

Rapid Research Note

Composition dependence of the phase transition temperature in $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$

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The temperature dependence of the spontaneous polarization in strontium–barium–niobate single crystals with varying Sr/Ba ratio is presented. The temperature of the relaxor phase-transition is determined from the inflexion point of the curve of the ferroelectric polarization versus temperature. The influence of the Sr/Ba ratio in the crystal on the transition temperature is discussed within an effective field approach.

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1 Introduction Ferroelectric strontium–barium–niobate (SBN, $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$) has a large spontaneous polarization P , huge electrooptic coefficients as well as pronounced pyroelectric and piezoelectric properties. Therefore, SBN is used in applications such as pyroelectric detectors or holographic data storage systems [1, 2]. Since many physical parameters connected with the polar structure reach a maximum in the vicinity of the transition temperature T_C separating the ferroelectric from the paraelectric phase, it is desirable to use SBN as close as possible to T_C . An exact determination of T_C is difficult, since SBN is a relaxor ferroelectric: There is for example no sharp peak of the dielectric permittivity χ' at T_C , but only a broad maximum which strongly depends on the frequency used [3, 4]. This relaxor behavior prevents all properties of SBN to change in a step-like manner.

While the phase transition has been examined extensively for doped and undoped SBN61, there exist only few reports that deal with crystals with different x . It is shown that for Sr fractions of $0.25 \leq x \leq 0.75$ in the melt T_C increases with decreasing x [1, 5]. Therefore, a variation of x allows to selectively influence the phase transition behavior without being forced to accept the sometimes unfavorable crystal properties associated with doping, like the optical absorbance [6], or photorefractive properties [2, 7]. Furthermore, a variation of the Sr/Ba ratio can reveal the physical nature of the internal fields causing the relaxor transition [8].

Here, we present phase transition temperature measurements in SBN single crystals with various Sr fractions x . We examine the temperature dependence of the polarization, $P(T)$, using pyroelectric surface-charge measurements. It has been shown that the temperature T_1 of the inflexion point of $P(T)$ is a meaningful parameter for characterizing the relaxor phase-transition [9]: Although T_1 is not necessarily identical with the actual phase transition temperature T_C , it has been shown to be a suitable approximation. A slightly non-linear dependence of T_1 on x is observed and explained using an effective field approach [10].

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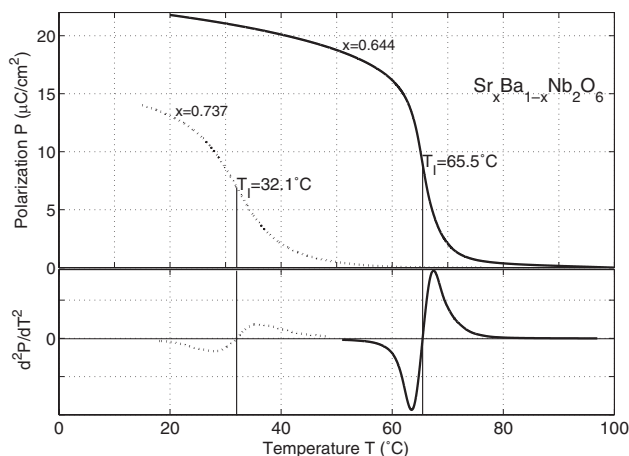


Fig. 1 $P(T)$ curves of $\text{Sr}_{0.644}\text{Ba}_{0.356}\text{Nb}_2\text{O}_6$ and $\text{Sr}_{0.737}\text{Ba}_{0.263}\text{Nb}_2\text{O}_6$. The temperature T_I of the inflexion point was determined from the null of the second derivative d^2P/dT^2 , shown in the lower part of the figure.

2 Experiment and results $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ crystals were grown by the Czochralski method from melts with a Sr fraction in the range of 0.19 to 0.84, which corresponds to 0.32 to 0.82 in the samples. The composition x of the corresponding crystals was determined by X-ray fluorescence with an accuracy of about 0.003 and will be used throughout this work. The crystals were cut into platelets with a thickness of 1 mm along the crystallographic axis. To obtain a fully poled sample, the crystal was heated up to a temperature exceeding the expected T_C , estimated from a linear interpolation of known data, by about 50°C . Then an electric field of 350 V/mm was applied parallel to the c -axis, and the samples were cooled back to room temperature in 90 min with the field applied. After this poling procedure, the sample was fixed into a temperature-controlled holder with one c -face connected to the ground, the other one to a charge amplifier. The temperature was increased from 20°C to 250°C with a heating rate of $0.01^\circ\text{C}/\text{s}$. During this time, the charge change on the c -faces of the sample, which is proportional to the polarization change of the sample, was recorded.

Figure 1 exemplarily shows $P(T)$ for two samples with $x = 0.644$ and $x = 0.737$. The temperature T_I of the inflexion point is marked by the zero crossing of the second derivative d^2P/dT^2 which is shown in the lower part of Fig. 1. The relaxor behavior is well emphasized in $P(T)$ and the second derivative. It is most pronounced for larger x and decreases with decreasing Sr^{2+} concentration. Even a small variation of the Sr content of less than 0.1 results in a remarkable change of the shape of $P(T)$, see Fig. 1. For very high temperatures, the determination of $P(T)$ became less reliable due to the high electric conductivity of all samples: It was not possible to compensate external electric fields below the mV scale. In the paraelectric phase the electric conductivity of the samples became so large that these small fields were

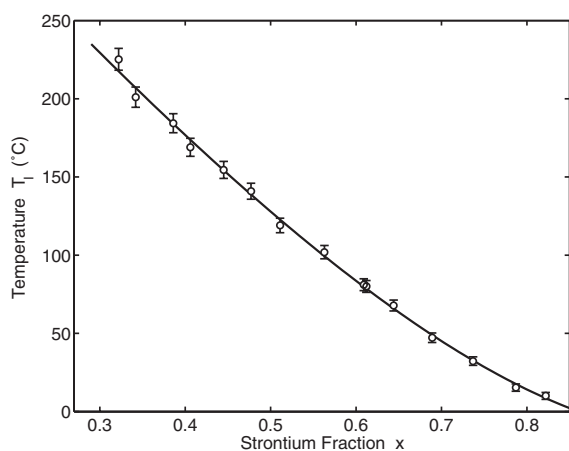


Fig. 2 Temperature T_I for SBN in dependence on the Sr fraction x .

sufficient to cause electric currents which made effective surface charge measurements of the polarization impossible. However, direct measurements of the conductivity showed that this problem arose only at $T > T_1 + 15 \text{ }^\circ\text{C}$.

Figure 2 shows the dependence of T_1 on the Sr fraction x . The continuous line, describing the measured data very well, represents a fit within the framework of an effective field approach, which will be discussed below.

3 Discussion The decrease of T_1 with increasing Sr content qualitatively agrees with observations reported in the literature [1, 5]. However, the transition temperatures shown here deviate from the literature values: We observe higher T_1 for small values of x and lower T_1 for high values of x . A possible explanation lies in the uncertainty of the composition of the samples used for earlier studies, where generally only the Sr content in the melt is given. We have found that the actual Sr content x in the sample tends to shift closer to the congruently melting composition, $x = 0.61$. This explains the systematic deviation of our T_1 from earlier literature values. Furthermore, the transition temperatures reported earlier stem from dielectric measurements and are less reliable due to their frequency dependence [3, 11].

The nonlinear behavior of $T_1(x)$ can be explained by structure induced polarization changes. SBN belongs to the structure type of the tetragonal tungsten bronzes, i.e., the structure consists of corner-linked NbO_6 octahedra forming pentagonal, tetragonal and trigonal channels [12, 13]. Large Ba^{2+} ions occupy only the pentagonal channels, of which there are 4 per unit cell, while smaller Sr^{2+} ions occupy both the pentagonal and the tetragonal channels, of which there are 2 per unit cell. Approximately 72% of the tetragonal channels are occupied independent of the composition x with Sr^{2+} . However, the pentagonal channels are occupied by roughly 85% only with Ba^{2+} for $x = 0.33$, which decreases to circa 31% for $x = 0.75$, while the Sr^{2+} content increases from zero to about 57%, respectively. Because of the only Sr containing tetragonal channel and the strong variation of the Sr/Ba ratio in the pentagonal channel it is tempting to regard the compositional changes of $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ as being caused by three sublattices. Sublattice (1) may be devoted to Sr in tetragonal sites, (2) to Sr in pentagonal ones, while (3) is devoted to Ba. Within an effective field approach [10] the polarization of m coupled systems is described by m equations of the form

$$P_i = N_i \mu_i \tanh \left(\frac{\left(E + x_i \beta_i P_i + \sum_{k \neq i} (x_k \alpha_{ik} P_k) \right) \mu_i}{k_B T} \right) \quad (1)$$

The parameters α_{ik} describe the coupling strength between the subsystems with polarization P_i , the number of elementary dipoles N_i , the dipole moments μ_i and the effective fields β_i , while $k_B T$ has the usual meaning. The relative portions are x_i and $\sum_i x_i = 1$. For temperatures approaching T_C the polarization approaches zero, the hyperbolic tangent can be approximated by its argument. Summarizing several parameters in $T_i = \beta_i N_i \mu_i^2 / k_B$, which might be regarded as the Curie temperatures of the ‘pure’ sublattices, Eqs. (1) transform to

$$(a_{ki} - \delta_{k,i} T) P_i = b_i E_i \quad \text{with} \quad a_{ki} = \begin{cases} x_i T_i & \text{for } k = i \\ x_i T_i \alpha_{ki} / \beta_k & \text{for } k \neq i \end{cases}, \quad b_i = T_i / \beta_i. \quad (2)$$

The polarizations should be able to approach any value at T_C at zero field. Therefore the determinant of the coefficients must vanish. For $m = 3$ we derive $T_C^3 - s_2 T_C^2 + s_1 T_C - s_0 = 0$ with

$$s_2 = \sum_i a_{ii}; \quad s_1 = \sum_{i,k>i} (a_{ii} a_{kk} - a_{ik} a_{ki}); \quad s_0 = \sum_{i \neq k \neq l \neq i} (a_{i1} a_{k2} a_{l3} (-1)^{np(ikl)}), \quad (3)$$

wherein $np(ikl)$ is the number of permutations necessary to produce the index set $\{i, k, l\}$ from $\{1, 2, 3\}$. Because an exact solution is awkward to manage, we linearize the third order equation by substituting $s_2 + \Delta$ for T_C and omitting all nonlinear terms in Δ . Physically this is well justified as s_2 is the ‘classical’

Curie temperature, the weighted sum over the Curie temperatures of the ‘pure’ sublattices $s_2 = \sum_i a_{ii} = \sum_i (x_i T_i) = T_C^{\text{classical}}$ and only minor deviations are expected. We obtain

$$T_C = s_2 + \frac{s_0 - s_1 s_2}{s_1 + s_2^2} \quad \text{with} \quad s_1 s_2 \gg s_0 \quad \text{and} \quad s_2^2 \gg s_1 \quad \text{and thus} \quad T_C = s_2 - \frac{s_1}{s_2}. \quad (4)$$

The parameter s_1 is a slightly more complex sum, but replacing the quotients $(\alpha_{ik}\alpha_{ki})/(\beta_i\beta_k)$ therein by an appropriate average factor λ^2 we arrive for the Curie temperature finally at

$$T_C(x_i) = T_C^{\text{classical}} - \frac{1 - \lambda^2}{T_C^{\text{classical}}} \sum_{i,k>i} (x_i x_k T_i T_k). \quad (5)$$

We point out that for a system with two sublattices, the parameter $(\alpha_{ik}\alpha_{ki})/(\beta_i\beta_k)$ reduces to $(\alpha_{12}\alpha_{21})/(\beta_1\beta_2) = \lambda^2$, because of $\alpha_{12} = \alpha_{21}$ and thus Eq. (5) equals that in [14] after some appropriate linearizing.

In Fig. 2 the transition temperature T_1 is presented as a function of the strontium fraction $x = x_1 + x_2$. For a fit of our data with Eq. (5) we took into account a constant contribution of Sr on tetragonal sites by setting $x_1 = 0.29$, which corresponds to about 72%, and $x_3 = 1 - x$. The fit yields $\lambda = 0.51$, $T_1^{\text{tet}}(\text{Sr}) = T_2^{\text{pent}}(\text{Sr}) = 304$ K, and $T_3(\text{Ba}) = 668$ K, respectively. Allowing $T_1^{\text{tet}}(\text{Sr}) \neq T_2^{\text{tet}}(\text{Sr})$ simply results in an additional parameter without improving the quality of the fit. This means that constant polarization contributions like Sr on tetragonal sites or niobium–oxygen octahedra are implicitly included by an appropriate change of the temperature constants. Therefore the temperatures given should be regarded as fit parameters only. A λ less than 1 means that in this mixed system the coupling strength between the sublattices is weaker than the average value of the coupling strength within each sublattice. Such a reduction may be due to random internal strain fields in the crystal lattice introduced by the different ionic sizes of Sr and Ba.

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