

Relaxation mechanisms in $\text{Sr}_{0.3}\text{Ba}_{0.7}\text{Nb}_2\text{O}_6$

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Strontium barium niobate $\text{Sr}_{0.3}\text{Ba}_{0.7}\text{Nb}_2\text{O}_6$ exhibits a complex dielectric behavior. Measurements performed over a wide frequency range (10^2 – 10^9 Hz) and as a function of temperature have allowed a complete description of the relaxation mechanisms observed. At low frequency and below the temperature of the maximum of ϵ'_r ($T_m = 303$ K), a relaxor behavior is detected and correlated to the cationic disorder in pentagonal and tetragonal sites of the tungsten bronze structure. Moreover a network relaxation is clearly observed at high temperature in the paraelectric phase in the radio frequency range (10^8 Hz). By analogy with perovskites, it can be related to the motion of Nb^{5+} ions in octahedral sites. The two relaxation mechanisms are described through both thermal evolution of the corresponding relaxation frequencies (Arrhenius-type behaviour) and comparison of the dielectric spectra (Cole–Cole type relaxations).

Introduction

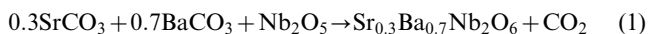
Among the large group of compositions known as ferroelectric relaxors, those having the tungsten bronze structure (TKWB) are of particular interest. Strontium barium niobate solid solutions $\text{Sr}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6$ [SBN], are attractive owing to their outstanding properties and are used in many applications such as pyroelectric detectors and piezoelectric devices.^{1,2} The SBN relaxor behavior is now well known and related either to compositional fluctuations or more recently to the freezing of randomly oriented and mutually interacting polar clusters (heterophase fluctuation model).^{3,4} Considering the strong anisotropy which characterizes TKWB materials, polar fluctuation mechanisms are more critical than, for instance, in perovskite type relaxors such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$.

A complete understanding of the complex dielectric behavior in tungsten bronze-type compounds requires an investigation performed over both a wide temperature and frequency range. The selected composition, $\text{Sr}_{0.3}\text{Ba}_{0.7}\text{Nb}_2\text{O}_6$ is rich enough in barium to present relaxor characteristics. An important aspect of this work is experimental and concerns the use of different set-ups in a continuous frequency range from 10^2 to 10^9 Hz to quantify and characterize the relaxation mechanisms. A discussion based on the possible origin of the observed dielectric relaxations is proposed.

Experimental

Sample preparation

$\text{Sr}_{0.3}\text{Ba}_{0.7}\text{Nb}_2\text{O}_6$ ceramics were prepared using a conventional mixed oxide process [eqn. (1)]:



The initial reaction mixture was ground and calcined at 1200°C under oxygen atmosphere for 15 h. Disks of 9 mm of diameter were then sintered at 1400°C under oxygen atmosphere for 2 h and compactness of the sample reaches 90%. Dilatometry analysis was performed on the calcined powder under oxygen atmosphere. The use of different sintering additives (Li_2CO_3 , Nb_2O_5) did not lead to significant improvement of ceramic densification. X-Ray diffraction analysis showed the sample to be single phase of TKWB type structure. The values of the cell parameters a and c were 1.2433 and 0.3916 nm, respectively.⁵

Dielectric measurements

Measurements were performed under vacuum. At low frequency (10^2 – 3×10^5 Hz) a Wayne–Kerr 6425 component analyzer was used and the permittivities were deduced from capacitance and loss tangent values. A Hewlett–Packard 4194A impedance gain phase analyzer was used for measurements between 10^4 and 10^7 Hz while the use of an HP8753A analyzer allowed a continuous sweep of the frequency range from 10^6 to 10^9 Hz. The complex permittivity of the sample was derived either from the complex impedance or from the reflection coefficient. An air line was used for high frequency measurements at temperature ranging from 200 to 450 K. The end section of this line was filled by a disk-shaped ceramic sample of 7 mm diameter in a short circuit holder. For all the devices used, careful calibrations were performed prior to the measurements.

Results and discussion

The atomic disorder resulting from the partial filling of the A (C.N. 15) and B (C.N. 12) sites by Sr^{2+} and Ba^{2+} ions, explains the diffuse transition observed for the thermal dependence of ϵ'_r (Fig. 1).⁵ The value of the temperature of the maximum of ϵ'_r , $T_m = 303$ K, is close to room temperature at 10^2 Hz, in good agreement with previous work.⁵ A significant increase of T_m occurs as the frequency is raised to 10^8 Hz. Simultaneously, the

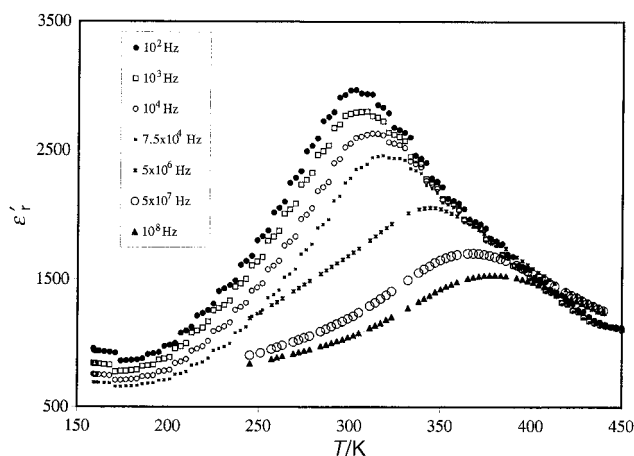


Fig. 1 Temperature dependence of ϵ'_r at various frequencies.

value of $\epsilon'_{r\max}$ decreases as is usually observed in relaxor type materials. Heterogeneity of composition in A and B sites is associated with a breakdown of translational symmetry and is generally responsible for relaxor character.

The low frequency relaxation behavior at low temperatures, $T < T_m$, is similar to that observed in the well known PMN characterized by a large and diffuse maximum of ϵ''_r .⁶ The shape of the ϵ''_r peak does not reflect relaxation behavior described by a single relaxation time (Debye-type) and generally the Cole–Cole relation [eqn. (2)] is a more accurate description:⁷

$$\epsilon_r^* = \epsilon'_\infty + \{(\epsilon'_s - \epsilon'_\infty) / [1 + (i\omega\tau)^{1-\alpha}]\} \quad (2)$$

where $\tau = 1/2\pi f_r$ is the average relaxation time ϵ'_s is the permittivity at $f \ll f_r$, ϵ'_∞ that at $f \gg f_r$ and α is an exponent taking values between 0 and 1 and characteristic of the deviation from the Debye model. The value of α is representative of the distribution width of the relaxation time. The frequency spectrum is very complex in the ferroelectric phase and is strongly temperature dependent. As the temperature increases from 240 K to T_m , the low frequency relaxation f_r (LF) increases. It was difficult to fit the curves using a simple Cole–Cole model. Since the ϵ''_r maximum can be seen as an overlap of different maxima, it is logical to use eqn. (3) which takes into account the contribution of two relaxations:⁸

$$\epsilon_r^* = \epsilon'_\infty + \left(\epsilon'_{01} / [1 + (if/f_{r1})^{1-\alpha_1}] + \epsilon'_{02} / [1 + (if/f_{r2})^{1-\alpha_2}] \right) \quad (3)$$

ϵ'_{01} and ϵ'_{02} represent the contribution of each relaxation to the static permittivity: $\epsilon'_s = \epsilon'_\infty + \epsilon'_{01} + \epsilon'_{02}$. Determination of the temperature dependence of the low frequency relaxation in the range $T < T_m$ was thus possible.

In the paraelectric phase and sufficiently far from T_m , dielectric dispersion is not observed below 10^6 Hz. This result confirms that the dispersion at low temperature is related to the relaxor character of the material. As the temperature increases from T_m , the maximum of ϵ''_r becomes sharper reflecting the presence of a single relaxation. This high frequency relaxation appears close to f_r (HF) = 3×10^8 Hz at 365 K (Fig. 2). Measurements performed between 10^6 and 10^9 Hz complete the frequency dielectric characterization of $\text{Sr}_{0.3}\text{Ba}_{0.7}\text{Nb}_2\text{O}_6$ ceramics. The variation of ϵ'_r with both frequency and temperature is represented on a three-dimensional diagram (Fig. 3) which summarizes the high frequency investigation (10^6 – 10^9 Hz), showing the temperature maximum of ϵ'_r as well as the dielectric dispersion, *i.e.* the strong decrease of ϵ'_r as the frequency increases, at each temperature. The determination of f_r (HF) is extracted from the theoretical curves which show full agreement with the experimental ones (same values for the maxima of ϵ''_r) using the Cole–Cole model [eqn. (2)]. The relaxation appears to be essentially monodisperse with values

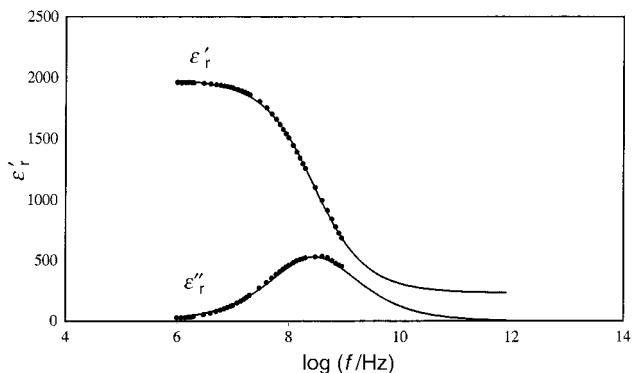


Fig. 2 Frequency dependences of ϵ'_r and ϵ''_r at 365 K: (●) experimental points, (—) theoretical curves.

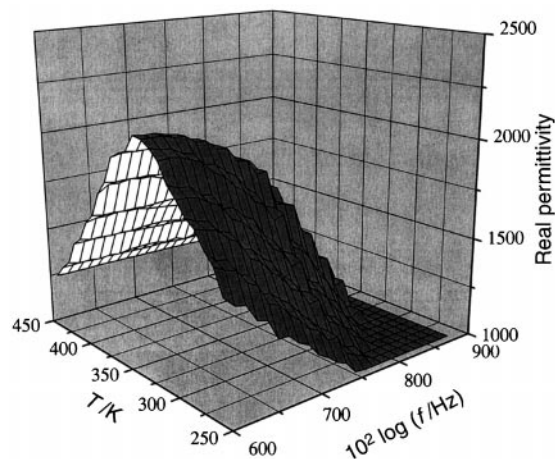


Fig. 3 Frequency and temperature dependences of ϵ'_r .

of the relaxation time distribution α , close to 0.3 at 365 K and *ca.* 0.1 at 430 K. The f_r (HF) value increases with temperature for $T > T_m$. Such network relaxation has already been observed in $\text{Sr}_{0.4}\text{Ba}_{0.6}\text{Nb}_2\text{O}_6$ and confirmed by other workers in $\text{Ba}_2\text{NaNb}_{5(1-x)}\text{Ta}_{5x}\text{O}_{15}$ crystals.^{9,10} An analogy with perovskite compounds for which a relaxation of close to 10^8 Hz is also observed can be made.¹¹ This relaxation is attributed to the cooperative and anharmonic motion of Nb^{5+} ions in a double-well potential. On using the correlation chain model, the decrease of f_r (HF) with decreasing temperature from 450 to 340 K could result in an increase of the number of cooperative Nb^{5+} ions involved in the relaxation mechanism (Fig. 4).¹²

The more complex part of the dielectric response of $\text{Sr}_{0.3}\text{Ba}_{0.7}\text{Nb}_2\text{O}_6$ is located between *ca.* 290 and 340 K. As an example, the complete dielectric response in a wide frequency range (10^2 – 10^8 Hz) is shown near T_m at 298 K without any discontinuities thanks to the three different devices used (Fig. 5). Such a good agreement, in particular, suggests the good quality and validity of the delicate high frequency measurements. Frequency dependences of real and imaginary parts of the permittivity show a decrease of ϵ'_r associated with an increase of ϵ''_r as early as 10^5 Hz. The shape of the ϵ''_r peak seems to be characteristic of the overlap of two LF and HF relaxations and the values remain high up to 10^8 Hz. The proximity of the two relaxations makes it difficult to precisely determine the relaxation frequency values.

Finally, a significant difference between the two relaxation mechanisms is evident from Fig. 4. Two regimes can be clearly observed between the thermal evolution of LF and HF relaxation frequencies on considering the break in the slope close to 300 K. As explained previously, while the origin of LF relaxation is related to relaxor behavior the HF relaxation appears to be thermally activated as shown by the good fit

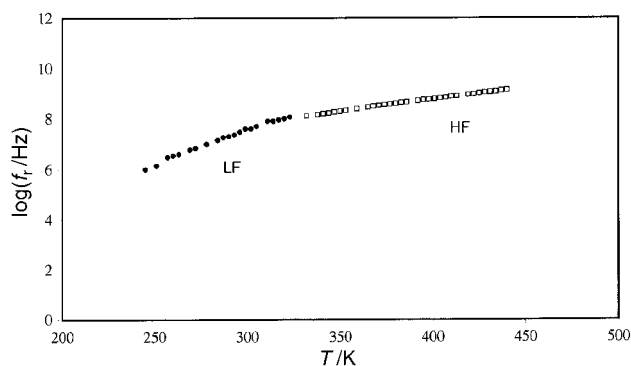


Fig. 4 Relaxation frequency vs. temperature: (●) low frequency relaxation, (□) high frequency relaxation above T_m .

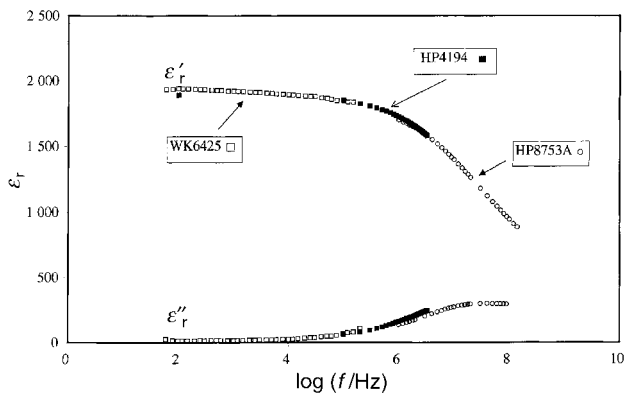


Fig. 5 Frequency dependences of ϵ'_r and ϵ''_r obtained using the different devices indicated in the range 10^2 – 10^9 Hz at 298 K.

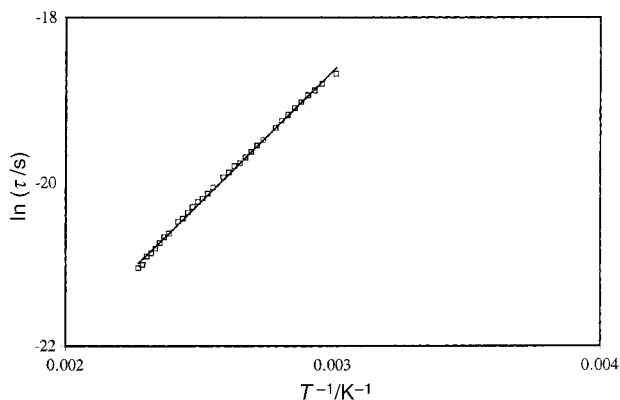


Fig. 6 Arrhenius plot for the high frequency relaxation.

obtained using an Arrhenius law (Fig. 6). The values of both activation energy, E_a , and attempt frequency, f_0 , for the HF process are 0.276 eV and 1.9×10^{12} Hz respectively. A higher activation energy corresponds to the LF mechanism ($E_a = 0.46$ eV). This result reflects stronger interactions between polar units, in relation with the relaxor behavior. This is in good agreement with the polydisperse nature of the low frequency relaxation observed ($T \leq T_m$). For example, the value of α reaches 0.65 at temperatures close to 260 K.

Conclusion

A complete study of the dielectric properties of the TKWB type $\text{Sr}_{0.3}\text{Ba}_{0.7}\text{Nb}_2\text{O}_6$ ceramic allowed us to distinguish two

relaxation mechanisms. One of them is observed at low frequency ($f_r \leq 10^7$ Hz) and below T_m ; its origin is probably related to the relaxor behavior of this material resulting from the cationic disorder of Sr^{2+} and Ba^{2+} in A and B sites. The activation energy associated with this process is rather high and a strong deviation from a single Debye behavior is apparent at lower temperatures. This accounts for the existence of both strong correlations between dipoles and significant polar fluctuations. The second relaxation occurs at high frequency ($f_r \geq 10^8$ Hz) and its origin may be ascribed to the crystalline network considering the motion of ferroelectric active Nb^{5+} ions. The description of this high frequency relaxation was possible thanks to high frequency measurements performed between 200 and 450 K. In the temperature range close to T_m , the dielectric response is much more complex. A large and diffuse maximum of ϵ''_r is obtained, with values near 10^8 Hz still high, suggesting the probability of a peak outside of the scope of the measured frequency range. It would thus be interesting to use equipment scanning an even higher frequency range. Another solution would be to use the cavity method to obtain the value of ϵ''_r above 10^9 Hz. Such measurements would be also useful in order to confirm the obtained values of ϵ''_r at high temperature. Another possibility would be to decrease $f_r(\text{HF})$ using suitable ionic substitution. A theoretical approach based on chemical bonding considerations is currently being undertaken.

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