The relaxant phase transition of $Li_{0.7}Na_{0.3}NbO_3$

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Abstract. Alternating-current complex impedance measurements have been carried out to characterize a relaxant phase transition of $Li_{0.7}Na_{0.3}NbO_3$ solid solution crystal as a function of frequency in the temperature range from 25 °C to 700 °C. The results were described using an equivalent-circuit model based on simple combinations of ideal elements of a pure resistor R and an ideal capacitor C. The ferroelectric transitions exhibit unusual properties compared with those of a ferroelectric relaxor. The diffusive character in the phase transition is a result of polarization fluctuation due to two distinguishable cations. No T_{max}-shift results from the absence of confirmable slowing down coupled with the soft mode. The dielectric relaxation occurs on the high-temperature side of the dielectric maximum with the result that the point defect thermally activated at high temperature gives rise to the low-frequency relaxation. The dielectric dispersion that occurs on heating is due to the high degree of ionic hopping transport accompanied with a large thermal expansion.

Ferro–antiferroelectric mixtures $Li_{1-x}Na_xNbO_3$ are expected to exist in the form of the frustrated states due to the competition between two kinds of order–disorder arrangement. Polycrystalline $Li_{1-x}Na_xNbO_3$ has been investigated by various workers over the years in the compositional range $0.80 \leqslant x$ [1, 2, 3, 4]. A few results have also been reported for crystalline $Li_{1-x}Na_xNbO_3$ with low concentrations of Li^+ ions ($0.97 \leqslant x$) [5, 6, 7]. Also sol–gel processing was developed by Balbaa and Gowda [8]. But no detailed studies have been reported for rich concentrations of Li^+ ions.

We have grown the mixed crystal $Li_{1-x}Na_xNbO_3$ in the range $0 \leqslant x \leqslant 0.7$ from the melt by the Czochralski method. Investigations in this laboratory have been carried out already on the mixed crystals $Li_{0.9}Na_{0.1}NbO_3$ [9, 10, 11], $Li_{0.8}Na_{0.2}NbO_3$ [12] and $Li_{0.7}Na_{0.3}NbO_3$ [13]. Previous studies revealed that the structures and the phase transitions of $Li_{0.9}Na_{0.1}NbO_3$ and $Li_{0.8}Na_{0.2}NbO_3$ are similar to those for $LiNbO_3$ with the exception of the larger thermal coefficients and lower transition temperatures with increasing x. $Li_{0.7}Na_{0.3}NbO_3$, however, is orthorhombic with a unit cell of dimensions $a = 5.374(9)$ Å, $b = 5.152(1)$ Å and $c = 16.738(0)$ Å at 25 °C, and undergoes the ferroelectric phase transition from orthorhombic to tetragonal at about $T_C = 480$ °C. The phase transition of $Li_{0.7}Na_{0.3}NbO_3$ confirmed by the pyroelectric and dielectric measurements is very strange and diffusive as shown in figure 1. And also, some ambiguities as regards the diffusive phase transition of $Li_{0.7}Na_{0.3}NbO_3$ remain. The dielectric constant maximum T_{max}-shift as a function of frequency is negligible in the measured frequency range. And a characteristic frequency dispersion of the dielectric constant in the vicinity of T_{max} (=337 °C and 450 °C on cooling and heating, respectively) is observed on its higher-temperature side in contrast to what is found for the typical ferroelectric relaxor [14]. Moreover, though this diffusive effect can be interpreted assuming the compositional heterogeneity suggested by some workers [14, 15],
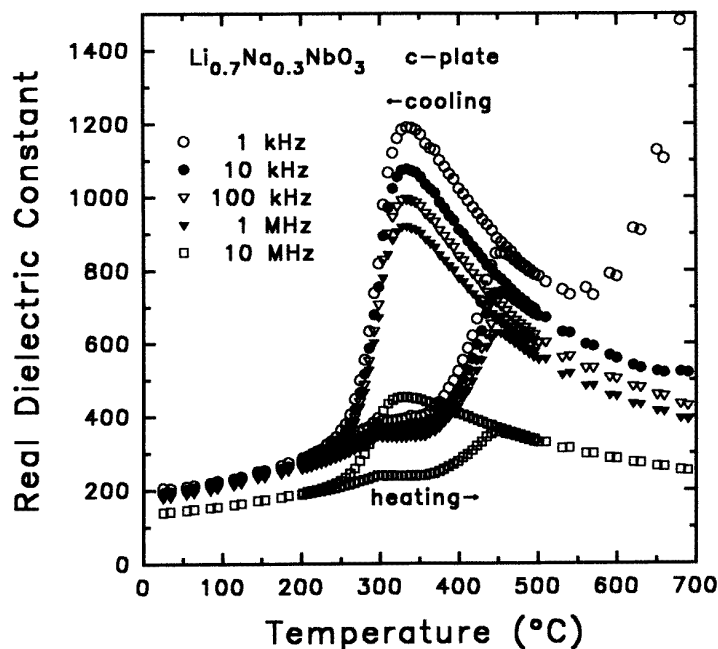
Figure 1. The dielectric constants ε_{33} of $Li_{0.7}Na_{0.3}NbO_3$ measured at several frequencies as functions of the temperature. Two strange anomalies are observed at 298 °C and 450 °C on heating, but this is reduced to one anomaly at 337 °C on cooling. A pronounced broadening of the dielectric constant occurs at around the dielectric maximum T_{max}.

it is incorrect to interpret the difference between the anomalous character of the dielectric constant on heating and that on cooling in the same way.

Since the broad dielectric anomaly is related to a slowing down and a broadening of a dielectric relaxation in the frequency space, a more detailed analysis of the dynamic response of the dielectric constant was indicated. Preliminary studies revealed the existence of a high ionic conductivity over a wide temperature range around the diffusive transition temperature for $Li_{0.7}Na_{0.3}NbO_3$. This result induced us to utilize the ac complex impedance method for characterizing the phase transition of $Li_{0.7}Na_{0.3}NbO_3$.

The mixed crystal $Li_{0.7}Na_{0.3}NbO_3$ was grown from a stoichiometric melt of 99.99% Li_2CO_3, Na_2CO_3, and Nb_2O_5 by the Czochralski method. The as-grown crystal was translucently milky and had a rectangular symmetry along the c-axis. The typical diameter and length of the as-grown crystals were 10 mm and 40 mm, respectively.

The sample used for the measurements was cut into plates perpendicular to the c-axis. Two kinds of electrode on the large faces were made with platinum paste fired at 900 °C to diminish the effect of residual resistance of the electrodes in the initial warm-up, and with vacuum-evaporated gold. The complex impedances $Z^*(\omega)$ were determined in the frequency range from 10 Hz to 10 MHz, using a Hewlett–Packard impedance analyser 4192A. The sample was placed in the electric furnace and connected by 10 cm parallel Pt lead wires with HP standard test cable. A personal computer was adopted to control the measuring system and processing of data. Measurements of $Z^*(\omega)$ were carried out in the temperature range from 25 °C to 700 °C. At each measuring temperature T the sample was maintained at $T \pm 0.3$ °C for 5 min before collecting the data. To ensure reproducibility

the measurements were carried out five times in the same conditions. The measured value of the impedance measurements was not affected by the boundary between the electrodes and the crystal, nor by the type of electrode in our experimental conditions.
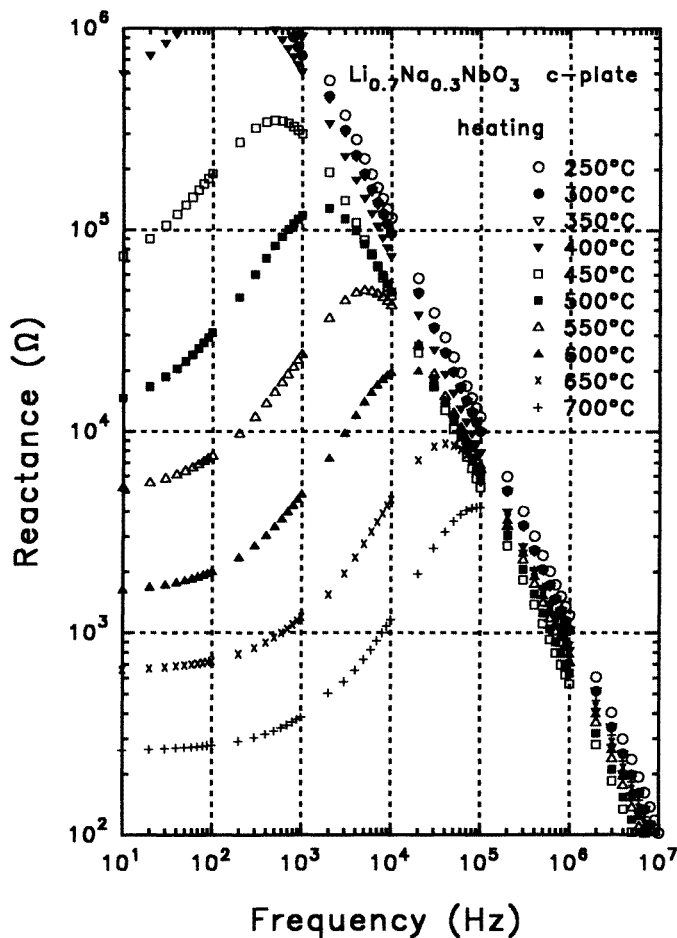
Figure 2. The imaginary part of the impedance as a function of frequency at several temperatures for Li$_{0.7}$Na$_{0.3}$NbO$_3$.

To get a more quantitative insight into the dielectric results, we carried out an impedance analysis in the frequency space. Figure 2 presents the variation of the imaginary part of the impedance for several temperatures on heating as a function of frequency using a double-logarithmic scale. A relaxation covering several frequency decades is observed. The logarithmic peak frequency increases with increasing temperature in both the ferroelectric and paraelectric regions. A careful examination of figure 2 shows that the absolute value of the high-frequency slope is very close to unity and seems to be independent of the temperature. On the low-frequency side, however, the slope has a temperature-dependent value lower than unity and goes to zero asymptotically as the frequency goes down to low extremes. Since these asymmetric behaviours cannot be described by the Debye expression, it is necessary to propose an appropriate relaxation model for Li$_{0.7}$Na$_{0.3}$NbO$_3$. An assumption that the movable ions, which give rise to an impedance relaxation, are Li$^+$

ions and Na^+ ions, and that these cations may be thermally activated in the same framework of $Li_{0.7}Na_{0.3}NbO_3$ independently, could suggested that two dispersion mechanisms may be involved.
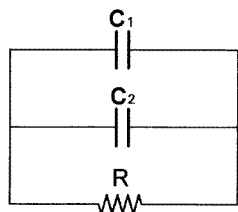

Figure 3. The equivalent-circuit model proposed for $Li_{0.7}Na_{0.3}NbO_3$.

Considering the existence of two dispersion mechanisms and the bulk resistance R_0 of the material, an equivalent circuit shown in figure 3 is proposed where C_1 and C_2 are the universal capacitances introduced by Jonscher [16]. The impedance may, therefore, be written in the form

$$Z^*(\omega) = \frac{1/R_0}{1 + (i\omega\tau_1)^{1-\alpha} + (i\omega\tau_2)^{1-\beta}} \tag{1}$$

where $\tau_1 = R_0C_1$ and $\tau_2 = R_0C_2$ are characteristic relaxation times, corresponding, respectively, to Li^+ ions and Na^+ ions. And considering that the Li^+ ion is lighter than the Na^+ ion, one can suppose that $\tau_1 < \tau_2$. The exponents α and β take values over the entire range $0 \leqslant \alpha, \beta \leqslant 1$ and may be functions of the temperature. The exponent reflects the deviation from an ideal capacitance or from a pure conductance (resistance) [16].

In figure 4, fitting has been carried out using the imaginary data on the basis of equation (2) and is drawn as a solid line. Since the fitting leads always to a value of β close to zero and independent of temperature, it is possible to take the value of β as zero to diminish the fitting flexibility. The four parameters obtained, R_0, τ_1, τ_2, and α, were then introduced into the real part of the formula to check whether the calculated values are also in agreement with the measured values. The good agreement between experimental and calculated values of the impedance over all the temperatures measured confirms that the model proposed here is adequate for $Li_{0.7}Na_{0.3}NbO_3$. The values of α are always larger than zero and rather sensitive to temperature changes for all temperatures as shown in figure 5.

According to a theory based on many-body interaction processes given by Dissado and Hill, the exponent α (or β) characterizes the magnitude of the correlation in a single dipole reorientation [17, 18]. The zero value corresponds to fully correlated transitions and the unity value to fully uncorrelated transitions. The above result from our experiments, therefore, allows us to attribute one mechanism corresponding to the exponent β to the nearly intrinsic polarization process. The other mechanism, corresponding to the exponent α, is correlated with the reorientation of the charge-carrier polarization in the ferroelectric phase; however, it is uncorrelated in the paraelectric region.

In the transition region, two anomalous variations of α are observed for both heating and cooling. A minimum is observed at T_C, while a maximum is observed at 310 °C for both heating and cooling. According to lattice dynamics theory [19], one of the soft modes is weakened and the restoring force tends to zero at the ferroelectric transition temperature. Therefore, if one assumes that the charge carriers couple with the soft mode, one may expect the carriers to become very mobile at T_C, implying a higher energy loss and a smaller energy storage. Considering the universal capacitance introduced by Jonscher [16], the exponent should tend to a maximum at the transition temperature. In our cases, however, the fact that α tends to a maximum at 310 °C, much below than T_C, and to a minimum at T_C
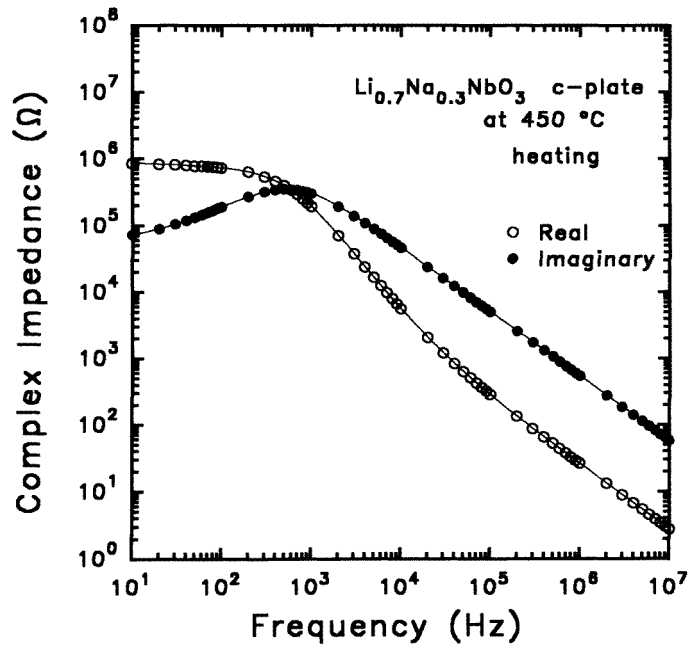
Figure 4. Real and imaginary parts of the impedance as a function of frequency at 450 °C for $Li_{0.7}Na_{0.3}NbO_3$. The solid line indicates the theoretical results obtained by using equation (2). The fitting parameters are: $R_0 = 1.50 \times 10^6$ Ω, $\tau_1 = 5.58 \times 10^{-4}$ s, $\tau_2 = 5.58 \times 10^{-4}$ s, and $\alpha = 0.90$.
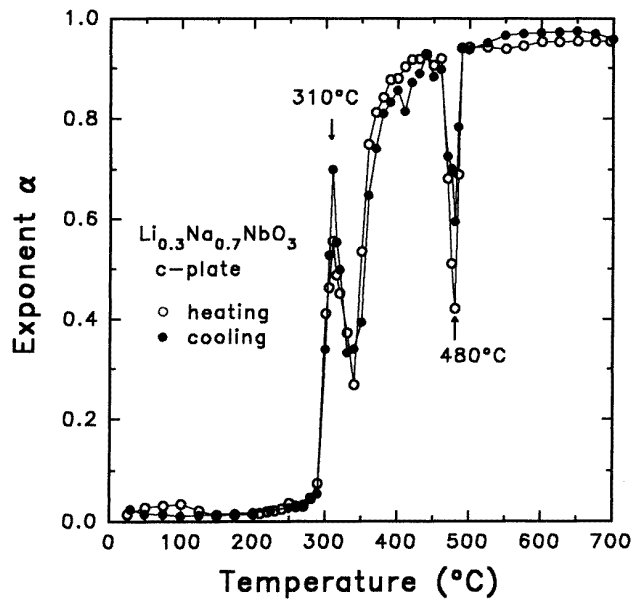
Figure 5. Variations of the exponent α as a function of temperature for $Li_{0.7}Na_{0.3}NbO_3$.

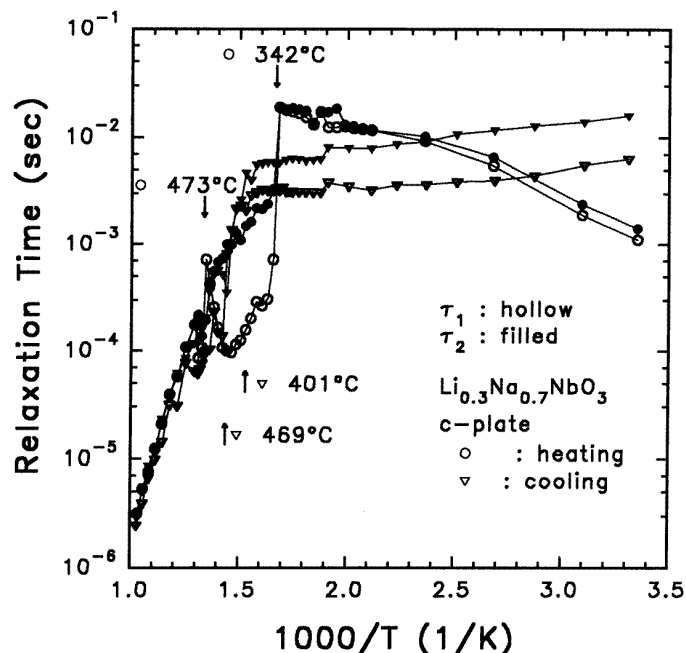**Figure 6.** An Arrhenius plot of the two relaxation times τ_1 and τ_2 for $Li_{0.7}Na_{0.3}NbO_3$.

in contrast suggests that no charge-carrier coupling with the soft mode is allowable and that the dielectric constant maximum T_{max}-shift as a function of frequency is negligible in the measured frequency range. The maximum of α at 310 °C means that the Li^+ charge reorientation is very active at this temperature, and then Li^+ charge polarization starts to disappear. With increasing temperature, the fluctuation of polarization is completely removed in the paraelectric phase above T_C.

The absence of a T_{max}-shift to higher temperature with increasing frequency is the reason for the dielectric dispersion not occurring at low frequencies on the low-temperature side of the dielectric maximum. On the other hand, it is believed that the low-frequency relaxation due to the point defect thermally activated at high temperature causes the dielectric dispersion on the high-temperature side as shown in high-T_C ferroelectrics [14, 15]. This result is distinctly different to findings for the ferroelectric relaxor. The diffusive character in the phase transition of $Li_{0.7}Na_{0.3}NbO_3$ is believed to arise as a result of polarization fluctuation due to two distinguishable cations. Though clear experimental confirmation of a microheterogeneity in the distribution of cations was lacking, it is considered that the domain rearrangements give rise to a great difference between the dielectric anomalies found on heating and on cooling.

The temperture dependences of the relaxation times τ_1 and τ_2 are plotted in figure 6. The results cannot be well described by an Arrhenius law. An anomaly occurs near the dielectric maximum T_{max} where the maximum in τ_1 is observed or its slope changes. However, a typical slowing-down behaviour of the relaxation times associated with the ferroelectric phase transition as expected in ferroelectric materials such as $AgNa(NO_2)_2$ and Pb-based oxides is not observed [20, 21]. The convergence of these results indicates that the above-mentioned anomalous behaviours of the relaxation times are less informative than that of the exponents—at least, in our samples.

In the high-temperature paraelectric region, in which the slopes of relaxation times have large values, the movable ions are more stable than at lower temperature. However, in the ferroelectric region, the absolute values are very small and the cations become very mobile. Moreover, the sign of the slope depends on the heating or cooling process implying that the dielectric relaxation in the ferroelectric phase is closely related to its large thermal expansion coefficient. Thus the low-temperature dielectric maximum at about 337 °C on heating seems to be caused by a charge-carrier hopping process arising from the large thermal expansion.

In conclusion, the ferroelectric transition of Li$_{0.7}$Na$_{0.3}$NbO$_3$ is characterized not by an abrupt structural transition, but rather by a gradual, diffusive transition due to a polarization fluctuation which occurs over a wide temperature range. At temperatures in the ferroelectric phase well below this range the high ionic conduction accompanied with a large thermal expansion gives rise to a dielectric dispersion on heating, while at temperatures in the paraelectric phase well above the Curie range the movable cations become more stable. However, within the Curie range the crystals exhibit unusual dielectric and impedance properties compared with those of a ferroelectric relaxor. The temperature at which the dielectric peaks is independent of the measuring frequency, and this does not coincide with the maximum of the relaxation time but coincides with minimum of the exponent. The absence of confirmable slowing down coupled with the soft mode seems to forbid any T_{max}-shift to higher temperature with increasing frequency. Finally, the dielectric relaxation occurs at low frequency on the high-temperature side of the maximum with the result that the point defect thermally activated at high temperature gives rise to the low-frequency relaxation.

Acknowledgment

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