

Relaxor or classical ferroelectric behaviour in ceramics with composition $\text{Ba}_{1-x}\text{Na}_x\text{Ti}_{1-x}\text{Nb}_x\text{O}_3$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2000 J. Phys.: Condens. Matter 12 5951

(<http://iopscience.iop.org/0953-8984/12/27/313>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.221

The article was downloaded on 16/05/2010 at 05:19

Please note that [terms and conditions apply](#).

Relaxor or classical ferroelectric behaviour in ceramics with composition $\text{Ba}_{1-x}\text{Na}_x\text{Ti}_{1-x}\text{Nb}_x\text{O}_3$

Hamadi Khemakhem[†], Annie Simon[‡], Régnauld Von Der Mühl[‡]
and Jean Ravez[‡]

[†] ICMCB–CNRS, Avenue du Dr A Schweitzer, 33608 Pessac, France

[‡] Laboratoire de l'Etat Solide, ENIS, 3038 Sfax, Tunisia

Received 7 February 2000, in final form 25 April 2000

Abstract. Ceramics with composition $\text{Ba}_{1-x}\text{Na}_x\text{Ti}_{1-x}\text{Nb}_x\text{O}_3$ are of either classical ferroelectric (for $0 \leq x < 0.075$) and ferro- or antiferroelectric (for $0.55 < x \leq 1$) or relaxor ferroelectric type (for $0.075 \leq x \leq 0.55$), the transition at T_c being only diffuse without any frequency dispersion for this last region. All the corresponding dielectric characteristics, i.e. diffusivity of the ferroelectric–paraelectric transition, frequency dispersion of ϵ'_r , shift of T_m with frequency deviation from the Curie–Weiss law, are determined. The relaxor behaviour is more relaxor the more the composition deviates from BaTiO_3 and NaNbO_3 . This study is in the field of preparation of relaxor ceramics free from lead in the interest of the environment, which present a transition temperature close to room temperature.

1. Introduction

Due to their advantageous properties on one hand and their nontrivial character on the other hand, relaxors have been a subject of intense research for many years. In perovskites, the relaxor behaviour occurs dominantly in lead-based compositions [1–4]. Research is now in progress to obtain such lead-free ceramics, which are relaxor at room temperature. In another way, BaTiO_3 and NaNbO_3 are well known as classical non-relaxor ferro- or antiferroelectrics. Some properties of the physics relaxors are still not well understood and the microscopic picture is not complete.

The aim of the present work is to study the temperature and frequency dielectric responses of the $\text{Ba}_{1-x}\text{Na}_x\text{Ti}_{1-x}\text{Nb}_x\text{O}_3$ solid solution for compositions between BaTiO_3 and NaNbO_3 . Such compositions, free from lead, could be of relaxor type due to the simultaneous occupation of the two 12 and 6 coordination number (C.N.) sites by Ba^{2+} and Na^+ cations, and Ti^{4+} and Nb^{5+} cations respectively.

2. Preparation

Materials with composition within the system $(1-x)\text{BaTiO}_3 + x\text{NaNbO}_3$ were prepared from dry reagent grade BaCO_3 , TiO_2 , Na_2CO_3 and Nb_2O_5 . Calcinations at 1150°C for 15 h were followed by sintering of disc-shaped pellets at 1200 – 1400°C , depending on the values of x and for 3 h. Both treatments were performed under oxygen. The relative diameter shrinkages obtained by measurement of the green and sintered bodies $(d_g - d_s)/d_g$ are in the range 0.14 – 0.16 .

3. Dielectric and ferroelectric studies

Dielectric measurements were performed on ceramic discs after deposition of gold electrodes on the circular faces by cathodic sputtering. The relative real and imaginary permittivities ϵ'_r and ϵ''_r were determined as a function of both temperature and frequency in the ranges 77–500 K and $20\text{--}2 \times 10^5$ Hz respectively. These variations were determined using a Wayne–Kerr 6425 component analyser. Three different behaviours were obtained:

- For compositions in the range $0 \leq x < 0.075$, only one of the three anomalies related to the phase transitions (rhombohedral–orthorhombic–tetragonal–cubic) for BaTiO_3 has been observed at T_c (figure 1). The values of both ϵ'_r and T_c are not dependent on frequency implying these compositions to be classical ferroelectric type.

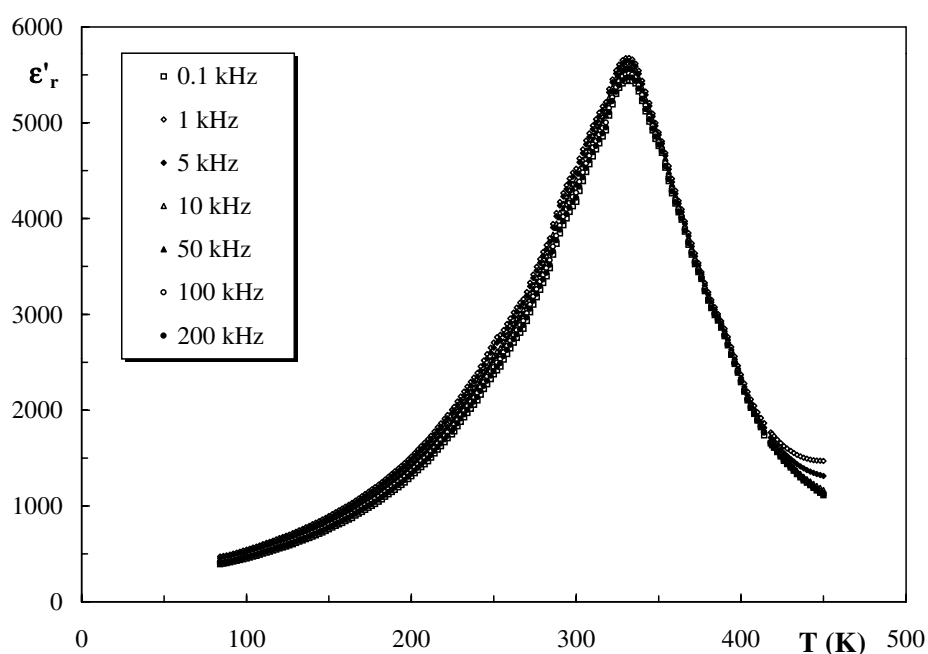


Figure 1. Temperature and frequency dependence of ϵ'_r for the composition $x = 0.025$.

- For compositions in the range $0.075 \leq x \leq 0.55$, there is only one broad peak of ϵ'_r and ϵ''_r at T_m (figures 2 and 3). When frequency increases, a decrease of ϵ'_r and an increase of T_m were observed. The frequency dispersion of ϵ'_r goes with a relatively high value of ϵ''_r for the relaxor phase ($T < T_m$). In addition, there is a deviation from the Curie–Weiss law (figure 4). All these observations suggest these compositions to be of relaxor type [1]. However the stoichiometric disorder for compositions in the region $0.075 \leq x \leq 0.55$ shows a different behaviour combining a strong frequency dispersion and a sharp drop of permittivity.

The frequency (f) dependence of T_m can be fitted with the Vögel–Fulcher relation: $f = f_0 \exp[-E_a/(T_m - T_f)]$ where f_0 , E_a and T_f are constants and T_m is the temperature of the dielectric permittivity maximum. The parameter T_f is often called freezing temperature. A value of $T_f = 93.4$ K, $\log(f_0) = 12.6$ and a thermal activation energy $E_a = 0.094$ eV were obtained in the case of $x = 0.30$.

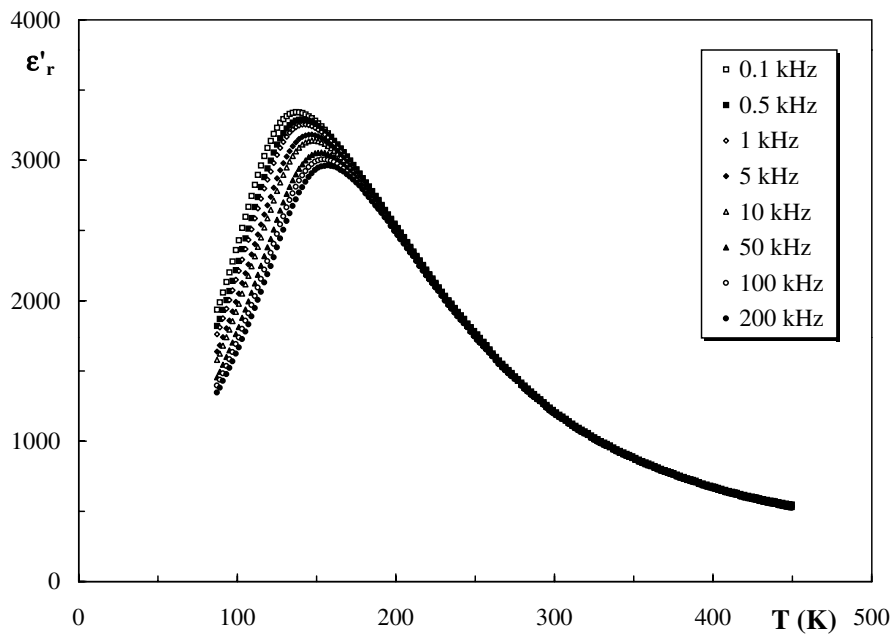


Figure 2. Temperature and frequency dependence of ϵ'_r for the composition $x = 0.30$.

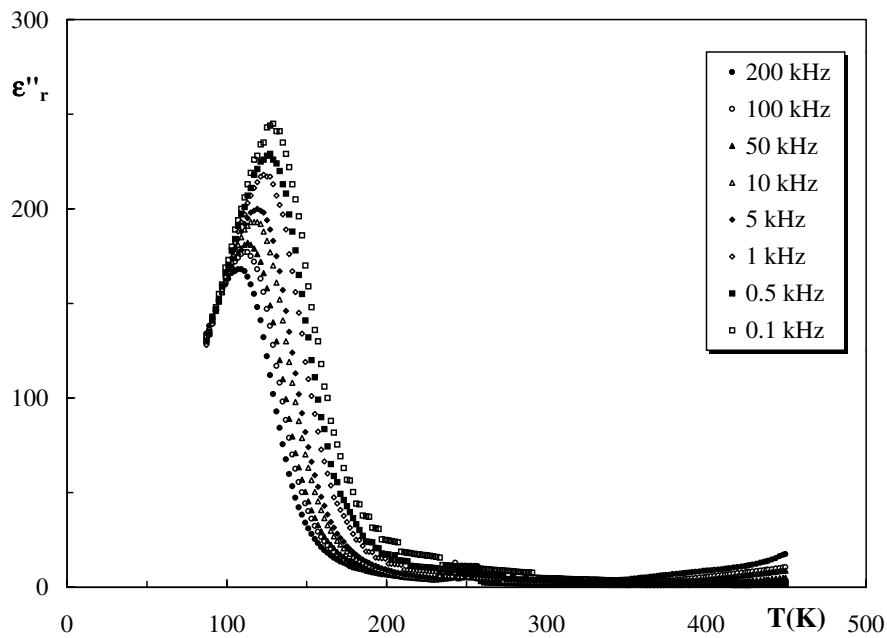


Figure 3. Temperature and frequency dependence of ϵ''_r for the composition $x = 0.30$.

The variations of T_c (or T_m) (tetragonal–cubic) with the composition at 10^3 Hz are shown in figure 5. T_c (or T_m) decreases when x increases from $x = 0$ with a minimum at $x = 0.40$

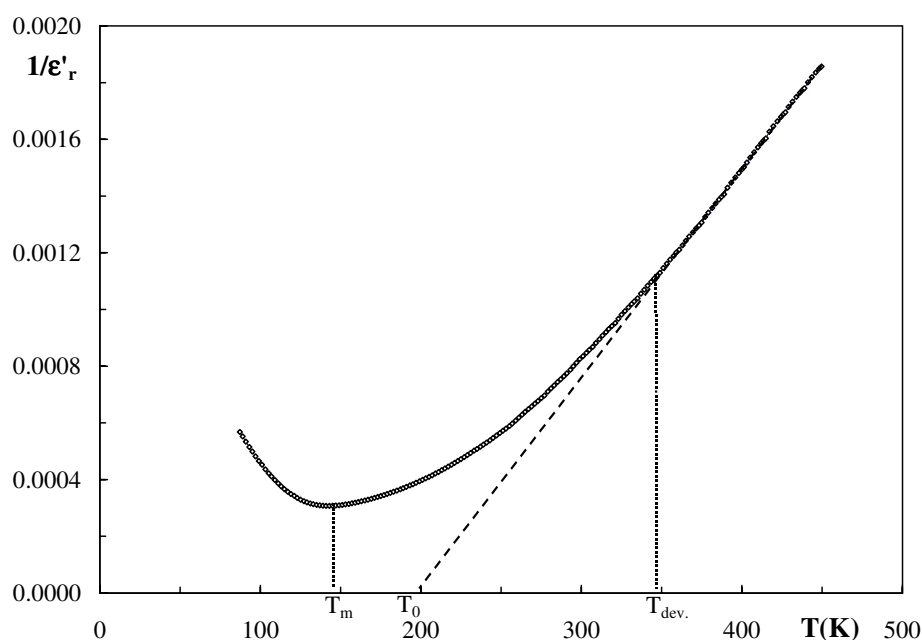


Figure 4. Variation of $1/\epsilon'_r$ as a function of temperature, at 10^3 Hz, for the composition $x = 0.30$.

then increases. This decreasing is related to the larger size of Nb which limits the shift within the octahedron and thus leads to decreasing Δz and to lower T_c ($r_{\text{Nb}^{5+}} = 0.64 \text{ \AA}$ and $r_{\text{Ti}^{4+}} = 0.605 \text{ \AA}$ in the six-coordination site [5]).

- For compositions in the region $0.55 < x \leq 1$, three anomalies were observed at T_1 , T_2 and T_c . No frequency dispersion occurred for $T < T_c$ implying a classical ferroelectric behaviour. The highest temperature represents the ferroelectric or the antiferroelectric transition. Figure 6 shows as an example the temperature dependence of ϵ'_r for a ceramic with composition corresponding to $x = 0.90$; for that composition, the x-ray powder diffraction spectrum should be indexed with the tetragonal system and parameters $a = 3.9198(4) \text{ \AA}$ and $c = 3.9543(7) \text{ \AA}$.

4. Pyroelectric and piezoelectric studies

The sodium niobate is antiferroelectric at room temperature with a value of $T_c = 620 \text{ K}$ [6]. Ceramics with composition close to NaNbO_3 showed a sharp peak of ϵ'_r without dielectric dispersion. The value of T_c is decreasing as composition deviates from NaNbO_3 . Nevertheless it was not possible to conclude by dielectric measurement if the low temperature phase is either antiferroelectric as NaNbO_3 or ferroelectric. Previous works performed on the NaNbO_3 – LiNbO_3 system showed that the Li^+ – Na^+ substitution induces ferroelectric phase [7].

In the present work, in order to raise the ambiguity, pyroelectric and piezoelectric studies were undertaken on a poled ceramic with the composition $\text{Ba}_{0.1}\text{Na}_{0.9}\text{Ti}_{0.1}\text{Nb}_{0.9}\text{O}_3$. The ceramic sample was poled using a dc electric field of 10 kV cm^{-1} at 450 K for 10 min and then short circuited for several hours in order to eliminate any residual space charge.

The pyroelectric current and the temperature of the poled sample were measured simultaneously either during heating–cooling cycles (figure 7) or during a complete heating

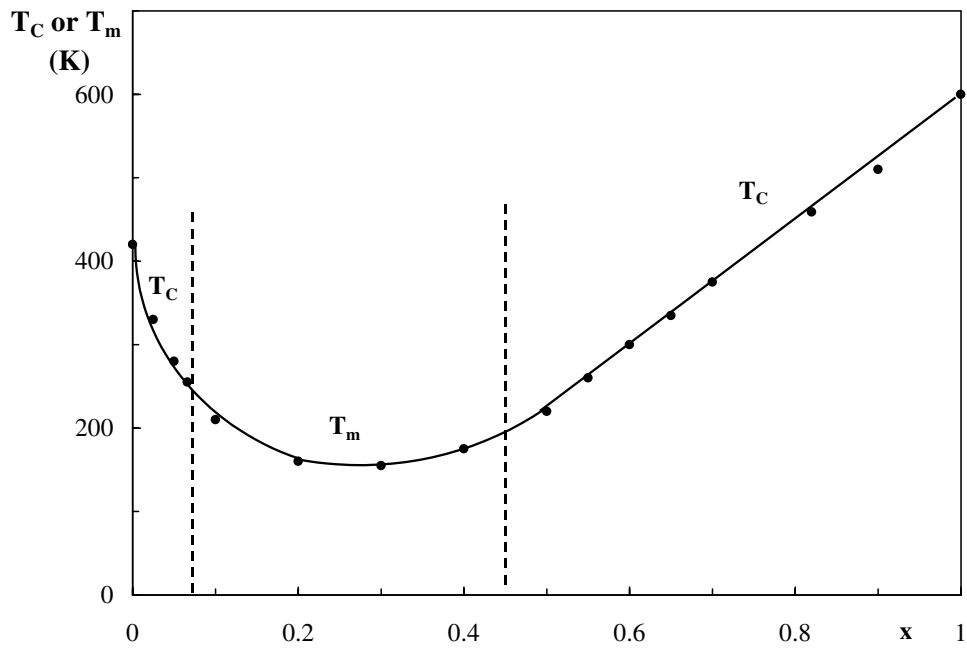


Figure 5. Variation of T_c (or T_m) (tetragonal-cubic) with composition.

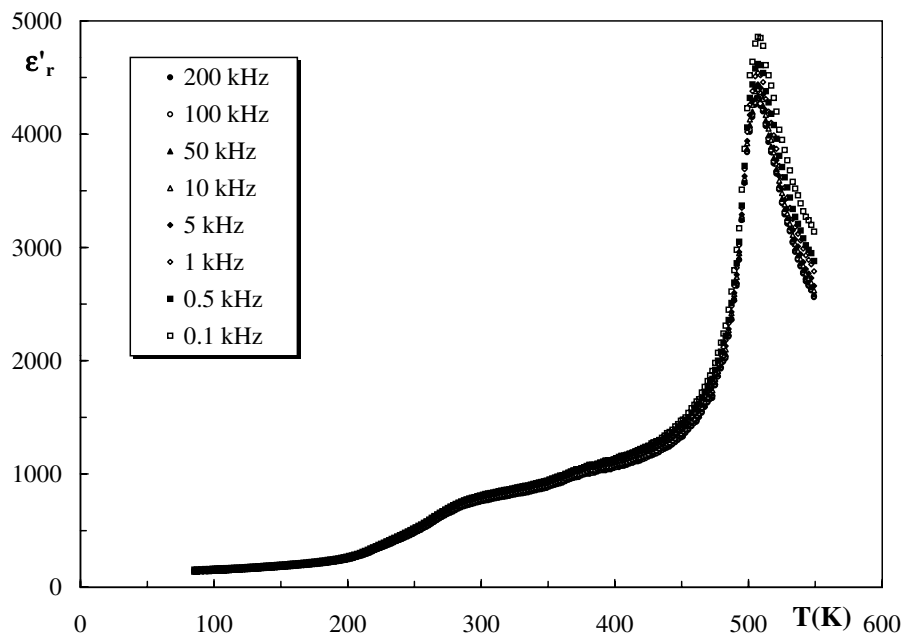


Figure 6. Temperature and frequency dependence of ϵ'_r for the composition $x = 0.90$. The temperature dependence of $d\epsilon'_r/dT$ is given for a frequency of 100 Hz.

experiment between 77 and 600 K at a rate of 5 K min^{-1} (figure 8). The heating-cooling cycles show clearly the pyroelectric behaviour of the sample following the relation $i(T) = p(T)sb$

Table 1. Piezoelectric characteristics of a ceramic with composition $\text{Ba}_{0.1}\text{Na}_{0.9}\text{Nb}_{0.1}\text{Ti}_{0.9}\text{O}_3$.

Thickness e	1.18 mm
Diameter D	6.74 mm
Density d	4.271
Compactness (= % of theoretical density)	88
Radial resonance frequency f (R, 1)	526.3 kHz
Poisson's ratio σ	0.31
Plane coupling coefficient K_p	0.21
Velocity of sound v	5156 m s ⁻¹
Youngs modulus $1/s_{11}$	1.135×10^{11} N m ⁻²
Piezoelectric coefficient d_{31}	30.8 pC N ⁻¹

where i is the current, s the area of an electrode, p the pyroelectric coefficient and $b = dT/dt$ the heating (+) or cooling (-) rate. It can be seen in figure 7 that the current reverses when the sign of b changes. The thermal variation of the apparent spontaneous polarization of the sample was calculated by integration of the thermal variation of p versus T . The thermal variations of p and P_s (figure 8) show anomalies corresponding to the phase transitions in the ferroelectric domain: one close to 200 K and the ferroelectric–paraelectric transition at $T_c \approx 500$ K.

Piezoelectric measurements were performed at 300 K on the same sample—polarized again—using the resonance method for the main radial resonance. The results are reported in table 1.

The value obtained for the transverse piezoelectric coefficient d_{31} is quite interesting despite the poor compactness of the sample and also to be considered is the relatively high value of T_c which allows a good stability of the performance versus temperature. Taking into account that the spontaneous polarization disappears only at 550 K, the piezoelectric properties may persist until this temperature. If we consider that P_s remains relatively high up to 400 K, the value of the piezoelectric coefficient d_{31} will remain also high in this temperature range.

5. Dielectric relaxor characteristics

Figure 2 shows clearly for $x = 0.30$, the broad peak of ϵ'_r at T_m , the dispersion of ϵ'_r and the shift of T_m when the frequency increases from 10^2 to 10^5 Hz. Always for the same composition, figure 9 shows the frequency variations of ϵ'_r and ϵ''_r . In the relaxor phase ($T = 120$ K $< T_m$), the value of ϵ'_r decreases continuously and almost linearly with $\log f$, but in the paraelectric phase ($T = 300$ K $> T_m$), ϵ'_r does not change. We observe that the value of the imaginary part ϵ''_r of the permittivity is relatively important for $T < T_m$; in contrast its value is very weak and does not vary for $T > T_m$. This behaviour confirms the ferroelectric relaxor character of the materials.

Figure 4 shows the variation of $1/\epsilon'_r$ as a function of temperature for the composition $x = 0.30$. In contrast to a classical ferroelectric, there is a strong deviation from the Curie–Weiss law. The Curie–Weiss behaviour is observed only in the $T > T_{dev}$ region. When $T < T_{dev}$. (= 320 K), the observed deviation from the Curie–Weiss law is characteristic of dipole–dipole interactions of some type of short-range order. The large curvature of $1/\epsilon'_r$ around T_m implies a diffuse phase transition. This is another characteristic of a relaxor type ferroelectric. In table 2, all relaxor characteristics are reported for some compositions as the frequency relative dispersion $\Delta\epsilon'_r/\epsilon'_r = [\epsilon'_r(10^2 \text{ Hz}) - \epsilon'_r(10^5 \text{ Hz})]/\epsilon'_r(10^2 \text{ Hz})$ at $T_m(10^2 \text{ Hz})$ and the T_m shift $\Delta T_m = T_m(10^5 \text{ Hz}) - T_m(10^2 \text{ Hz})$. From the variation of relaxor characteristics

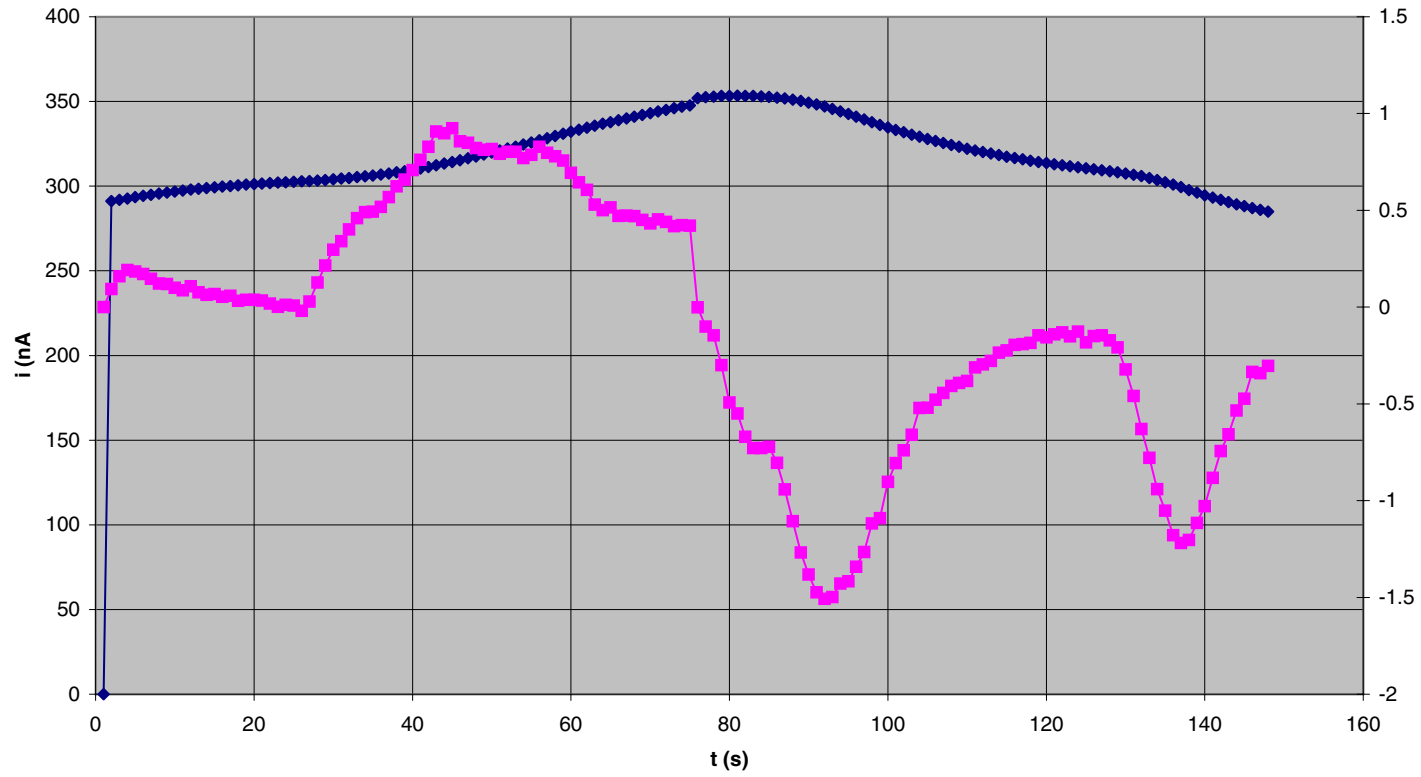


Figure 7. Variations of pyroelectric current and temperature versus time during one heating/cooling cycle for a poled ceramic with composition $x = 0.90$.

Relaxor behaviour of $Ba_{1-x}Na_xTi_{1-x}Nb_xO_3$

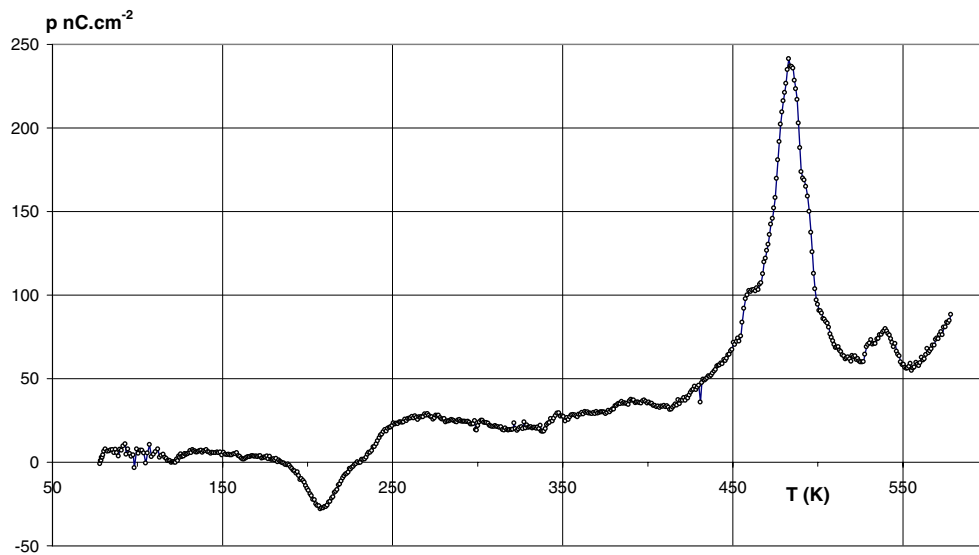


Figure 8. Thermal variations of pyroelectric coefficient and spontaneous polarization on heating for a poled ceramic with composition $x = 0.90$.

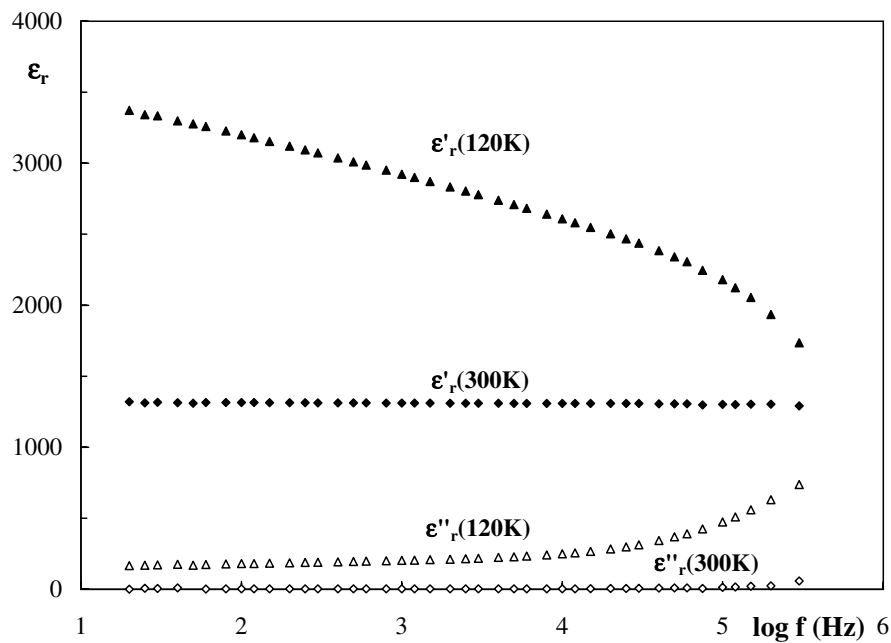


Figure 9. Real and imaginary part (ϵ'_r and ϵ''_r) variations with frequency for the composition $x = 0.30$.

it can be deduced that the relaxor character increases from $x = 0.10$ to $x = 0.40$ then it decreases. This behaviour can be interpreted as follow: the relaxor character is related to the inhomogeneity introduced by the substitution of Nb^{5+} by Ti^{4+} . Our material can be considered

as a good relaxor ferroelectric by comparison with the well known PMN ($PbMg_{1/3}Nb_{2/3}O_3$) [8]. In addition we observe an increase as x increases the value of the characteristic deviation from the Curie–Weiss law ($T_{dev.} - T_m$) at 10^3 Hz.

Table 2. Values of the frequency dispersion $\Delta\varepsilon'_r/\varepsilon'_r$ at $T < T_m$ and $\Delta T_m = T_m(10^5 \text{ Hz}) - T_m(10^2 \text{ Hz})$ for some compositions of ceramics with relaxor behaviour.

x	$\Delta\varepsilon'_r/\varepsilon'_r$	ΔT_m (K)
0.10	0.0928	7.5
0.20	0.1152	20
0.30	0.1216	21
0.40	0.1306	16.5
0.50	0.1120	20
0.55	0.1070	10.6

6. Conclusion

Dielectric studies of the $(1-x)BaTiO_3/xNaNbO_3$ diagram allowed us to prepare three new domains of solid solutions with derived perovskite structure. In the two extreme regions $0 \leq x < 0.075$ and $0.55 < x \leq 1$, we observe a classic ferroelectric or antiferroelectric–paraelectric phase transition implying a ferroelastic–paraelastic character in relation to changes of crystalline system. For the third region $0.075 \leq x \leq 0.55$, the phase transition is diffuse and of ferroelectric relaxor–paraelectric type.

The variation of T_c (or T_m) results from two competitive effects leading to either an increase or a decrease of T_c according the two types of substitution. The consistent increase in T_m goes with no decrease of the typical relaxor characteristic ΔT_m (the variation of T_m with frequency, here from 10^2 to 10^5 Hz).

Ferroelectric relaxor ceramics are used as dielectric for capacitors and as actuators, due to either high permittivity and high electrostrictive coefficients, respectively. The values of T_m obtained in the present work are however in the vicinity of room temperature for some compositions and this is an important result for applications.

References

- [1] Cross L E 1994 *Ferroelectrics* **151** 305
- [2] Hilton A D, Randall C A, Barber D J and Shrout T R 1989 *Ferroelectrics* **93** 379
- [3] Setter N and Cross L E 1980 *J. Appl. Phys.* **51** 4356
- [4] Ardnt H, Sauerbier F, Schmidt G and Shebanov A 1988 *Ferroelectrics* **79** 145
- [5] Shannon R D 1976 *Acta Crystallogr. A* **32** 751
- [6] Megaw H D 1969 *Acta Crystallogr. B* **25** 581
- [7] Von der Mühl R, Sadel A, Ravez J and Hagenmuller P 1979 *Solid State Commun.* **31** 151
- [8] Elissalde C, Ravez J and Gaucher P 1992 *Mater. Sci. Eng. B* **13** 327