Phase transition of the uniaxial disordered ferroelectric \( \text{Sr}_{0.61}\text{Ba}_{0.39}\text{Nb}_2\text{O}_6 \)

S N Gvasaliya\(^1\), R A Cowley\(^2\), L I Ivleva\(^3\), S G Lushnikov\(^4\), B Roessli\(^5\) and A Zheludev\(^1\)

1. Introduction

Relaxor ferroelectrics are disordered crystals with an anomaly in the dielectric permittivity \( \varepsilon \) that is broad in temperature and frequency-dependent. Remarkably, this anomaly does not necessarily link to any macroscopic changes of symmetry [1]. Due to very high values of \( \varepsilon' \), large piezoelectric constants and electro-optic coefficients, the relaxors have been a focus of intense experimental and theoretical studies [2–5]. It is commonly accepted that the unique properties of relaxors are related to the disordered chemical structure. However, a consistent model of the relaxor behavior has not so far been developed. In particular, it is unclear how large the chemical disorder has to be for a ferroelectric material to become a relaxor. We report below a neutron scattering study of the ferroelectric phase transition of \( \text{Sr}_{0.61}\text{Ba}_{0.39}\text{Nb}_2\text{O}_6 \). We show that despite strong and relevant chemical disorder this crystal largely behaves as an ordinary ferroelectric.

Strontium Barium Niobate, \( \text{Sr}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6 \) (SBN), is one of a group of disordered ferroelectrics with the tetragonal tungsten bronze structure [6]. The dielectric anomaly associated with the phase transition in SBN is strongly affected by the relative amount of Sr/Ba ions. At high concentrations of Sr the dielectric anomaly in SBN occurs at lower temperatures, extends over two hundreds degrees and shows pronounced frequency dispersion. Upon increasing the Ba content the peak in the dielectric constant shifts towards higher temperature, becomes sharper and its dispersion nearly vanishes. This suggests that the higher the Sr/Ba ratio the closer the shape of \( \varepsilon' \) of SBN to that of relaxor ferroelectrics. Contrary to the observations for conventional cubic relaxors a spontaneous polarization \( P_s \) develops in SBN as a result of the phase transition. This polarization is however unusual in several aspects. The value of \( P_s \) at saturation and the critical exponent \( \beta \) depend on how the poled state is prepared [7, 8]. Moreover, both rejuvenation and memory...
effects are observed in the ferroelectric state of SBN [7, 9]. Dielectric aging observed in SBN contrasts sharply that of cubic relaxors, presumably due to different behavior of the fluctuations orthogonal to the net polarization [7]. These properties are characteristic of glasses rather than that of the ordered crystals. The observations for SBN have yet to be explained.

2. Crystal structure and the experimental details

The units cell of Sr$_{1-x}$Ba$_x$Nb$_2$O$_6$ is tetragonal for 0.25 < x < 0.75. Above $T_c$, the space group of SBN is 4mm, while below the phase transition temperature the space group is 4 mm because the inversion centre is lost in the ferroelectric phase. The unit cell contains five formula units and the five Sr/Ba ions are distributed over six different sites. The structure is a network of distorted Nb/O octahedra connected together so that there are pentagonal, square and triangular tunnels which can be occupied by the Sr/Ba ions. These two ions have considerably different ionic radii [10] and are distributed in the pentagonal and square tunnels. As a result, this structure has some of the Sr ions and all of the Ba ions randomly distributed in the pentagonal tunnels and the remaining Sr ions are randomly located in the square tunnels. Thus SBN is disordered both chemically and in the position of the Sr/Ba ions. Since the Sr$^{2+}$ and Ba$^{2+}$ ions have formally the same charge there are no strong electrostatic forces related with the chemical randomness of the Sr and Ba ions. This is in contrast with the cubic relaxors, such as PbMg$_{1/3}$Nb$_{2/3}$O$_3$ (PMN) where the disordered ions Mg$^{2+}$/Nb$^{5+}$ have different charges.

We report below a neutron scattering study of Sr$_{0.61}$Ba$_{0.39}$Nb$_2$O$_6$ (SBN-61) for which the transition temperature is $T_c \approx 350$ K. The experiments were performed with the cold neutron 3-axis spectrometer TASP [11], situated at the end of a curved guide at the SINQ facility (PSI, Switzerland). The energy of the scattered neutrons was kept fixed to 8.04 meV and a PG filter was installed in front of the analyzer. Most of the data was collected with the collimation in the horizontal plane from reactor to detector as open-80°-sample-80°-80°, giving the energy resolution of 0.40 meV. Some data was taken with a tighter collimation: open-20°-sample-20°-20°, improving the resolution to 0.2 meV. A part of the data was collected with the wave-vector transfers near to the (001) Bragg reflection, while the majority of the data was obtained with the wave-vector transfers near the (002) Bragg peak. These Bragg positions were chosen because they have very different neutron structure factors ($|F_{001}| = 9.6$ and $|F_{002}| = 26.9$), while the spontaneous dielectric polarisation of SBN-61 is along the (0, 0, 1) direction.

The large single crystal of SBN-61 had dimensions of 2 × 1.5 × 1.5 cm$^3$ and there was no sign of cracking. The mosaic spread was within the resolution of the spectrometer used for these experiments. The sample was mounted so that the (0, 0, 1) and the (1, 1, 0) directions defined the scattering plane. The lattice parameters of SBN-61 at $T = 300$ K are $a = b = 12.488$ Å, and $c = 3.938$ Å. The sample was mounted in a displex refrigerator that enabled the temperature to be controlled between 20 K and 480 K. Higher temperature data was obtained by using a furnace that allowed for temperature to be as high as 800 K.

3. Temperature dependence of the excitations

On approaching the ferroelectric phase transition the susceptibility of the transverse polarization fluctuations should diverge. Since in SBN the polarization appears along the c-axis, we studied the transverse modes propagating along the $(q, q, 0)$ direction. Figure 1 shows the neutron spectra for a wave-vector transfer of (0.35, 0.35, 2) at temperatures above, near, and below the phase transition $T_c \approx 350$ K. The data show two peaks, one of which is elastic scattering while the other is an inelastic peak at an energy that increases as the wave-vector transfer is increased.

To quantitatively analyze the spectra we establish a minimal required model. Attempts were made to fit the data with a Gaussian peak centred at zero energy and a damped harmonic oscillator (DHO) describing the inelastic scattering. This model failed to describe the experimental data satisfactorily, especially at low energy transfers where there was considerably more scattering than that given by the model. The scattering function was...
therefore extended by including a Lorentzian peak with a variable energy width and centred on zero energy transfer:

$$S(Q, \omega) = A_{\text{EDS}}(Q) \delta(\omega) + \frac{1}{\pi} [n(\omega) + 1] \cdot \text{Im}(B(Q)_{\text{DHO}} \chi_{\text{DHO}})$$

$$+ C(Q) \chi_{\text{TA}}$$

(1)

In equation (1) the first term describes the elastic diffuse scattering (EDS). The energy width of this scattering is limited by the experimental resolution. The second and third terms are the phonon scattering and the energy-resolved component of the diffuse scattering (IDS). Both of these terms have a finite energy width and so they contain the detailed balance factor namely 

$$\delta(\omega) + \frac{1}{\pi} [n(\omega) + 1] \cdot \text{Im}(B(Q)_{\text{DHO}} \chi_{\text{DHO}})$$

$$+ C(Q) \chi_{\text{TA}}$$

The damping $\gamma(q, \omega)$ and the scale factors $A_{\text{EDS}}$, $B(Q)_{\text{DHO}}$, and $C(Q)$ were allowed to have any constant value for each different wave vector. The scattering function equation (1) was convoluted with the resolution function by using ResLib4.2 library [12] and a constant background was added. The best fits were obtained for a locally constant dispersion of the TA phonon. The fitted results gave a good description of the data as shown in figure 1.

We now qualitatively describe the behavior of each component of the neutron spectra for SBN-61. A weak IDS does not exhibit any regular dependence as a function of reduced wavevector $q$. As a function of temperature its intensity gradually decreases (see figure 1). Such behavior suggests this scattering is not related to the ferroelectric transition of SBN-61 and we are not going to further consider the properties of this excitation. Due to the relatively low tetragonal symmetry the phonons in SBN are strongly anisotropic. Because of this a reliable parametrisation of the data as a function of the wavevector is not exhibited (see figure 1). This additional contribution is clearly different from IDS as it rapidly increases in intensity upon cooling. Thus, this broader component of the elastic scattering is the EDS associated with the slow fluctuations and produces the elastic peak in the spectra shown in figure 1.

A critical scattering above $T_c$ is commonly described by a Lorentzian function. We shall assume that the fluctuations associated with the TA phonon have a finite energy width and so they contain the detailed

$$\chi_{\text{EDS}}(Q, \omega)$$

with susceptibility $\chi_{\text{EDS}}(Q, \omega)$ given by

$$\chi_{\text{EDS}}(Q, \omega) = \frac{\chi(q = 0, T)}{1 - (\omega / \Gamma_q)^2} (1 - i \omega / \Gamma_q)^{-1}$$

(3)

In equations (2) and (3) $Q$ is the total wavevector transfer, $\tau = Q \pm q$ is the appropriate reciprocal lattice point, $\chi(q = 0, T)$ is the susceptibility at the $q = 0$, $\xi = 1/\kappa$ is the correlation length, and $\Gamma_q$ is the wavevector-dependent damping. This scattering is integrated over the energy transfer because the spectrometer resolution is much larger than the relevant energy scales of the EDS. The intensity is then adequately approximated by

$$I_{\text{EDS}} = \chi(q = 0, T) \cdot T \cdot \frac{\kappa}{\kappa^2 + q^2}$$

(4)

The scattering profiles shown in figure 3(b) were fitted to a Gaussian Bragg peak together with an additional peak fitted to a Lorentzian curve convoluted with the Gaussian width that was determined from the Bragg reflections to be approximately the resolution width. The results for the width of the diffuse scattering are shown in figure 4. They are difficult to extract

4. Diffuse scattering above $T_c$ and the dielectric anomaly

The elastic neutron scattering was measured around the (0, 0, 1) and (0, 0, 2) Bragg reflections by performing scans along the $(q, q, 0)$, transverse, direction. At high temperatures, above about 450 K, the scattering consists of a sharp
reliably above a temperature of 400 K and below 350 K. A surprising feature of the results is that the width does not decrease to zero when the sample is cooled from a temperature of 400 K to \( T_c \). At most phase transitions the width of the critical scattering decreases to a very small value. Another unexpected result is that the widths of the diffuse scattering observed near the (0,0,2) Bragg reflection are wider by approximately 30\%, than those observed near the (0,0,1) Bragg reflection (see inset to figure 4). This difference is not related to possible gradients in the composition of the sample as the radial, transverse and longitudinal scans through the (1,1,0) and the (0,0,2) reflections appear to be of the resolution width and their shapes do not show appreciable changes with the temperature. The ratio of the widths is about 1.3 and is unexpected because for most structural phase transitions it would be unity. On the other hand, if the increase of the width is caused by the strain, the ratio of the widths would be as high as two. Our result is intermediate and suggests that somewhat different components of the ionic displacements contribute to the critical scattering around the (0,0,1) and the (0,0,2) Bragg peaks.

One of the main results of this study is the similarity in the divergence of the EDS and dielectric anomaly observed in the paraelectric phase. The temperature dependence of the integrated intensity of the EDS scattering \( I_{\text{EDS}}/T \sim \chi(q = 0, T) \) is shown in figure 5 where it is compared with the real part of the low-frequency dielectric susceptibility measured along the ferroelectric \( c \)-axis, \( \varepsilon' || c \). The agreement in the temperature dependences suggests that the diverging dielectric constant and the neutron elastic diffuse scattering have the same origin. Moreover, as no important changes were observed in the inelastic scattering probed near the (0,0,1) and the (0,0,2) Bragg peaks, it becomes apparent that slow fluctuations drive the phase transition of SBN-61 and are responsible for the ferroelectric anomaly. Based on the energy resolution in our experiments the upper time-scale of these fluctuations is \( \sim 10^{-11} \) s.

The inverse correlation length of the diffuse scattering obtained in our study is larger, on average, by a factor as high as four than that deduced for SBN-60 [13]. The major reason for this discrepancy is that in our experiments a much better signal-to-noise ratio was achieved. Indeed, Borisov \textit{et al} [13] could follow the DS up to the wavevector transfer of...
The elastic scattering in the ferroelectric phase of SBN is more reliable. The neutron diffuse scattering in SBN is more reliable.

5. Diffuse scattering from ferroelectric domain walls

The elastic scattering in the ferroelectric phase of SBN is more difficult to analyze. Below the phase transition temperature, it becomes complicated to distinguish the Bragg peaks and the diffuse scattering since the latter becomes more intense close to \( q = 0 \). Furthermore, one should expect at least two contributions to the diffuse scattering below, but near \( T_c \). The first contribution comes from the critical scattering. As we have shown for \( T > T_c \), the intensity of the DS follows well \( \varepsilon \) and a similar behavior is expected for \( T < T_c \). An inspection of Figure 5 suggests that the critical scattering should become negligible at \( T \lesssim 300 \) K. Second, below \( T_c \) the sample breaks up into ferroelectric domains, which causes intense diffuse scattering from the domain walls. Finally, due to the relief of extinction, a change in the Bragg intensity near \( T_c \) is expected. In order to reliably describe the data, the temperature range was restricted to \( T \lesssim 300 \) K. In this regime we can expect the EDS to be dominated by the scattering from the the ferroelectric domain walls.

The distribution of the EDS in the \([H, H, L]\) plane was measured by scanning along several directions and around a number of the Bragg peaks. In particular, longitudinal scans were performed around the \((0,0,1), (0,0,2),\) and \((2,2,0)\) Bragg positions. The EDS is not observed in this geometry. Also, the scans along the \((q, q, 0), (0, 0, q),\) and \((q, q, q)\) were performed in the vicinity of the \((1,1,1),\) and \((1,1,2)\) Bragg peaks. The diffuse scattering was detected only for the \((q, 0, 0)\) directions. Our observations are in agreement with previous reports on the distribution of the DS in SBN [13, 15, 16] and show the diffuse scattering is sharp along the \((0,0,q)\) direction.

Here we recall the results for the scattering from domain walls [17–20] and introduce the necessary modifications. If no electric field is applied to the sample when the temperature passes through \( T_c \) from above, the structure breaks up into ferroelectric domains. For a uniaxial ferroelectric a plausible assumption is that the adjacent domains with opposite polarizations along the c-axis, thus representing the so-called 180° structure. In this way the problem is reduced to the scattering by the walls with the normals perpendicular to the c-axis. In order to obtain an analytical expression for the scattering function, a further simplification is helpful. We shall assume that the spontaneous polarization along an arbitrary direction \( x \), \( P_x \), is proportional to the displacement field \( P_x \sim u(x) \) with \( u(x) = u_0 \tan h(x/\lambda) \). This leads to the scattering function having the form

\[
S(q_x) = \frac{D \lambda^2}{\sinh^2(q_x \lambda/2)}
\]

(5)

In this approach, \( \lambda \) is a half of the average thickness of the domain walls along \( x \) direction, and \( D \) is a constant proportional to the density of the domain walls.

In order to properly account for the effects of instrument resolution, the model represented by equation (5) has to be extended to 4D \((Q, \omega)\) space. To this end equation (5) can be rewritten in the following way:

\[
S(Q, \omega) = \frac{D \lambda^2}{\sinh^2(q_x \lambda/2)} \delta(q_x) \delta(q_y) \delta(q_z) \delta(\omega)
\]

(6)

The \( \delta \)-functions in equation (6) are now considered. The \( \delta(\omega) \) is directly applicable for the convolution as the EDS is resolution-limited in energy. The EDS along the \((0, 0, q)\) direction is sharp and appears to be also resolution limited. For this reason the \( \delta(q_x) \) in equation (6) is approximated by a sharp (much narrower than the calculated resolution) Lorentzian. Finally, we assume that the domain walls are randomly distributed in the \( a-b \) plane of the crystal and hence do not produce interference effects. This allows us to average the \( 1/\sinh^2(0.5q_x \lambda) \delta(q_x) \) term in equation (6) leading to the following scattering function:

\[
S(Q, \omega) = D \frac{1}{|q|} \frac{\lambda^2}{\sinh^2(q \lambda/2)} \frac{\kappa_x}{q^2 + \kappa_x^2} \delta(\omega)
\]

(7)
The time scale of this scattering is slower than \(10^{-11}\) s. The wavevector width of the scattering reduces as the sample is cooled but does not reach zero at the ferroelectric phase transition. In the ferroelectric phase the neutron diffuse scattering could be described by scattering from sharp domain walls. Our results suggest that despite apparent chemical disorder SBN-61 behaves as ordinary order-disorder uniaxial ferroelectric with slow critical fluctuations.

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6. Conclusions

We have studied the ferroelectric phase transition of SBN-61 by neutron scattering. Measurements of the transverse acoustic mode as a function of temperature showed very little change in the dispersion and did not give any evidence for the soft optic phonon. We did observe critical scattering with a temperature dependence similar to that of the low-frequency dielectric constant. The time scale of this scattering is slower than \(10^{-11}\) s. The wavevector width of the scattering reduces as the sample is cooled but does not reach zero at the ferroelectric phase transition. In the ferroelectric phase the neutron

\[(\pm \tau)\]

Figure 7. The width of the ferroelectric domain walls in SBN-61 in the temperature range 220–300 K. The vertical lines denote the phase transition \(T_c\) and the temperature where the critical contribution to the DS becomes negligible. The horizontal line shows the value of the lattice constant.

In equation (7) the reduced wavevector \(q\) runs from respective Bragg peak, \(q = Q \pm \tau\), and in our treatment \(\kappa_z\) was fixed to the value 0.0005 rlu. Equation (7) was convoluted with the resolution function of the spectrometer and the best fit results are shown in figure 6. The points in the scans that are clearly a part of the Bragg peak (shaded areas in figures 3(b) and 6) were excluded from the fitted range. The model reproduces the generally expected (atomically) sharp domain walls in ferroelectrics and is similar to the results obtained for SBN-70 by Prokert [21] and for other uniaxial ferroelectrics [17, 22, 23].

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