sub>3</sub>; the lattice instability which gives rise to the diffuse streaks running between the  $\Gamma$  and M points involves the displacements of Pb and Sc/Nb ions, and an AF response also occurs. Therefore, the freezing pattern at the M point of PSN is most probably not M<sub>3</sub>. But no mode assignment has been made yet, and the work is still ongoing.



**Figure 7.** Comparison between the observed and calculated intensities of the peaks at the M points in different Brillouin zones.



**Figure 8.** A schematic representation of the ordering of dipoles at the B sites. The AF region is given by an array of squares. One side of the square corresponds to the lattice parameter, and the dipoles are shown as arrows in the figure.

#### 4. Conclusions

Our x-ray scattering study on ordered PSN indicates lattice instabilities at the  $\Gamma$  and M points in one temperature region, and the investigation of the dielectric constants suggests coupling of the two modes.

The work on disordered PSN and a comparison of the results with those for the ordered system inform us of another aspect of the mechanism of dielectric response of relaxors. Unlike

the case for PMN [5], the dielectric behaviours appear through frustration between the FE and AF dipole orders. This is the same mechanism as is operative in the FE–AF mixed-crystal systems [18–20]. But disordered PSN is not a mixture of any FE and AF phases, as is seen from the chemical formula, and the pre-existence of the AF regions in the paraelectric state is caused by self-accommodation of the size-effect lattice distortions, which is an effect unique to this system. The distortions are found to appear gradually through an interaction with the soft mode, and the interaction is thought to be essential for the occurrence of the diffuse transition.

### Acknowledgments

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