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Piezoelectric properties and equivalent circuits of ferroelectric relaxor single crystals

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Temperature dependent piezoelectric properties of ferroelectric relaxor single crystals, particularly the cerium-doped strontium barium niobate compositions (SBN60: Ce), were investigated by resonance and anti-resonance technique. Characteristic resonant frequencies ($f_r - f_a$, $f_s - f_p$, and $f_m - f_n$) were studied using equivalent circuit simulation. Piezoelectric resonance in a relaxor resonator persists into temperatures much higher than T_m (the temperature at which dielectric constant, κ, has a maximum at 1 kHz) in comparison with the normal ferroelectrics such as TGS. The parameters in an equivalent circuit, however, are phenomenally different from a normal resonator like a TGS, near and above the transition temperature region. The significance and understanding of the piezoelectric resonance characteristics in ferroelectric relaxor are discussed.

1. Introduction

Strontium barium niobate ($Sr_{0.6}Ba_{0.4}Nb_2O_6$: SBN60) is a relaxor material having a tetragonal structure with its space group P4bm both below and above the dielectric maximum temperature, T_m [1, 2]. Little attention has been paid to the piezoelectric study of relaxor materials, especially above the dielectric constant maximum temperature. The temperature and frequency dependences of the dielectric permittivity of $Sr_xBa_{1-x}Nb_2O_6$ (SBN), as well as its relaxor ferroelectric characteristics [1, 2], near the ferroelectric-paraelectric phase transition, have been studied extensively. At any specific temperature, a ferroelectric relaxor may still preserve its macroscopic homogeneous chemical composition and crystalline symmetry, but local chemistry may deviate from the global chemistry, and local symmetry may be lower than global symmetry, as a result of local polarization fluctuation [3, 4]. It is well known that the ferroelectric crystals are subspecies of a piezoelectric family. After proper poling, a macroscopic polarization is sustained at a temperature below the Curie temperature, along the polar direction. Above the Curie temperature, a ferroelectric undergoes a transition from a ferroelectric (polar) state to paraelectric (non-polar) state, and the piezoelectricity vanishes. However, the spontaneous polarization in a relaxor ferroelectric is not suddenly lost at a specific Curie temperature, but slowly decays with increasing temperature. The diffuse nature of the transition has been postulated to be due to a partially disordered distribution of cations in relaxor ferroelectrics, so that a mixture of ferroelectric and paraelectric microphase exists over a wide temperature range [5]. The present work studied the piezoelectric behaviour of a typical relaxor single-crystal SBN approaching and above the Curie transition temperature region.

2. Experimental procedure

A resonance and anti-resonance method was performed to measure the piezoelectric parameters of SBN60 from room temperature to 200 °C, and from room temperature to 100 °C for alanine-doped TGS. Before piezoelectric measurement, the SBN60 sample was poled at 140 °C for 15 min with 10 kV cm^{-1} field, and cooled down to 50 °C by maintaining the electric field. Just after poling, the d_{33} value measured by a d_{33}-meter was 158×10^{-12} C N^{-1}. Piezoelectric parameters, impedance, $|Z|$, and phase angle, θ, were precisely measured in order to determine the characteristic resonant frequencies $f_r - f_a$, $f_s - f_p$, and $f_m - f_n$, respectively. Each piezoelectric parameter is defined as follows: f_m is the frequency at maximum admittance (minimum impedance), f_s the motional (series) resonance frequency $= 1/2\pi(L_1C_1)^{1/2}$, f_r the resonance frequency (reactance $X_e = 0$), f_a the anti-resonance frequency (reactance $X_e = 0$), $f_p =$ the parallel resonance frequency $= [(1 + 1/r)/L_1C_1]^{1/2}/2\pi$, and $f_n =$ the frequency at minimum admittance (maximum impedance), where C_1 is the motional capacitance, L_1 the motional inductance, R_1 the motional resistance, C_0 the shunt (parallel) capacitance and $r = C_0/C_1$ is the capacitance ratio. Based on the measured basic parameters, which are impedance, $|Z|$, and phase angle, (θ), at each temperature, other necessary parameters are converted using IRE standard formalism [3].

TGS single crystal was also measured as a normal ferroelectric resonator for comparison with the relaxor ferroelectrics SBN. Dielectric constant measurement was done to ensure T_m (temperature of dielectric maximum) and to calculate the piezoelectric coefficient, d_{31}. Before dielectric measurement, the sample was annealed to eliminate the pre-stress during the poling. The same sample was used in both dielectric and piezoelectric measurements for consistency of results. Sample dimensions for both measurements were $3.71 \times 1.16 \times 0.77$ mm^3 (in a, c, b direction). All data were stored into the computer through a GPIB interface connected to an HP impedance analyser (HP 4194A, USA).

3. Results and discussion

Fig. 1a–e show the results of piezoelectric parameters measured by the resonance and anti-resonance method from room temperature to 200 °C for relaxor Ce: SBN60, and from room temperature to 100 °C for normal ferroelectrics TGS. Fig. 1a shows the impedance variation, Fig. 1b the phase angle variation of Ce: SBN60, and Fig. 1c and d for TGS doped with a few per cent of alanine as a function of frequency. Fig. 1a and c insets show the impedance variation in the temperature range from 70–120 °C for SBN, and from 50–65 °C for TGS, respectively. Impedance peak disappeared completely at 160 °C for SBN, and 60 °C for TGS.

Diffusiness ($D \equiv$ temperature of piezo-peak disappearance/temperature of dielectric maximum) of SBN and TGS are 2.1 and 1.2, respectively. This diffusiness indicates the degree of persistency of piezoelectric characteristics up to far above the transition temperature (Fig. 1e). The higher the diffusiness, the more persistent is the piezoelectric peak in the paraelectric phase. In the case of relaxor SBN, impedance has a minimum between 780 and 790 kHz depending on the temperatures, and these minima shift to lower frequency in the ferroelectric phase and to higher frequency in the paraelectric phase. The phase angle has a sign change in a resonance frequency range below T_m (76.02 °C at 1 kHz in dielectric measurement).

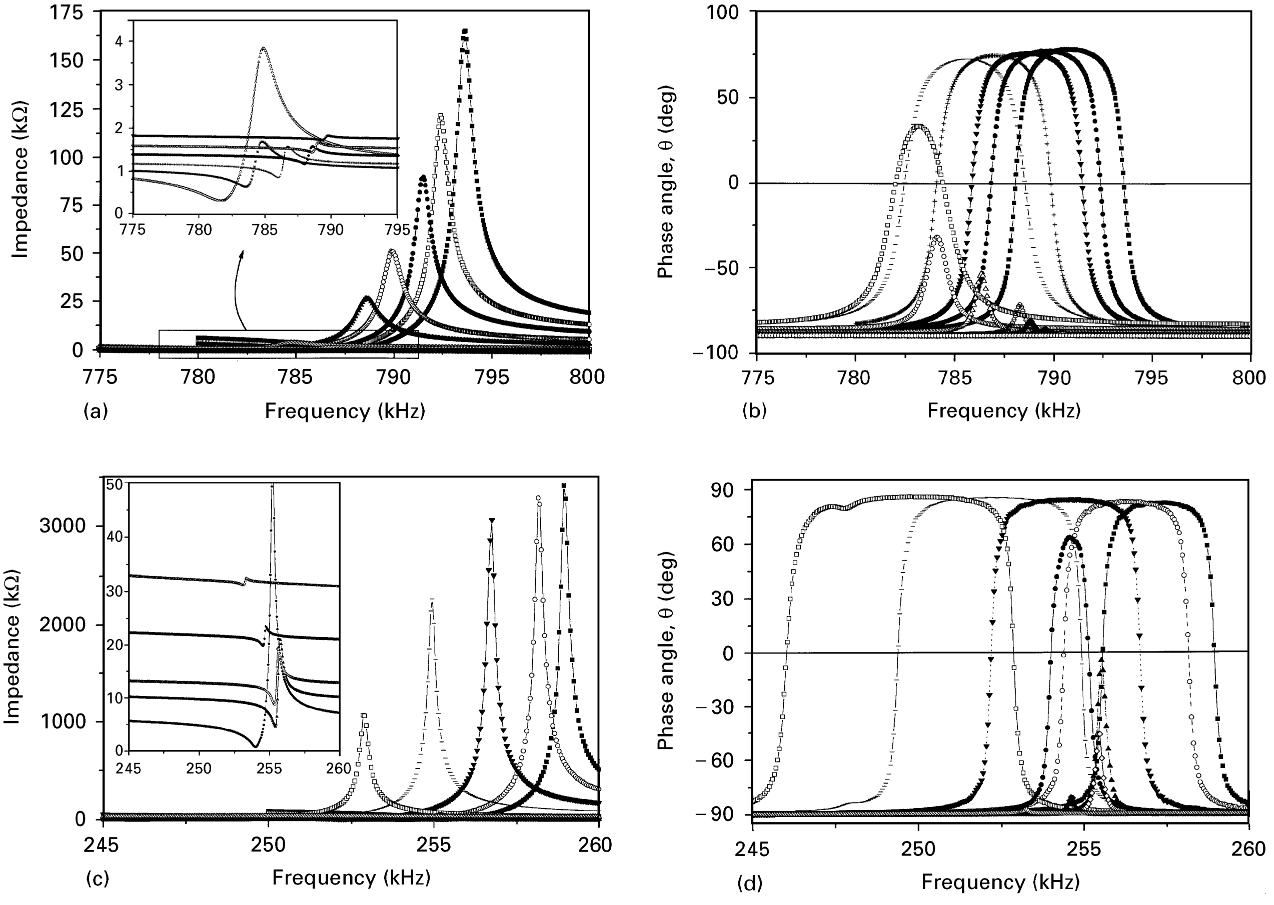

Figure 1 (a) Impedance variation of Ce: SBN60 as a function of frequency around resonance at different temperatures. The inset shows the impedance variation in the temperature range 70–120 °C. (■) 25 °C, (□) 30 °C, (●) 40 °C, (○) 50 °C, (▲) 60 °C, (△) 70 °C, (▼) 80 °C, (▽) 90 °C, (◆) 100 °C, (+) 110 °C, (∗) 120 °C. (b) Phase angle variation of Ce: SBN60 as a function of frequency around resonance at (■) 25 °C, (●) 30 °C, (▼) 40 °C, (+) 50 °C, (—) 60 °C, (□) 70 °C, (○) 80 °C, (△) 90 °C, (θ) 100 °C, (◆) 120 °C. (c) Impedance variation of alanine: TGS as a function of frequency around resonance at different temperatures. The inset shows the impedance variation in the temperature range 50–65 °C. (■) 25 °C, (○) 30 °C, (▼)35 °C, (—) 40 °C, (□) 45 °C, (●) 50 °C, (▲) 53 °C, (◇) 55 °C, (◆) 60 °C, (△) 75 °C. (d) Phase angle variation of alanine: TGS as a function of frequency around resonance at (■) 25 °C, (○) 30 °C,(▼) 35 °C, (—) 40 °C, (□) 45 °C, (●) 50 °C, (▲) 53 °C, (◇) 55 °C, (◆) 60 °C, (△) 65 °C. (e) Impedance variations of (□) SBN and (■) TGS as a function of temperature showing second-order and diffuse phase transition characteristics.

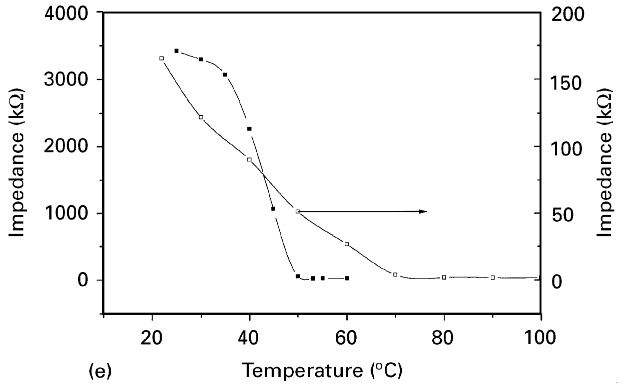

Figure 1 (Continued).

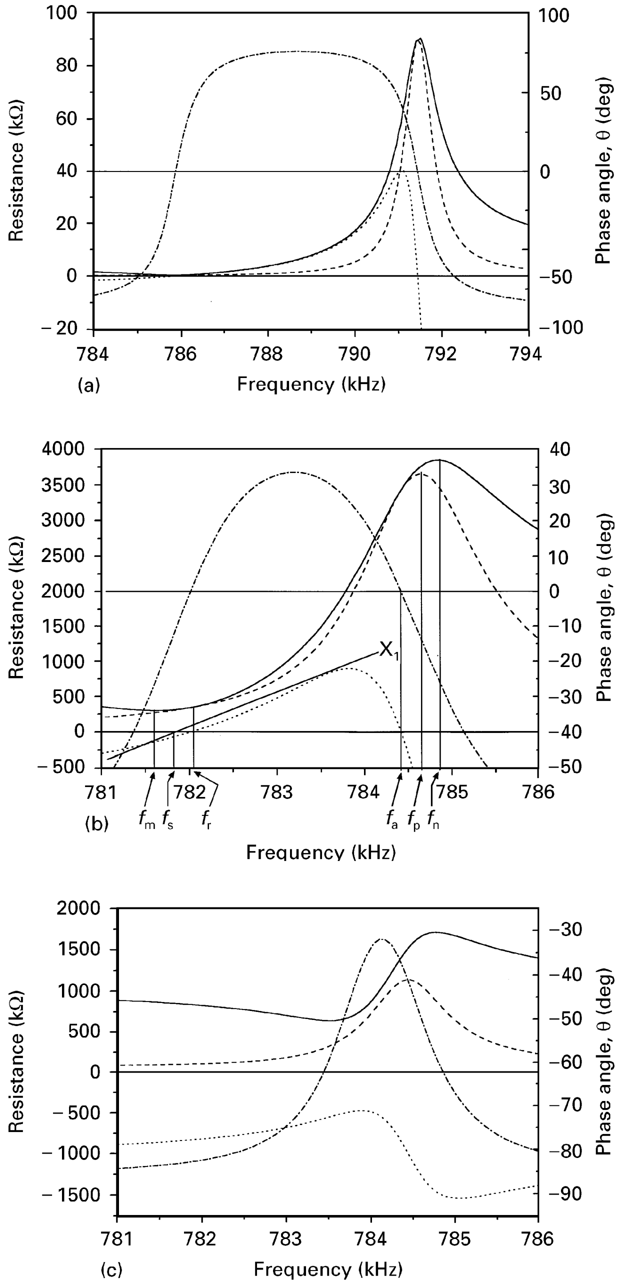

Figure 2 (—) Impedance, (- - -) reactance and (— — —) susceptance variation (left axis), and (— - —) phase angle variation (right axis) (a) at 40 °C and (b) 70 °C for Ce: SBN60. At 40 °C, f_a, f_p and f_n are too similar to be distinguished, whereas at 70 °C, f_a, f_p and f_n are very clearly distinguishable. (c) Impedance, reactance and susceptance variation (left axis) and phase angle variation (right axis) at 80 °C showing all susceptance has negative values.

Just after T_m, the phase angle exhibits no sign change throughout the resonance frequency range. The normal ferroelectric TGS, on the other hand, has a sharper impedance peak (smaller FWHM), and has a sign change up to T_c in phase-angle measurement. Impedance peak frequency decreases in the ferroelectric phase and begins to increase at the beginning of paraelectric region, but decreases again after reaching the perfect paraelectric region. From this point of view, SBN does not reach a perfect paraelectric region up to 160 °C.

These results were simulated by an equivalent circuit model, as shown in Fig. 2. Fig. 2a–c show the piezoelectric parameters of impedance, $|Z|$, reactance, (R_e), and susceptance, X_e, and phase angle, θ, at the temperature of 40, 60 and 80 °C, respectively. Below T_m, the reactance, R_e, and susceptance, X_e, of SBN satisfied the typical piezoelectric resonator response, and susceptance has a sign variation $-f_r$ and f_a can be determined at the position where the susceptance will be zero. Below 70 °C, there was only a slight difference between f_a, f_p and f_n, see Fig. 2a, so these three parameters were treated as the same frequency. At the 70 °C, f_a was clearly distinguishable from f_p and f_n (Fig. 2b). Piezoelectric coefficients, therefore, like k_{31}, s_{11}^E and d_{31}, can be calculated using these frequencies using the relations

$$\frac{k_{31}^2}{1-k_{31}^2} = \frac{\pi f_a}{2f_r}\tan\frac{\pi\Delta f}{2f_r} \qquad \Delta f = f_p - f_s \qquad (1)$$

$$s_{11}^E = \frac{1}{4l^2\rho f_s^2} \qquad (2)$$

$$d_{31}^2 = \kappa_{31}^2\varepsilon_{33}^T s_{11}^E \qquad (3)$$

Above T_m, on the other hand, susceptance shows no sign change in phase angle, hence we could not obtain the actual coupling constant, k_{31}, and the other piezoelectric coefficients. The results are summarized in Fig. 3a and b. Fig. 3a shows the coupling constant, k_{31} and Fig. 3b, shows s_{11}^E and d_{31}. In these figures, the broken lines mean that there was a discontinuity at that temperature, because susceptance could no longer change sign above T_m. Above T_m, all piezoelectric coefficients were calculated by using not a real $X_e = 0$ frequency, but frequencies of Z_{max} and Z_{min} – these values represent f_n and f_m, respectively. An impedance Cole–Cole plot around the resonance frequency range indicated this effect more clearly as shown in Fig. 4. At 70 °C, all the piezoelectric parameters, f_m, f_s, f_r, f_a, f_p and f_n, can be determined because susceptance has positive values. Namely, f_r and f_a can be determined by the intercept of susceptance with the zero line. At 80 °C, all the data points were below the zero line, so f_a and f_r could not be determined. f_r and f_a are really essential piezoelectric parameters in a piezoelectric resonant equivalent circuit. Therefore, there was no longer a real piezoelectric resonance above 80 °C, although it appears like piezoelectric resonance peaks up to far beyond T_m. Nevertheless, relaxor ferroelectrics are seen to have a more profound effect up to far above T_m in comparison with the normal ferroelectrics like TGS. Although TGS also has f_p and f_n

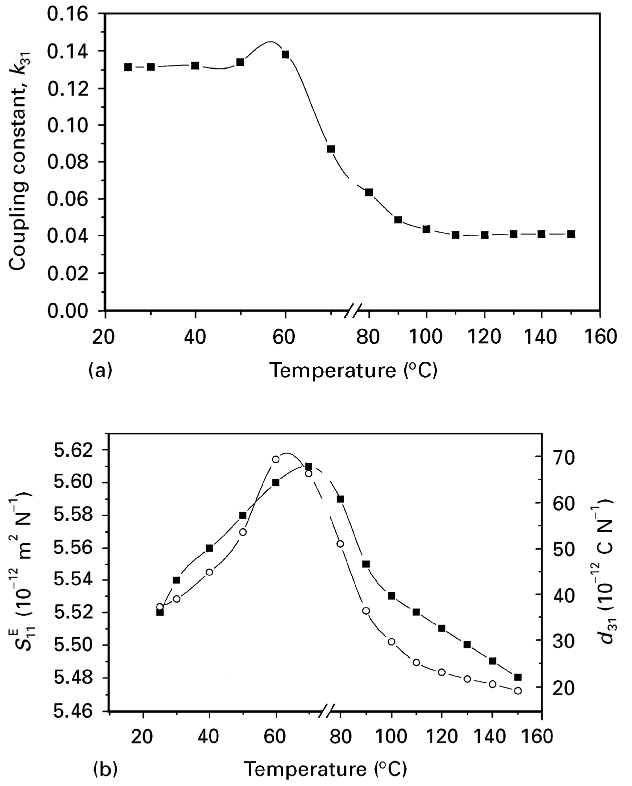

Figure 3 (a) Coupling constant versus temperature of Ce: SBN60 indicating some discontinuity just above T_m because of loss of resonance and anti-resonance frequency. (b) (■) s_{11}^E and (○) d_{31} versus temperature of Ce : SBN showing the same effect as in (a).

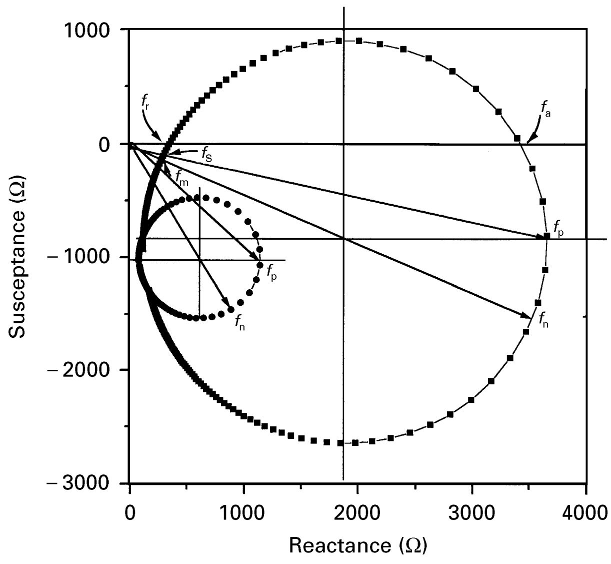

Figure 4 Impedance Cole–Cole plot at (■) 70 and (●) 80 °C which are the temperatures just below and above T_m.

frequencies up to 65–15 °C higher than its T_C (Curie temperature of TGS), the magnitude of these are very small in comparison to the values of below T_c. Therefore, in the case of TGS, f_p and f_n can be negligible, and hence the impedance as a function of temperature shows second order transition behaviour (see Fig. 1e). On the other hand, the impedance of SBN as a function of temperature has a very wide transition temperature region (Curie range) and a very slow decreasing slope. The magnitude of impedance is already negligible just below T_m in comparison to the room-temperature value, it persists into its intermediate state (partially paraelectric and partially ferroelectric state), longer than normal ferroelectrics.

4. Conclusion

Piezoelectricity does not vanish at a specific temperature, T_m, but decays over a certain temperature region. The resonance and anti-resonance conditions (zero reactance), however, are no longer satisfied above a specific temperature, T_m. The piezoelectricity vanishes at a temperature when presumably the coherence or interactions of neighbouring domains is diminished.

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