

Dielectric properties of $\text{Na}_{1-x}\text{K}_x\text{NbO}_3$ in orthorhombic phase

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Abstract. Pellets of ceramic, $\text{Na}_{1-x}\text{K}_x\text{NbO}_3$ ($x = 0, 0.2$ and 0.5), were prepared by conventional solid-state reaction method. Prepared samples were characterized using XRD and SEM. The frequency and temperature variation of dielectric constant, loss tangent and dielectric conductivity of prepared samples were measured in the frequency range from 10 KHz–1 MHz, and in the temperature range from 50–250°C for $x = 0.2$ and 0.5 , and between 50 and 480°C for $x = 0$ compositions. It was observed that the dielectric constant and loss tangent decrease, and conductivity increases with increasing frequency. Near the transition temperature the material shows anomalous behaviour for the observed properties, and the peaks of dielectric constant and loss tangent were observed shifting towards lower temperature with increasing frequency.

Keywords. Ferroelectrics; antiferroelectrics; perovskite; dielectric constant and loss; sintering; positive temperature coefficient of resistivity.

1. Introduction

Sodium potassium niobate ($\text{Na}_{1-x}\text{K}_x\text{NbO}_3$) (SPN) system shows interesting properties, e.g. a number of ferroelectric phases with high spontaneous polarization, low dielectric constant, high electromechanical coupling coefficients, etc (Wood 1951; Shirane *et al* 1954; Cross 1958; Egerton and Dillon 1959; Jaeger and Egerton 1962; Heartling 1967; Narayana Murty *et al* 1988, 1990). The constituents of this system are sodium niobate (NaNbO_3) and potassium niobate (KNbO_3). NaNbO_3 shows structural phase transitions at -100°C (rhombohedral to orthorhombic) (Wells and Megaw 1961; Darlington and Megaw 1973), at 360°C (orthorhombic to orthorhombic), at 480°C (orthorhombic to orthorhombic), at 520°C (orthorhombic to orthorhombic), at 575°C (orthorhombic to tetragonal) (Sakowski-Cowley *et al* 1969), and at 640°C (tetragonal to cubic) (Megaw 1974). KNbO_3 shows structural phase transitions at -10°C (rhombohedral to orthorhombic), at 225°C (orthorhombic to tetragonal), and at 420°C (tetragonal to cubic) (Hellwege and Hellwege 1981). At room temperature, NaNbO_3 , KNbO_3 and their mixtures basically show orthorhombic structure with a small perovskite subcell with monoclinic symmetry (Wood 1951; Shirane *et al* 1954; Tennery 1965). NaNbO_3 is anti-ferroelectric over a wide temperature range but below -100°C (rhombohedral structure) it shows ferroelectric behaviour (Megaw 1974). Doping of small amount ($< 2\%$) of K at Na site in NaNbO_3 makes it ferroelectric below around 400°C and its orthorhombic to orthorhombic

transition temperature shifts towards the orthorhombic to tetragonal transition temperature of KNbO_3 (Ahtee and Hewat 1975). When doped with 10–100% (mole) K, NaNbO_3 shows well-defined ferroelectric hysteresis loops between room temperature and 400°C . It also shows two transitions, orthorhombic to tetragonal at 200°C and tetragonal to cubic at 400°C (Cross 1958). Above 400°C it becomes paraelectric. Investigators have studied the temperature variations of dielectric properties of NaNbO_3 and KNbO_3 single crystals (Matthias and Remeika 1951; Shirane *et al* 1954; Cross 1958) and polycrystalline $\text{Na}_{1-x}\text{K}_x\text{NbO}_3$ (Egerton and Dillon 1959; Heartling 1967; Narayana Murty *et al* 1988, 1990). However, these studies were restricted to low range single frequencies.

In the present study pellets of $\text{Na}_{1-x}\text{K}_x\text{NbO}_3$ (for $x = 0, 0.2, 0.5$) were prepared by conventional solid-state reaction method. Characterization of the samples was made by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Dielectric measurements were carried out in the frequency range from 10 KHz–1 MHz, and in the temperature range from 50–250°C for $x = 0.2$ and 0.5 , and from 50–480°C for $x = 0$ compositions, using a temperature controller having an accuracy of $\pm 1^\circ\text{C}$.

2. Sample preparation

The starting materials used for preparing different compositions of $\text{Na}_{1-x}\text{K}_x\text{NbO}_3$ were sodium carbonate (Na_2CO_3), potassium carbonate (K_2CO_3) and niobium pentoxide (Nb_2O_5). Purity of all the starting materials was 99.95%. The starting materials were dried at 200°C for 1 h to remove absorbed moisture. Care was taken in handling K_2CO_3 so that it does not absorb moisture during material

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formation. Different compositions were prepared by weighing sodium carbonate, potassium carbonate and niobium pentoxide in stoichiometric proportion. Using mullet mortar and pestle, each composition was first manually dry mixed for 1.5 h and then wet mixed for 1 h in reagent methyl alcohol. The mixture was calcined in a platinum crucible, in air, at 950°C for 1 h. The calcined materials were weighed to ensure complete carbonate removal. The calcined mixture was ground and pressed, at 0.02 MPa, into pellets of 10 mm diameter. These raw pellets of the mixture were placed in a platinum crucible and sintered in air at 1050°C for 15 h, except NaNbO_3 . NaNbO_3 pellets were sintered at 1200°C due to its higher melting point, for 15 h. The sintered pellets were electroded, with air-drying silver paste, in metal–insulator–metal (MIM) configuration for dielectric measurements.

3. Characterization

Room temperature X-ray diffraction patterns of all the prepared samples were obtained on a SEIFERT 3000P, X-ray diffractometer using filtered $\text{CuK}_{\alpha 1}$ radiation of 1.540598 Å wavelength. Peak indexing was done by using Joint Committee on Powder Diffraction Standards (JCPDS) data cards. The perovskite subcell parameters were obtained using the relation provided by Azaroff (1968). The XRD characterization was carried out on 10–15 select samples of each composition ($x = 0, 0.2, 0.5$) of $\text{Na}_{1-x}\text{K}_x\text{NbO}_3$. All the samples show polycrystalline orthorhombic structure at room temperature (figure 1). The diffraction peaks were observed shifting towards lower angle with increasing x value. The calculated values of lattice parameters of NaNbO_3 were obtained as $a = 5.5738$ Å, $b = 15.4381$ Å and $c = 5.5116$ Å, which were close to the reported values (Vousden 1951; Wood 1951; Shirane *et al* 1954; Ahtee and Glazer 1976). SEM study was carried out using the model Philips PSEM 515

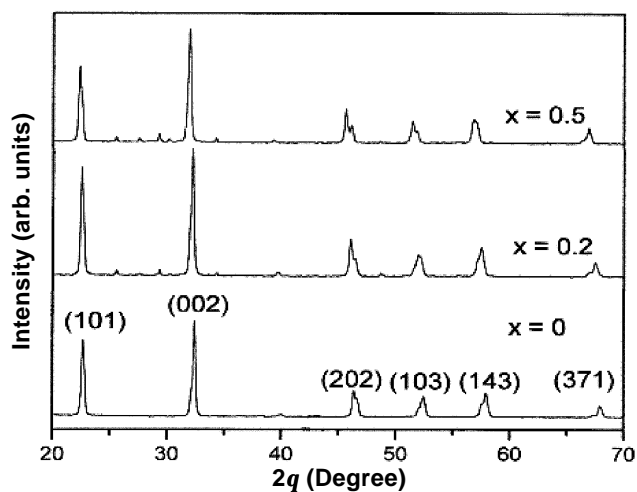


Figure 1. X-ray diffraction patterns of $\text{Na}_{1-x}\text{K}_x\text{NbO}_3$ for different x values, at room temperature.

(Holland). The obtained SEM results are given in figure 2. The average grain size for NaNbO_3 , $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ and $\text{Na}_{0.8}\text{K}_{0.2}\text{NbO}_3$ was found to be 8.1, 7.0 and 3.3 μm, respectively.

4. Dielectric measurements

Capacitance and loss tangent measurements were carried out in MIM configuration, using Fluke-PM6306 RCL

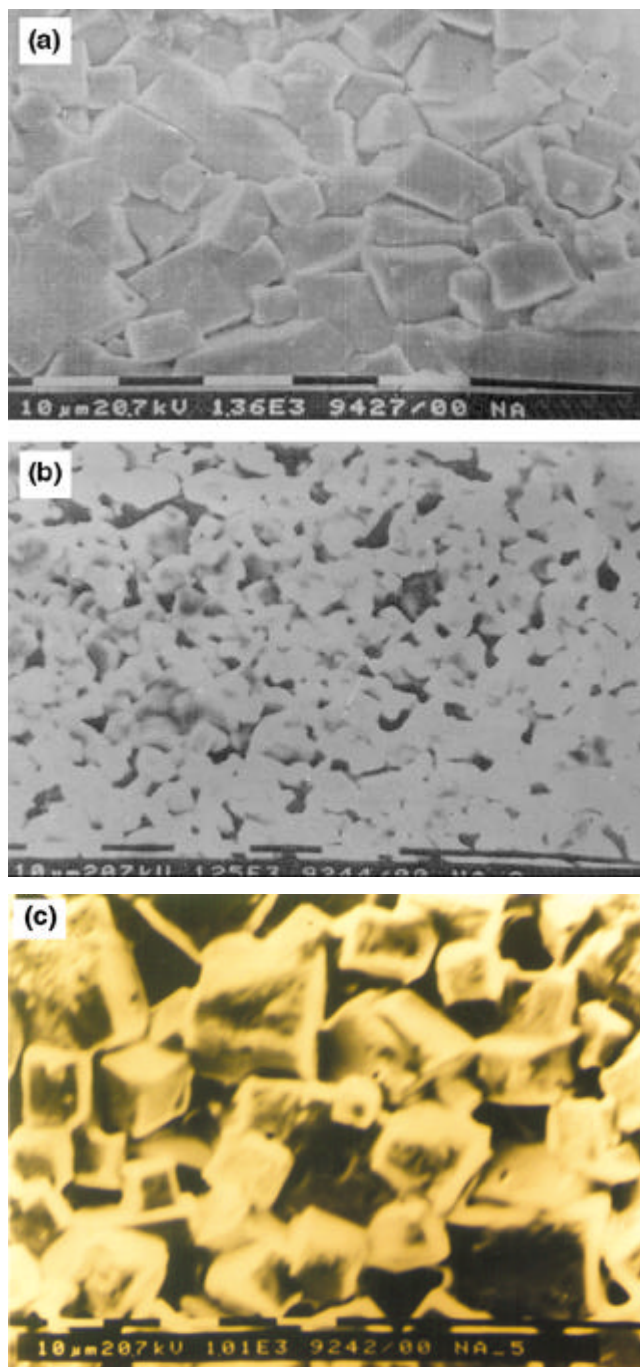


Figure 2. Scanning electron micrographs of $\text{Na}_{1-x}\text{K}_x\text{NbO}_3$ for different x values, (a) for $x = 0$, (b) for $x = 0.2$ and (c) for $x = 0.5$.

meter. The measurements were made, run to run on the same sample and sample to sample for all samples prepared with similar method. The observations were close to each other and the values were averaged. Dielectric constant (K) was calculated by the relation

$$K = C/C_0,$$

where C and C_0 are the capacitances of the electrodes with and without dielectric, respectively; C_0 is given by

$$C_0 = (0.0885 \pi r^2/d) \text{ pF},$$

where r (cm) is the radius of the electrodes and d (cm) distance between them. Dielectric conductivity (S) was calculated by the relation

$$S = \epsilon_0 \omega K \tan d,$$

where ϵ_0 is the permittivity of free space, $\tan d$ the loss tangent, and $\omega = 2\pi f$, f the applied frequency.

5. Results and discussion

Observed frequency dependence of dielectric constant and dielectric loss, at room temperature, for different x values in $\text{Na}_{1-x}\text{K}_x\text{NbO}_3$ samples has been shown in figures 3 and 4, respectively. Dielectric constant and loss

tangent, generally, decrease with increasing frequency. Dielectric constant and loss tangent were observed increasing with increasing x in $\text{Na}_{1-x}\text{K}_x\text{NbO}_3$.

The observed variation of dielectric constant with temperature is shown in figure 5 for NaNbO_3 pellets. It was observed that the dielectric constant increases with increasing temperature showing anomaly at the transition temperature. The peak height at the transition temperature was observed to decrease with increasing frequency and the dielectric constant peak shifted to lower temperature with increasing frequency, which indicated the relaxational behaviour of the material (Goodman *et al* 1991). Transition anomaly, for NaNbO_3 , was observed at 360°C with dielectric constant peak value, 661 for 10 KHz; at 350°C with peak value, 635 for 100 KHz; and at 340°C with peak value, 570 for 1 MHz. This anomaly is corresponding to a phase change, from orthorhombic to tetragonal structure (Egerton and Dillon 1959), and may be associated to the softening of a vibrational mode called the soft mode (Cochran 1959, 1960; Anderson 1960; Panwar *et al* 1989; Semwal and Panwar 1992).

Variation of the loss tangent with temperature, in NaNbO_3 , is shown in figure 6. Dielectric loss was observed increasing with increasing temperature and decreasing with increasing frequency. The loss tangent peaks were observed at 340°C (Peak value, 0.14) for 10 KHz, at

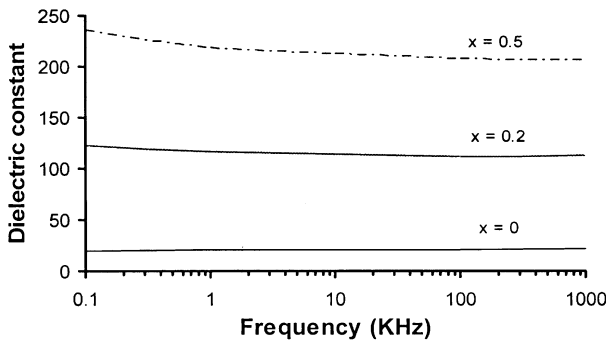


Figure 3. Frequency dependence of dielectric constant in $\text{Na}_{1-x}\text{K}_x\text{NbO}_3$ for different x values, at room temperature.

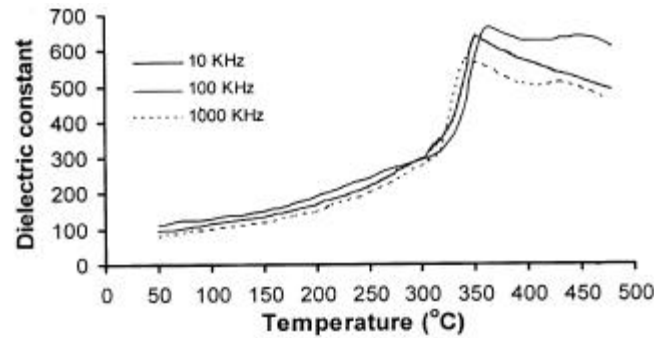


Figure 5. Temperature dependence of dielectric constant in NaNbO_3 , at different frequencies.

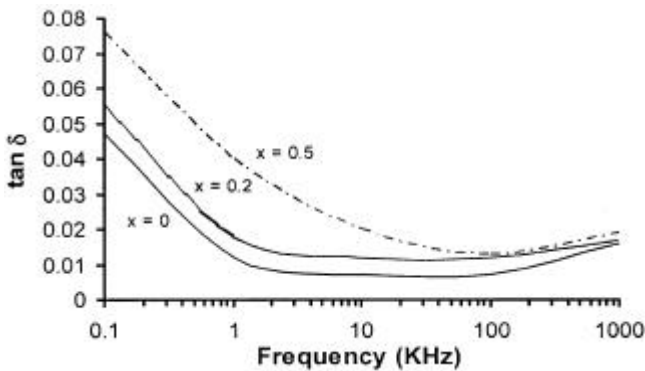


Figure 4. Frequency dependence of loss tangent ($\tan d$) in $\text{Na}_{1-x}\text{K}_x\text{NbO}_3$ for different x values, at room temperature.

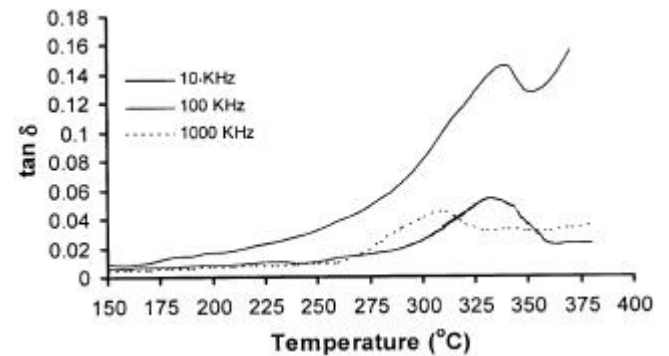


Figure 6. Temperature dependence of loss tangent in NaNbO_3 , at different frequencies.

330°C (peak value, 0.05) for 100 KHz, and at 310°C (peak value, 0.04) for 1 MHz. The loss tangent peak shifted to lower temperature with decreasing height and increasing frequency, showing the relaxational behaviour.

Figure 7 shows the observed temperature dependence of dielectric constant for $\text{Na}_{0.8}\text{K}_{0.2}\text{NbO}_3$ at different frequencies. In this composition also dielectric constant decreases with increasing frequency. Dielectric constant increases with temperature showing anomaly at transition temperature. The peak height decreases and shifts to lower temperature with increasing frequency. The dielectric peaks were observed at 215°C (peak value, 411) for 10 KHz, at 210°C (peak value, 380) for 100 KHz, and at 205°C (peak value, 118) for 1 MHz. At the transition temperature dielectric constant value increases sharply and thereafter remains almost constant with respect to temperature variation. The variation of loss tangent with temperature is shown in figure 8 for $x = 0.2$ composition. Loss tangent for this composition decreases with increasing frequency and increases with increasing temperature showing no significant anomaly near transition temperature as observed from the dielectric constant measurements.

Temperature dependence of dielectric constant for $x = 0.5$ composition is shown in figure 9. This composition also shows relaxational behaviour. The dielectric constant peaks were observed at 195°C (peak value, 704) for 10 KHz, at 190°C (peak value, 650) for 100 KHz, and at

185°C (peak value, 617) for 1 MHz. Beyond transition temperature dielectric constant value decreases slightly with increasing temperature. Figure 10 shows the variation of loss tangent with temperature for $x = 0.5$ composition. Loss tangent peaks for 10 KHz, 100 KHz and 1 MHz have been observed at 170°C with peak values 0.06, 0.03 and 0.02, respectively.

Dielectric constant and loss tangent peak heights decrease with increasing frequency, in all the prepared samples. Lossy dielectric can be represented by the circuit analog of a resistance in parallel with a capacitor (Goodman *et al* 1991). At higher frequency the capacitor offers low reactance to the sinusoidal signal, which minimizes the conduction losses in the resistor. Hence, the value of dielectric loss decreases at higher frequencies. The present observations were found in good agreement with the earlier reported results (Shirane *et al* 1954; Cross 1958; Egerton and Dillon 1959; Jaeger and Egerton 1962; Heartling 1967; Narayana Murty *et al* 1988, 1990). With increasing frequency the dielectric constant peaks were observed shifting to lower temperature in the present samples. However, for most of the relaxator ferroelectrics the peak of the dielectric constant shifts to higher temperature with increasing frequency, which has been attributed to the decreasing relaxation time with increasing temperature (Goodman *et al* 1991). For $\text{Na}_{1-x}\text{K}_x\text{NbO}_3$ system the relaxation time seems increasing with temperature, and

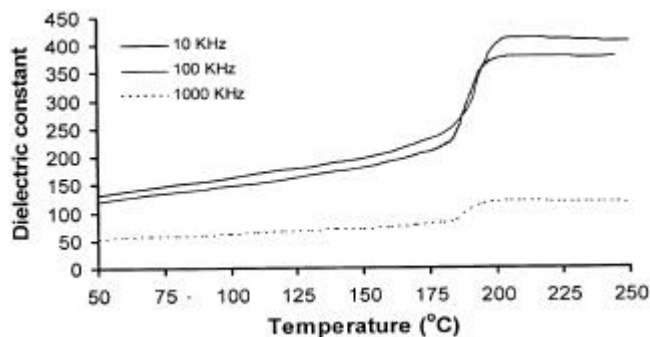


Figure 7. Temperature dependence of dielectric constant in $\text{Na}_{0.8}\text{K}_{0.2}\text{NbO}_3$, at different frequencies.

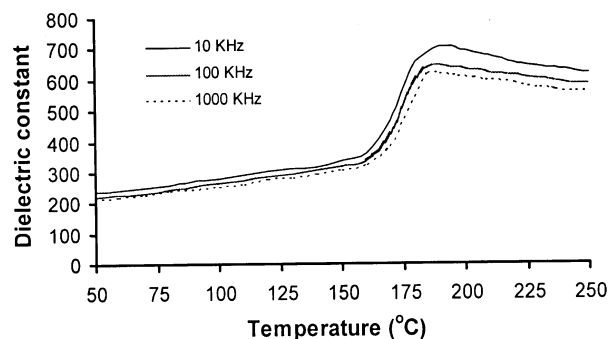


Figure 9. Temperature dependence of dielectric constant in $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$, at different frequencies.

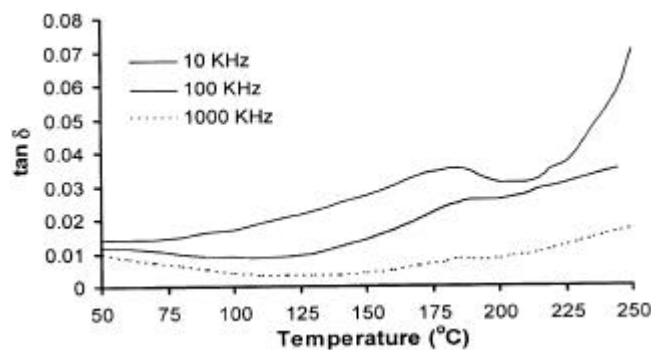


Figure 8. Temperature dependence of loss tangent in $\text{Na}_{0.8}\text{K}_{0.2}\text{NbO}_3$, at different frequencies.

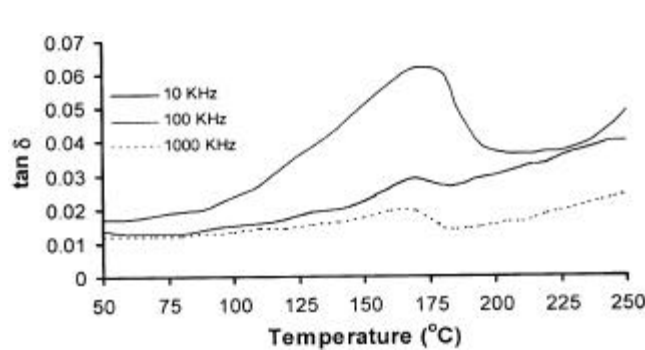


Figure 10. Temperature dependence of loss tangent in $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$, at different frequencies.

the observed shifting of the dielectric constant peak to lower temperature with increasing frequency can be due to the increasing relaxation time with temperature (Lingwal 2002).

The damping out of successive relaxation modes is attributed to the decreasing of peak height with frequency (Goodman *et al* 1991). The anomalous behaviour at certain temperature is due to structural change or phase transition of the material at that temperature (Cochran 1960; Cowley 1962, 1964, 1965; Pytte and Feder 1969; Feder and Pytte 1970; Pytte 1972). The phase transition in the perovskite type materials is, generally, assumed to be due to the instability of temperature dependent low frequency optical phonon—the soft phonon mode—at transition temperature. At the transition temperature, frequency of the soft mode tends to be zero and the lattice displacement associated with it becomes unstable. This explains the observed behaviour of dielectric properties near the transition temperature.

Using the Green's function and Dyson's equation method expressions for dielectric constant and loss tangent, in terms of soft phonon frequency and width, have been obtained for perovskites, elsewhere (Panwar *et al* 1989; Semwal and Panwar 1992). The soft mode concept has been extended to the relaxational systems (Blinic and Zeks 1979), wherein a mean field,

$$2p/t = w_{\text{relax}} \propto (T - T_c);$$

whereas

$$w_{\text{soft}} \propto (T - T_c)^{1/2}.$$

However, if soft mode is over damped its temperature dependence cannot be distinguished from a relaxational response (Dovner and Comes 1972). Where the soft mode is over damped, the relaxation rate, $t^{-1} = w_{\text{soft}}^2/\Gamma$ (where Γ is the phonon width), is found to be a more reliable parameter than the individual parameters, i.e. the soft phonon frequency and the width (Peercy 1975). The phonon frequency and width are the measure of relaxation behaviour in relaxator dielectrics, e.g. NaNbO_3 , NaTaO_3 and their K mixed systems. In the presence of resonant interaction the relaxation time ($t_I(q)$) with the phonon width ($\Gamma_I(q)$) is related as (Litov and Garland 1987)

$$t_I(q) = \Gamma_I(q)/\hat{\Omega}_I^2(q), \quad (1)$$

where $\hat{\Omega}_I(q)$ is the phonon frequency.

The relaxation time associated to $\hat{\Omega}_I(q)$ leads to the expressions for dielectric constant and loss tangent in these systems.

In the experimental range of frequencies ($w \ll \hat{\Omega}_I(q)$), the real part of dielectric constant ($K(w)$), and loss tangent ($\tan d$) (Panwar *et al* 1989; Semwal and Panwar 1992) can be expressed, using (1), as

$$K(w) = \frac{8p N m^2 \Omega_I(q)}{\hat{\Omega}_I^2(q) \{1 + \Omega_I^2(q) t_I^2(q)\}}, \quad (2)$$

and

$$\tan d = \frac{\Omega_I(q) t_I(q)}{\{1 + \Omega_I^2(q) t_I^2(q)\}}. \quad (3)$$

These equations are similar to the Debye expressions (Goodman *et al* 1991).

For the temperatures at which $\Omega_I(q) t_I(q) \ll 1$, i.e. the systems for which no relaxation effect is observed and the phonon mode damping is neglected, a discontinuity in the dielectric constant is obtained at $T = T_c$, since the soft phonon frequency, $\hat{\Omega}_I(q)$ is proportional to $|T - T_c|^{1/2}$. The factor $(1 + \Omega_I^2(q) t_I^2(q))$, in (2) and (3), smoothen out the discontinuity.

In some of the cubic perovskite crystals, e.g. BaTiO_3 , SrTiO_3 , etc no relaxation effect has been observed in the dielectric measurements up to microwave frequency range (Benedict and Durand 1958; Rupprecht and Bell 1962). Temperature dependence of microwave and low frequency ($w \ll \hat{\Omega}_I(q)$) loss tangent and dielectric constant, in these perovskites, can be associated with the temperature dependent optical soft mode frequency. A transverse radiation field drives the soft transverse optical mode of the material in a forced vibration. Energy is transferred from the electromagnetic field to this lattice mode and is then degraded into other vibrational modes. The anomaly near the transition temperature can be explained by the fact that soft mode frequency softens, giving the large value of dielectric constant and loss tangent, near the transition point.

For the real and imaginary parts of dielectric constant, maximum relaxation and loss occurs at $\Omega_I(q) t_I(q) = 1$ and slightly higher for the loss tangent peak (Goodman *et al* 1991). The frequency dispersion or change in dielectric properties with frequency and the corresponding circuit analogs for a general solid show several relaxation modes. The dielectric constant shows an expected decrease with frequency as successive polarization modes become damped out, and corresponding peaks occur in the loss spectra at the different relaxation and resonance frequencies. The resonance losses occurring for ionic and electronic oscillations at infrared and ultraviolet frequencies are associated with absorption interactions with the incident radiation at or near the natural vibration frequencies for the ions or electrons. Relaxation losses, conversely, are associated with dipolar orientation, ion jump, or electron hopping, and can occur over a wide frequency range. Space charge polarization losses typically occur at low frequency (< 1 KHz) and are associated with ion migration and electrode contact losses or with the presence of grain boundary or inhomogeneous phases in the dielectric. Space charge losses in the latter case can occur up to much higher ($\sim 10^5$ Hz) frequencies. Contributions to the overall dielectric constant and loss tangent from different polarization mechanisms can be related to the composition, porosity, grain morphology, frequency, and temperature of the diele-

ctric, and their relative effect can be held responsible for the observed dielectric behaviour of the material.

Temperature dependence of the observed dielectric conductivity has been shown in figures 11–13 for $\text{Na}_{1-x}\text{K}_x\text{NbO}_3$ ($x = 0, 0.2, 0.5$). Dielectric conductivity was observed to increase with temperature and frequency for the chosen compositions. Also, in the K doped samples dielectric conductivity was observed to increase with K concentration. The intrinsic defects, in ABO_3 perovskites, at A and O sites (Jaffe *et al* 1974) and their effective polarization determine the process of charge exchange with electrode. Increase of K concentration, in $\text{Na}_{1-x}\text{K}_x\text{NbO}_3$

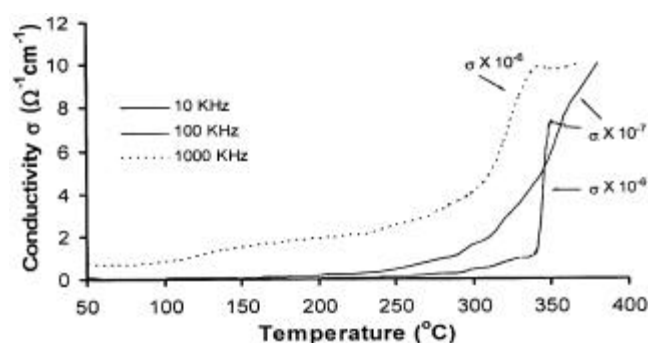


Figure 11. Temperature dependence of dielectric conductivity in NaNbO_3 , at different frequencies.

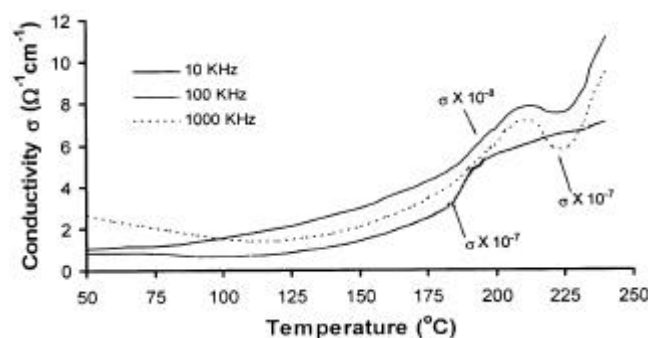


Figure 12. Temperature dependence of dielectric conductivity in $\text{Na}_{0.8}\text{K}_{0.2}\text{NbO}_3$, at different frequencies.

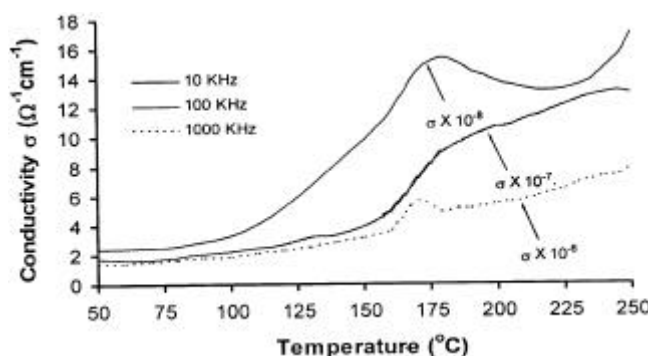


Figure 13. Temperature dependence of dielectric conductivity in $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$, at different frequencies.

system, increases the effective polarization and thereby increases the conductivity of the material. Also porosity and grain morphology greatly influence the conductivity of the material. Positive temperature coefficient of resistivity (PTCR) is observed, near the transition temperature in the present samples, i.e. below the transition temperature, resistivity decreases with increasing temperature, but near and above the transition temperature, it increases with temperature. Beyond a certain temperature above transition point, resistivity again begins to decrease with increasing temperature. Goodman (1963) observed that PTCR behaviour is intimately connected with the grain boundary. The origin of the PTCR in ceramics is usually explained on the basis of the Heywang (1961) model, which assumes that the acceptor type states of the grain boundaries create equivalent potential barriers associated with resistive depletion layers near the boundaries. The PTCR is a result of the dependence of barrier heights on dielectric constant of grain bulk in higher symmetry phase ($T > T_c$), the increase of dielectric constant, as $T \rightarrow T_c$, leads to decrease of the barrier heights and to the exponential increase of conductivity. In the region $T < T_c$, grain boundary barriers apparently do not play significant role. The decrease of barrier height below T_c is attributed to the compensation of the grain boundary charge by spontaneous polarization (Heywang 1983) or to the disappearance of the localized states at the grain boundaries in orthogonal phase (Kraskov and Valeev 1975). When the dielectric constant decreases with increasing temperature, above but near the T_c , the barrier height increases, which leads to an increase in resistivity with rise of temperature, until the potential barrier becomes equal to the activation energy of the surface terms. Beyond that temperature resistivity starts decreasing with further rise of temperature, as for semiconductors. The observed anomaly, near the transition temperature, in the conductivity measurements is consistent with the dielectric constant and loss tangent measurements.

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