Piezoelectric, pyroelectric, dielectric and ferroelectric properties of Ba0.3Na0.7Ti0.3Nb0.7O3

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Piezoelectric, pyroelectric, dielectric and ferroelectric properties of $Ba_{0.3}Na_{0.7}Ti_{0.3}Nb_{0.7}O_3$

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The ferroelectric, piezoelectric, and pyroelectric properties of $Ba_{1-x}Na_xTi_{1-x}Nb_xO_3$ with $x=0.70$ (BTNN0.70) lead-free ceramic were investigated. Polycrystalline sample with composition BTNN0.70 was prepared by using conventional dry ceramic technique. Sample was sintered at 1250 °C for 3 h under oxygen showed perovskite structure with high densities 4.92 g/cm^3 (~96% as relative density). X-ray analysis confirmed the formation of single-phase compound with cubic crystal structure. Dielectric properties were studied in detail as a function of frequency and temperature. From temperature variation of dielectric constant, Curie temperature (T_C) was determined. Discussion on hysteresis behavior for the sample at room temperature is presented. An essential relation between the piezoelectric properties and the ferroelectric nature of the ceramics was detected. The piezoelectric and pyroelectric coefficients of the ceramic were studied as a function of temperature. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2818146]

I. INTRODUCTION

The materials with a perovskite structure of general formula ABO_3, where A=mono- or divalent ion and B=tri-, tetra-, or pentavalent ion, have been found to be very useful and interesting for different solid-state devices.[1–3] The most widely used piezoelectric ceramics are lead-based ceramics especially $Pb(Zr,Ti)O_3$ (PZT) because of their superior piezoelectric properties. With concern in the environmental pollution of PbO evaporation, lead-free piezoelectric ceramics have recently attracted considerable interest to replace the lead-based material systems.[4] Pure $NaNbO_3$ (NN) is antiferroelectric at room temperature, with orthorhombic distorted perovskite structure; it easily becomes ferroelectric by low rate substitutions.[5–9] BTNN system ceramics are usually fabricated by the conventional solid-state method $[(1-x)BaTiO_3+xNaNbO_3]$.[10] Barium sodium niobate titanate, ceramic composition $Ba_{0.3}Na_{0.7}Ti_{0.3}Nb_{0.7}O_3$ (BTNN0.70), is a perovskite-type ferroelectric with a relatively high Curie temperature.[11] This lead-free compound could be of great interest as respectful materials for the environment in the scope of applications as dielectrics for capacitors or actuators and infrared detectors. Furthermore, BTNN0.70 system piezoelectric ceramic is essentially perovskite type ferroelectric and it is necessary to investigate the piezoelectric properties of the ceramic with respect to their ferroelectric properties. In this work, the relation between the piezoelectric properties and the ferroelectric nature of the BTNN0.70 system composition was studied and to confirm the ferroelectric phase, a pyroelectric measurement was realized on this composition.

II. EXPERIMENTAL CONDITIONS

A conventional ceramic fabrication technique was employed to prepare $Ba_{0.3}Na_{0.7}Ti_{0.3}Nb_{0.7}O_3$ (BTNN0.70) from dry reagent grade $BaCO_3$, TiO_2, Na_2CO_3, and Nb_2O_5. Calcination at 1150 °C for 15 h was followed by sintering of disk-shaped pellets at 1250 °C for 3 h. Both treatments were performed under oxygen. X-ray diffraction (XRD) measurements were performed on the milled ceramic powder using Cu $K\alpha$ radiation ($\lambda_{K\alpha_1}=1.540\,51$ Å and $\lambda_{K\alpha_2}=1.544\,33$ Å) at

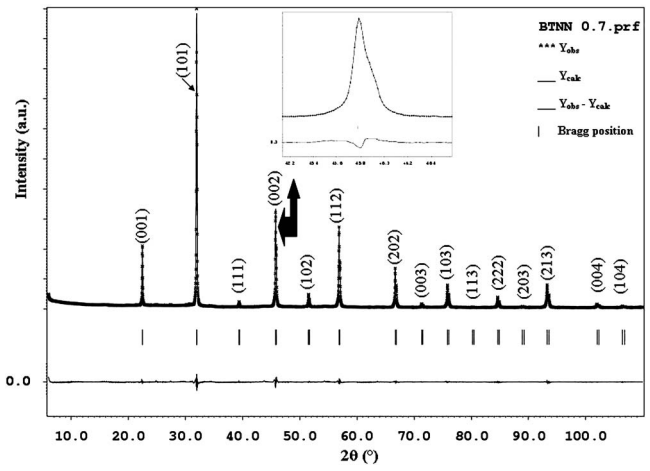

FIG. 1. XRD patterns for a cubic ceramic sample of $Ba_{1-x}Na_xTi_{1-x}Nb_xO_3$ with $x=0.70$.

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TABLE I. X-ray powder diffraction data for a ceramic with composition.

h k l	Bragg
0 0 1	22.4592
1 0 1	31.8911
1 1 1	39.3235
0 0 2	45.7247
1 0 2	51.4912
1 1 2	56.8275
2 0 2	66.6582
0 0 3	71.2922
1 0 3	75.8023
1 1 3	80.2241
2 2 2	84.5877
2 0 3	98.9200
2 1 3	93.2461
0 0 4	101.9800
1 0 4	106.4419

295 K. The scanning record was run at preset 2θ range of 6°–110° with 0.02° step and 150 s counting time. Data were analyzed by the Rietveld method[12] using the JANA program. The dielectric measurements were made on polished ceramic disks with evaporated gold electrodes. Dielectric properties at the various frequencies (0.1–200 kHz) were measured by a frequency impedance analyzer HP4194A conjuncted with a computer-controlled temperature chamber to measure capacitance as a function of temperature from 80 to 600 K. The piezoelectric properties were measured by means of the resonance-antiresonance method on the basis of IEEE standards using a precision impedance analyzer (HP4194A). The electromechanical coupling factor k_p was calculated from the resonance and antiresonance frequencies based on the formulas of Onoe and Jumonji.[13] Piezoelectric coefficients d_{31}, v, Q_m, and f_r were computed using measured parameters. Hysteresis measurements were done at different temperatures using an automatic *P-E* loop tracer based on modified Sawyer-Tower circuit.

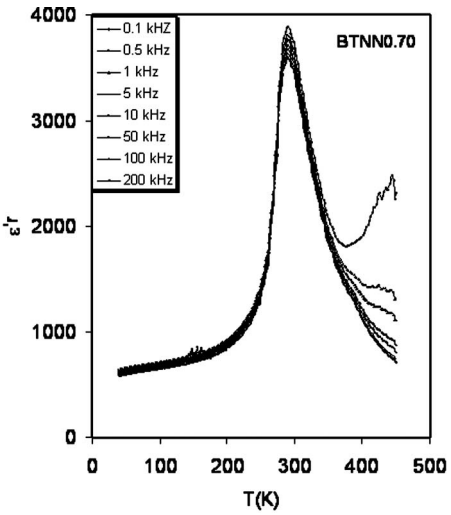

FIG. 2. Temperature dependence of the real part of the permittivity ε_r' for the ceramic composition $Ba_{0.3}Na_{0.7}Ti_{0.3}Nb_{0.7}O_3$.

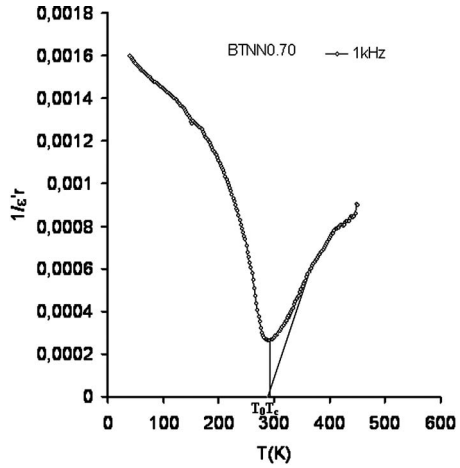

FIG. 3. Temperature dependence of $1/\varepsilon_r'$ at 1 kHz for a ceramic with composition $Ba_{0.3}Na_{0.7}Ti_{0.3}Nb_{0.7}O_3$.

III. RESULTS AND DISCUSSION

A. X-ray diffraction study

Figure 1 shows the XRD patterns of BTNN0.70 ceramic. A pure perovskite structure without any secondary impurity phases could be certified. XRD analysis shows that the sample to be single phase with cubic structure. For $x=0.70$, the x-ray powder diffraction spectrum should be indexed with the cubic space group $Pm\bar{3}m$ and parameter $a=3.9651$ Å and $Z=1$: the powder diffraction data are given in Table I. The diffraction spectra were measured at room temperature: they could be indexed with only one perovskite type phase. The observed values of 2θ plotted in Fig. 1 were obtained by weak profile analysis, the cell parameters well calculated by least square refinement.

Final atomic coordinates and thermal parameters are listed in Table II.

B. Dielectric study and ferroelectric properties

The relative dielectric constant corresponding to the sample BTNN0.70 sintered at 1250 °C for different holding

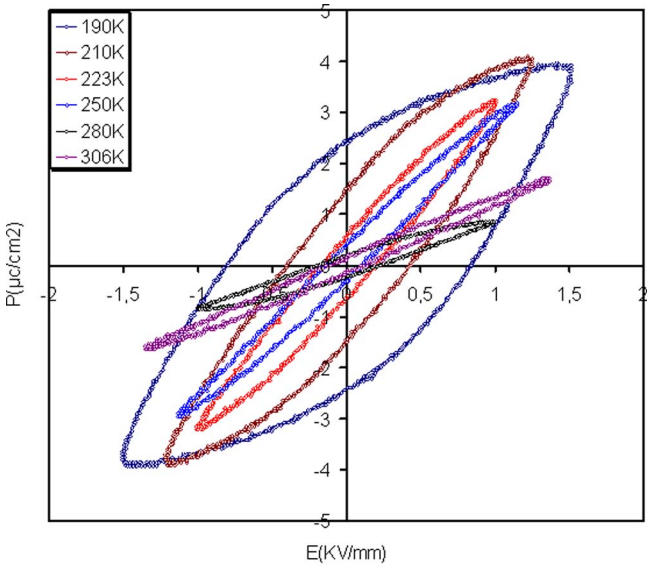

FIG. 4. (Color online) *P-E* hysteresis loops of BTNN0.7 sample sintered at 1250 °C.

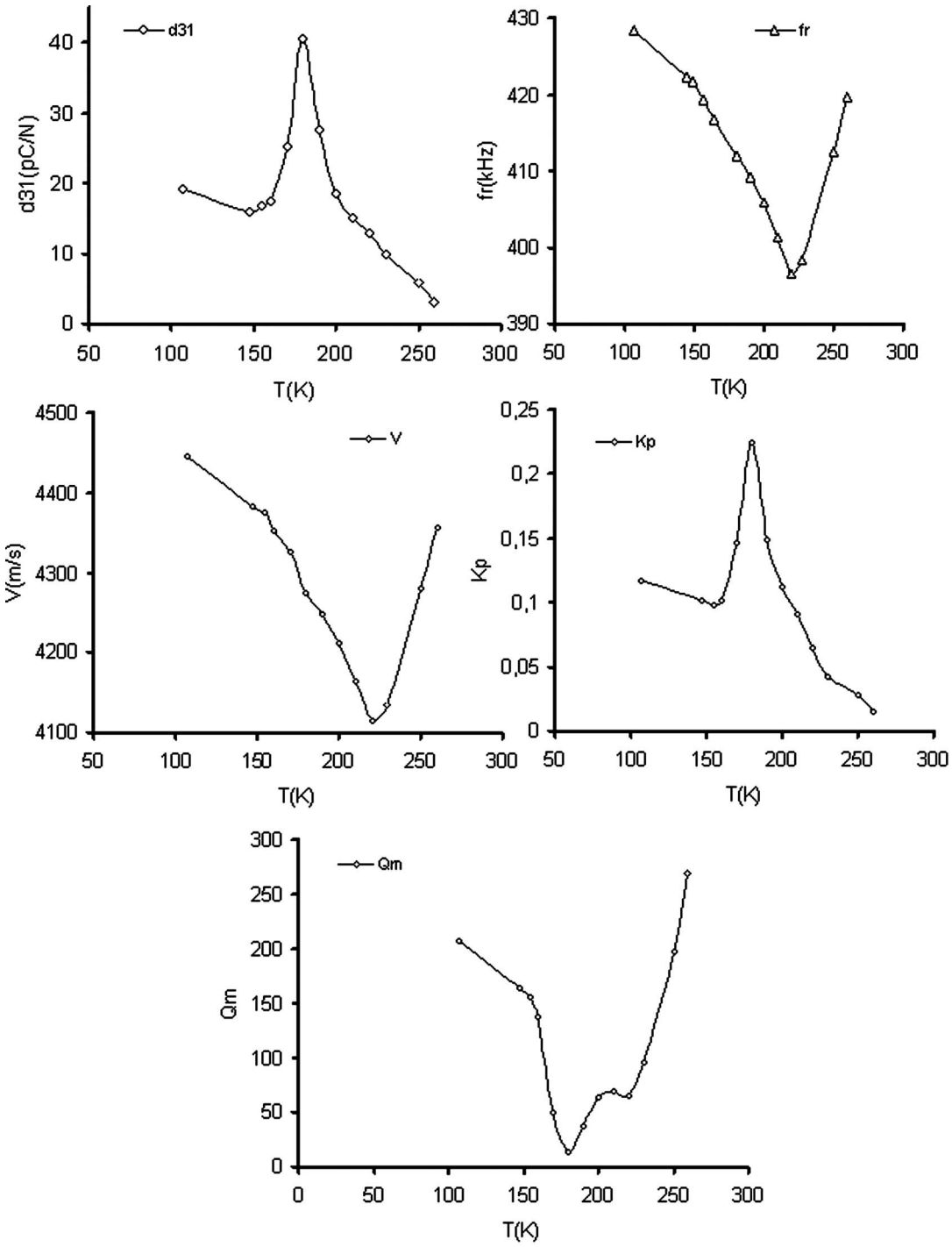

FIG. 5. The piezoelectric coefficients as a function of temperature of $Ba_{0.3}Na_{0.7}Ti_{0.3}Nb_{0.7}O_3$ ceramic.

times are shown in Fig. 2. There is no frequency dispersion. Ferroelectricity here is of the classical type. In addition, the thermal variation of $1/\varepsilon_r'$ is of Curie-Weiss type and is given in Fig. 3. The extrapolation of the high temperature part of the curve gives the Curie-Weiss temperature noted as T_0. The ferroelectric-paraelectric phase transition is of first order when $T_0 < T_C$ and is of second order when $T_C = T_0$, where T_0 is the Curie-Weiss temperature defined by $1/\varepsilon_r' = (T - T_0)/C$. The temperature dependence of $1/\varepsilon_r'$ at 1 kHz was also in good agreement with a Curie-Weiss law in the paraelectric region for $T > T_C$. Figure 3 shows the temperature dependence of $1/\varepsilon_r'$ for BTNN0.70 ceramic. The phase transition was clearly of the second order. All these physical properties are typical of a normal ferroelectricity,[14] as found in pure $BaTiO_3$ (BT).

C. Ferroelectric properties of BTNN0.70 ceramic

The *P-E* hysteresis loops of the BTNN0.70 ceramic measured at different temperatures because of its good dielectric properties under a 20 kV cm^{-1} applied electric field and 50 Hz are shown in Fig. 4. It is important to mention that saturation of polarization could not be achieved because the dielectric breakdown potential of the samples was lower than

TABLE II. Atomic coordinates and thermal parameters for BTNN0.70.

Ions	x	y	z	U_{iso}	Occ.
Ba^{+2}	0	0	0	0.008 56(6)	0.006 250
Na^{+1}	0	0	0	0.008 56(6)	0.014 583
Ti^{+4}	0.5	0.5	0.5	0.007 05(9)	0.006 250
Nb^{+5}	0.5	0.5	0.5	0.007 05(9)	0.014 583
O^{-2}	0	0.5	0.5	0.007 89(3)	0.062 500

the saturation field. This figure shows that the material has good ferroelectric nature. It is clearly evident that the shape of *P-E* loops varies greatly with the temperature. It can be seen that for low applied fields, the *P-E* loop is far from saturation. Sharp and well saturated squared *P-E* loop could be observed for increasing *E* showing full domain switching. The polarization loop of BTNN0.70 is well developed showing large remnant polarization P_r (remaining polarization when electric field is decreased to zero). The hysteresis loop is of a typical "square" form as a result of domain switching in an applied field. This is a typical characteristic of a phase that contains long-range interaction between dipoles in the ferroelectric microdomain state. This confirms that BTNN0.70 is of a normal ferroelectric phase. With increasing of temperature, the curves yield slimmer hysteresis loops with lower polarization values due to the ferroelectric-paraelectric phase transition. From the loop at room temperature, the remnant polarization P_r and the coercive field E_C (indicating and electric field required to zero the polarization) are determined to be 1.5 $\mu C/cm^2$ and 5 kV/cm, respectively.

D. Piezoelectric and pyroelectric properties

BTNN0.70 sample was first submitted to a dc field of about 7 kV cm^{-1} between 100 and 320 K for 5 min in dry helium atmosphere. The two electrodes were then short circuited for several hours in order to eliminate any residual space charge. Piezoelectric resonance experiments and pyroelectric current detection were then undertaken without positive results. The polarization treatment was then made at lower temperature from 320 to 100 K with a polarizing field increasing from 1 to 2.3 kV on cooling. The sample then shows piezo- and pyroelectric effects under 280 K. Figure 5 shows the piezoelectric parameters (piezoelectric coefficient d_{31}, coupling coefficient K_p, velocity of sound v, radial resonance frequency f_r, and mechanical quality factor Q_m) of poled BTNN0.70 ceramic. The thermal annealing behavior for BTNN0.70 ceramic is shown in Fig. 5, where the piezoelectric coefficient d_{31} is plotted against the annealing temperature. The transverse piezoelectric coefficient d_{31} and the electromechanical coupling factor k_p curves show a maxima in the ferroelectric part, then decrease to zero at the ferroelectric-paraelectric phase transition temperature. d_{31} of the BTNN0.70 is found to be 40 pC N^{-1}, which is the highest value among the NN modified BT-based piezoelectric ceramics, while comparing with other compositions (BTNN0.90).[11] When the annealing temperature is higher than 180 K, d_{31} of the BTNN0.70 piezoelectric ceramic decreases sharply and tends to zero when the annealing temperature is above the Curie temperature. The piezoelectric properties of the modified BT-based materials are obviously improved compared with those of the control material. Figure 5 also gives the mechanical quality factor (Q_m), planar electromechanical coupling factor (k_p), and radial resonance frequency f_r of the BTNN0.70 piezoelectric ceramic. It can be seen that all three of these factors for the BTNN0.70 are higher than those of the BTNN ceramics. The planar electromechanical coupling factor varies between 2.2% and 3.9%. The admittance circle recorded at 147 K is shown in Fig. 6 as an example and proves well that the BTNN0.70 ceramic is a piezoelectric material in the ferroelectric phase. Frequency variations at different temperatures of the admittance Y and the susceptance Y^* of $Ba_{0.3}Na_{0.7}Ti_{0.3}Nb_{0.7}O_3$ ceramic are given in Fig. 7. The decrease of the susceptance B curve as well indicate the ferroelectric-paraelectric phase transition. The thermal variation of the maximum of admittance at the transverse resonance decreases by increasing the temperature and vanishes close to 290 K, as shown in Fig. 8. The present sample is studied for pyroelectric activity using the static pyroelectric method. The pyroelectric depolarization current was measured on heating at a rate of about 2.2 K min^{-1} from 107 to 400 K. The temperature dependence of the pyroelectric coefficient (p) was calculated from the rate of variation of the temperature b and pyroelectric current i following the relation $p=i/sb$, where s is the area of an electrode. The pyroelectric current and the temperature of the poled sample were measured either during heating cycle (Fig. 9). The heat-

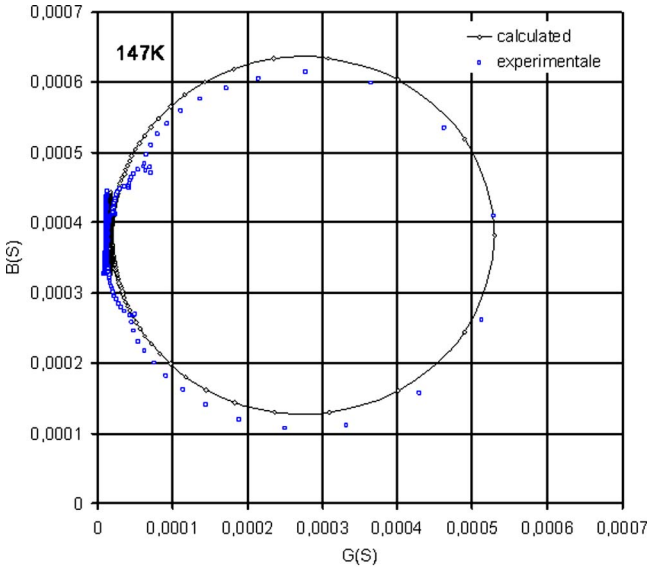

FIG. 6. (Color online) Piezoelectric admittance circle at the main radial resonance for a BTNN0.7 ceramic at 147 K.

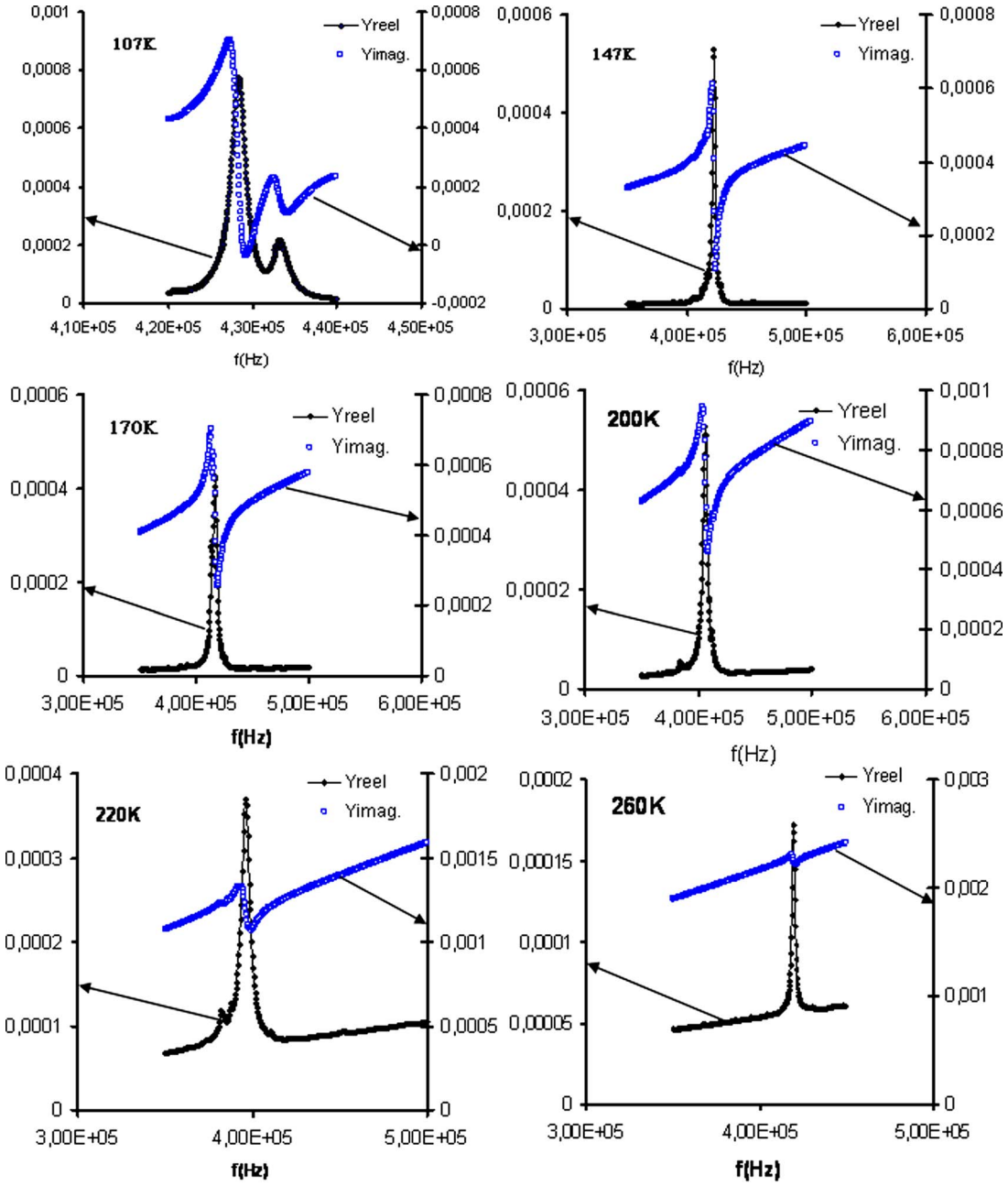

FIG. 7. (Color online) Frequency variations of the admittance Y and the susceptance Y^* at different temperatures of $Ba_{0.3}Na_{0.7}Ti_{0.3}Nb_{0.7}O_3$ ceramic.

ing cycle show clearly the pyroelectric behavior of the sample following the relation $i(T)=p(T)sb$, where i is the current, s the area of an electrode, p the pyroelectric coefficient, and $b=dT/dt$ the heating (+) or cooling (−) rate. The spontaneous polarization P_S was calculated by integration of the value of p versus T. Results are shown in Fig. 10. From this figure, it can be seen that the pyroelectric current has a broad maximum close to 285 K and then decreases until zero around 300 K. The pyroelectric coefficient changes insignificantly with the temperature up to about 270 K and starts increasing with the increase of temperature thereafter. The pyroelectric current as well as coefficient passes through a peak at a temperature slightly lower than the ferroelectric transition temperature. From Fig. 10, it is seen that the pyroelectric peak tends to become broader with the decrease of $NaNbO_3$ content.[11] The existence of pyroelectric current is also possible due to the permanent dipoles existing randomly in different regions beyond T_C. This can be correlated to the observed dielectric behavior, which may be due to the microheterogeneties in the composition. Figure 10 also shows the behavior of spontaneous polarization (P_S) calculated from the pyroelectric coefficient following the relation $P_S=\int pdt$. P_S presents a constant value at low temperatures and then tend to decrease to attain zero at a temperature near the T_C. The value of P_S at room temperature for $x=0.70$ is around 2 $\mu C/cm^2$. The spontaneous polarization becomes zero at 300 K, confirming that the present set of the compound is ferroelectric below this temperature. The value of $p(T)$ varies with the $NaNbO_3$ concentration.[11] The curve is seen to have the "classic" pattern characteristic of second order phase transition. These results indicate that the polar state of the sample disappears at a temperature close to

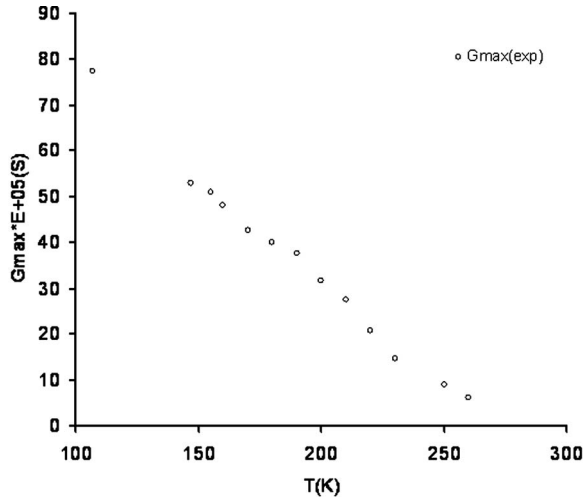

FIG. 8. Thermal variation of the maximum of admittance at the main radial piezoelectric resonance of a BTNN0.7 ceramic.

300 K. The piezoelectric effect is too weak to be calculated in this case, whereas pyroelectric effect can be detected. The peak position is found to be the same in both pyroelectric coefficient and dielectric behavior plots taken with the variation of temperature, which confirms that the phase transition is around 300 K.

IV. CONCLUSION

Ferroelectric cubic phase was identified by XRD method. The material belonging to the solid solution $Ba_{1-x}Na_xTi_{1-x}Nb_xO_3$ with composition $x=0.70$ shows a cubic perovskite structure with a lattice parameter a of about

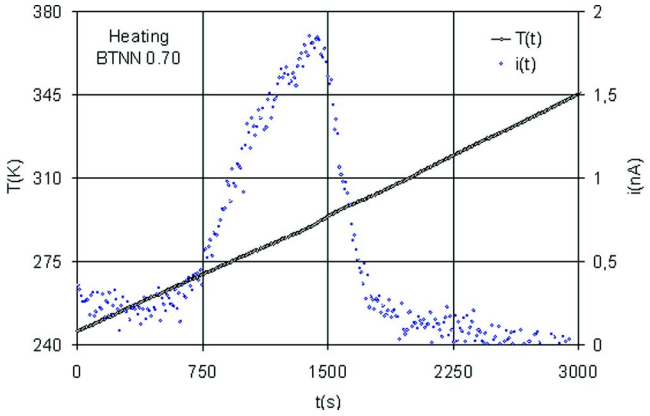

FIG. 9. (Color online) Variations of pyroelectric current and temperature vs time during one heating cycle for a poled BTNN0.7 ceramic.

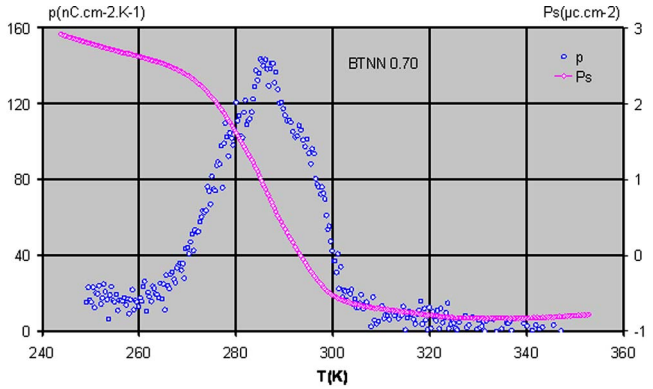

FIG. 10. (Color online) Temperature dependence of the pyroelectric coefficient and spontaneous polarization of a BTNN0.7 ceramic.

3.9651 Å. The fact that sample should be polarized by applying a dc field and the pyroelectric and piezoelectric behavior are in agreement with the ferroelectric properties of the ceramic. The value of T_C involves a good stability of the piezoelectric properties; this is an important result, while the material can be used for high power applications.

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