ac conductivity and conduction mechanism of NaNbO 3 semiconductor antiferroelectric ceramic: A relaxational approach at high temperature

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The electric properties of the sodium niobate perovskite ceramic were investigated by impedance spectroscopy in the frequency range from 5 Hz to 13 MHz and from room temperature up to 1073 K, in a thermal cycle. Both capacitance and conductivity exhibit an anomaly at around 600 K as a function of the temperature and frequency. The electric conductivity as a function of angular frequency $\sigma(\omega)$ follows the relation $\sigma(\omega)=A\omega^s$. The values of the exponent s lie in the range $0.15 \leq s \leq 0.44$. These results were discussed considering the conduction mechanism as being a type of polaron hopping. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1618016]

Sodium niobate is an oxide with perovskite-type structure exhibiting antiferroelectric characteristics. Structural, dielectric, and optical investigations have shown that NaNbO$_3$ undergoes several phase transitions;[1] a recent contribution to the sequence of successive phase transitions has been reported.[2,3] NaNbO$_3$ shows an orthorhombic symmetry at RT following through several phase transitions up to 913 K, at which point it becomes cubic. However, the electrical properties of polycrystalline niobates depend on the factors such as microstructure and thermal treatment,[4–9] which are strongly influenced by the preparation method. A wide variety of chemical methods for powder synthesis has been developed and optimized for preparing of electroceramic, including coprecipitation, sol–gel processes, and wet chemical methods using the hydrothermal synthesis[5] and the polymeric precursor method.[6] These advanced techniques of preparation are important, since they allow the preparation of stoichiometric, single phase, and highly specific surface-area powders. These characteristics have a high degree of influence on the improvement and reliability of the electrical and dielectrical behavior of the material. In this sense, the degree of densification of the sample exerts a significant influence on the electrical behavior. The porosity effects on the electrical properties have also been recently addressed.[7]

Recently, studies detailed involving dielectric properties of NaNbO$_3$ ceramics have reported a possible orthorhombic–orthorhombic distorted phase transition around 280 K.[2] Further works employing Raman scattering experiments have confirmed this phenomenon.[3] NaNbO$_3$ doping with Li$^+$ and K$^+$ cations gives rise to ferroelectricity at room temperature. Presently, few studies on the conductivity and its correlation with phase transition phenomenon are available in the literature concerning this semiconductor dielectric material in a polycrystalline form.

Recent investigations have shown a close correlation between dielectric properties and phase transitions in solid solutions of sodium niobates.[8] Nevertheless, at high temperature, the analysis of dielectric properties of sodium niobate is only partial,[4] possibly due to a high magnitude of dielectric loss. Similarly, there is some doubt if the major conduction mechanism is of the polaron hopping type and is its intrinsic characteristic.

The sodium niobate powder was synthesized by a chemical evaporation method. Sodium nitrate (NaNO$_3$), oxalic acid (H$_2$C$_2$O$_4 \cdot$2H$_2$O), ammonium hydroxide (NH$_4$OH), and a soluble niobium complex salt (NH$_4$H$_2$[NbO(C$_2$O$_4$)$_3$]$\cdot$3H$_2$O) provided by CBMM (Companhia Brasileira de Metalurgia e Mineração, Araxá-MG-Brazil), were used as starting reagents. A precursor salt was obtained after solvent evaporation of this starting solution. This precursor was calcined at 1173 K in air for 5 h. The x-ray powder analysis showed the diffraction lines only of the orthorhombic phase (JCPDS-Card 33-1270). The synthesis procedure—powder compaction, sintering, and electrode deposition—was described in detail elsewhere.[9] Ceramic with density of 95% of the theoretical density (4.55 g/cm^3) was prepared. Platinum electrodes were deposited on both faces of the sample by a platinum paste coating. The electrical measurements were performed in the frequency range 5 Hz to 13 MHz, using a Hewlett-Packard HP 4192-A impedance analyzer controlled by a personal computer. A 500 mV signal was applied. The sample was placed in a sample holder with a two-electrode configuration. The ac measurements were taken from RT to 1073 K in one thermal cycle: heating and cooling cycle. The temperature of measurements was held for 1 h prior to each measure. All the measurements represented by $Z^*(\omega)=Z'(\omega)+Z''(\omega)=Z_g^*(\omega)+Z_{gb}^*$, where $Z_g^*(\omega)$ and Z_{gb}^* correspond to the impedances of the grain and grain boundary, respectively, were carried out in a dry air flow. The capacitance C values were extracted by the following equation:

$$C=\varepsilon_0\varepsilon S/l, \tag{1}$$

where ε_0 represents the vacuum permittivity and S/l the geometric factor, where S is the electrode area and l is the thick-

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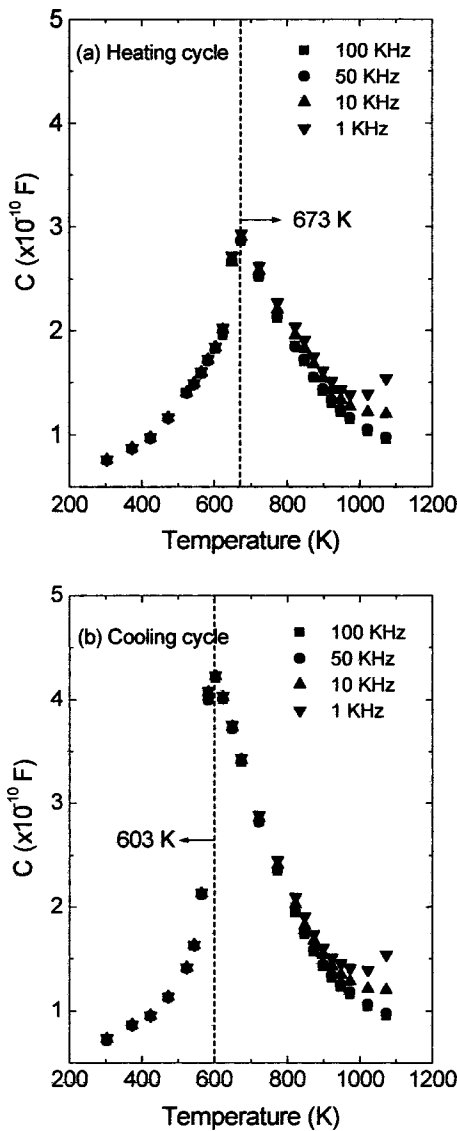[a)]Electronic mail: nobremal@prudente.unesp.br

FIG. 1. Capacitance values as a function of temperature at several frequencies: (a) heating cycle and (b) cooling cycle.

FIG. 2. Electric conductivity as a function of temperature at several frequencies: (a) heating cycle and (b) cooling cycle.

ness of the sample. The dielectric permittivity ε can be expressed in a conventional way being $\varepsilon^*(\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega)$, where $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ are the real and imaginary parts of the permittivity, respectively.

Figures 1(a) and 1(b) show the capacitance values as a function of temperature at several frequencies in a thermal cycle. During the cooling cycle, an increase of the polarizability occurs. Considering Fig. 1(a), an increase of the capacitance C can be seen between RT and a maximum at 673 K termed peak temperature T_p. Above 673 K and up to 1073 K, C values decrease gradually with increasing temperature. Figure 1(b) show that during cooling from 1073 to 823 K, the temperature dependence of C with frequency is identical to that recorded during the heating cycle. Between 823 and 523 K, all the capacitance values are higher than those derived during the heating cycle. Moreover, the T_p value shifts down to 603 K upon the cooling cycle. This effect is noticeable in a broad temperature range leading to the development of a thermal hysteresis, taking into account heating and cooling cycles. The maximum in the capacitance curve is at the same T_p for different frequencies and can be assigned to a
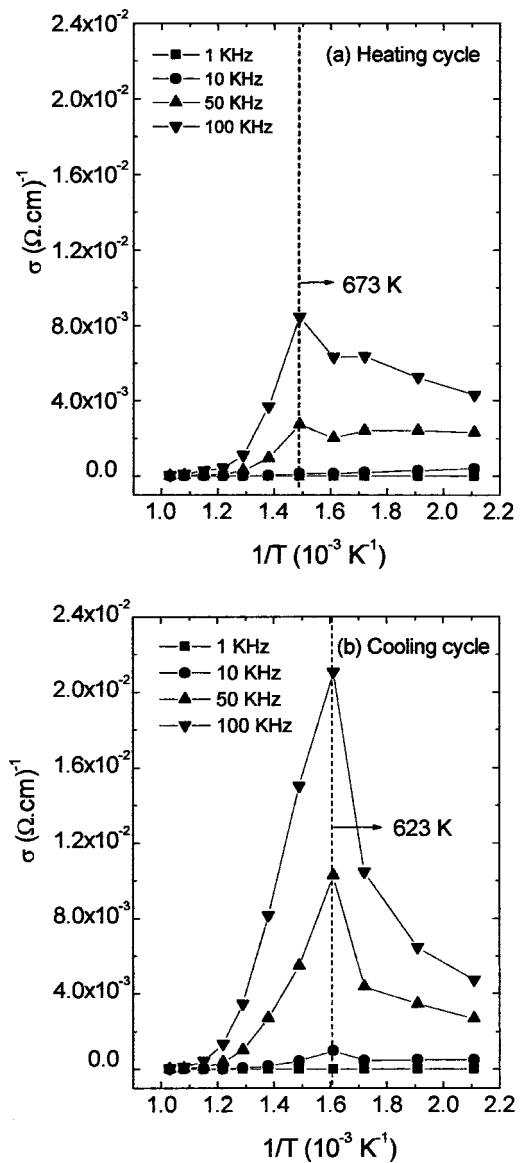
first-order phase transition from an antiferroelectric at low temperature to a paraelectric phase.[10] Both figs. 1(a) and 1(b) exhibit a dispersion of capacitance values at temperatures above 823 K for frequencies below 10^4 Hz and can be associated with dielectric losses, which might be correlated to conduction.

Figure 2 shows the dependence of ac conductivity with temperature at several frequencies. At frequency below 50 kHz, the conductivity is slightly dependent on the frequency and none anomaly is detected between 1 and 10 kHz [Fig. 2(a)]. However, at high frequency, an asymmetric peak develops as a function of temperature at $f \geqslant 50$ kHz. During the cooling cycle, the ac conductivity values are enhanced [Fig. 2(b)].

As an example, a shoulder is clearly observed at 10 kHz, which presents as an asymmetric peak from 50 kHz. This peak is positioned in the same temperature range, where the antiferroelectric–paraelectric (orthorhombic–tetragonal) phase transition in sodium niobate occurs, as reported earlier. The dependence of the electric conductivity with fre-
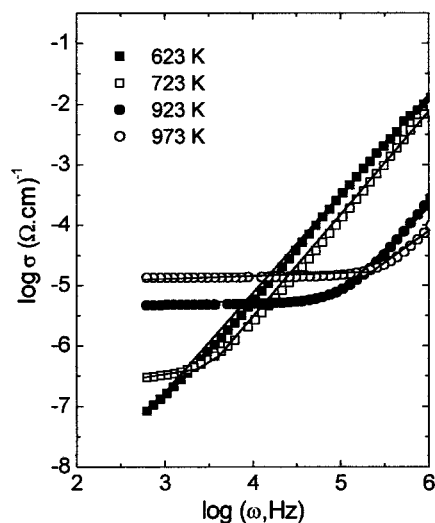
FIG. 3. Theoretical fitting of the electric conductivity as a function of frequency in double-logarithmic scale, in according to the Eq. (2) at several temperatures.

FIG. 4. Values of the s parameter as a function of temperature in one thermal cycle.

quency can be represented by the following equation:

$$\sigma_{tot}(\omega) = \sigma_{dc} + A\omega^s, \qquad (2)$$

where σ_{dc} is dc conductivity due excitation of electron from a localized state to the conduction bands, and $A\omega^s$ is the ac conductivity. The ac contribution is typically assigned to the hopping conduction. A is a frequency-independent constant and s a power with values $0.0 < s < 1.0$, both temperature dependent.

Figure 3 shows the conductivity as a function of frequency in a double-logarithmic representation with each respective theoretical fitting using Eq. (2). Excellent agreement between experimental data and theoretical fitting is observed. The frequency dependence of ac conductivity, σ_{ac} obeys a power relation $\sigma_{ac} \propto \omega^s$, at low temperature ($\leqslant 723$ K). The experimental observation of Eq. (2) indicates that the transport mechanism is due to the hopping of carriers via localized electron states,[11] ω^s term. Thus, up to 723 K, only localized conduction is detected, which is compatible with the presence of low symmetry structure. At high temperature (>723 K) and at low-frequency domain, a plateau can be observed. This behavior is further evidence of dc conductivity that is independent of the frequency. These data confirm previous expectative of high loss degree by conduction at high temperature, which has a strong influence on the dielectric permittivity. This feature is compatible with the development of a delocalized or low localization conduction mechanism.

The $M^*(\omega)$ parameter is represented by the equation $M^*(\omega) = j\omega C_0 Z^*(\omega)$, where $j = \sqrt{-1}$ and C_0 is the vacuum capacitance of the cell. The impedance data were represented using the variation of normalized parameters Z''/Z''_{max} and M''/M''_{max} as a function of logarithmic frequency (data not shown here). These representations permit analysis of apparent polarization by inspection of the magnitude of mismatch between the peaks of both parameters.[12] A slight mismatch was observed at low temperature between the $Z''(\omega)$ and $M''(\omega)$ peaks. However, the absence of a significant mismatch between these peaks is detected at high temperature. This indicates that the polarization process is
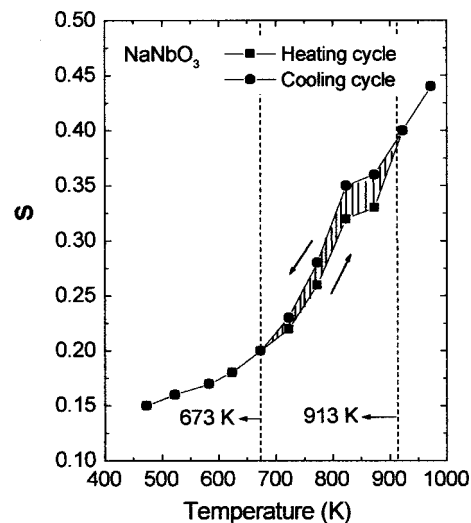
due to a localized conduction, which can be associated with the changing of the lattice symmetry and carrier mobility. In this sense, there is a transition or changing of conduction mechanism type from localized to a localized with low-lattice-coupling type. This phenomenon is in accordance with phase transition correlated to the development of structures with high symmetry.[1,9] Furthermore, this result provides evidence that the difficulties observed to attain high-temperature dielectric spectroscopy studies are due to the improvement of the degree of dc conductivity.

The s parameters derived in one thermal cycle are shown in Fig. 4. The values increase as the temperature increases. A thermal hysteresis is observed between 723 and 913 K, according to Figs. 1(a) and 1(b). The set of values of the exponent s derived lies in the range $0.15 \leqslant s \leqslant 0.44$, all of them lower than 0.5, which should correspond to the mechanism of the hopping type. The magnitude of values indicates a large effective mass m^* of electron due to its localization. Therefore, the values of $s \leqslant 0.5$ are further evidence of a type of conduction mechanism as small or large polaron hopping.

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