Journal of Alloys and Compounds 452 (2008) 451–455

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

New relaxor ceramic with composition $BaTi_{1-x}(Zn_{1/3}Nb_{2/3})_xO_3$

L. Khemakhem [a,*], A. Kabadou [a], A. Maalej [b], A. Ben Salah [a],
A. Simon [c], M. Maglione [c]

[a] Laboratoire des Sciences des Matériaux et d'Environnement, Faculté des Sciences de Sfax, BP 802, 3018, Sfax, Tunisia
[b] Laboratoire des Matériaux Ferroélectriques, Faculté des Sciences de Sfax, BP 802, 3018, Sfax, Tunisia
[c] Institut de Chimie de la Matière Condensée de Bordeaux Av. du Dr. A. Schweitzer, 33608 Pessac Cedex, France

Received 12 February 2007; received in revised form 9 March 2007; accepted 12 March 2007
Available online 16 March 2007

Abstract

New ferroelectric ceramics of ABO_3 perovskite type were synthesized in the $BaTi_{1-x}(Zn_{1/3}Nb_{2/3})_xO_3$ system by solid state reaction technique. The effect of the replacement of titanium by zinc (Zn) and niobium (Nb) in the B cationic site on structural and dielectric properties were investigated. As a function of composition, these compounds crystallize with tetragonal or cubic symmetry. The material is classical ferroelectric for $0 \leq x \leq 0.05$ and presents a relaxor behavior for $0.075 \leq x \leq 0.2$ and for $0.75 \leq x \leq 0.975$. Dielectric permittivity in the temperature range from 85 to 500 K with frequencies range from 0.1 to 200 kHz, was studied.

In the region when $0.75 \leq x \leq 0.975$, ΔT_m presents the important values which go more then 100 K for $BaTi_{0.05}(Zn_{1/3}Nb_{2/3})_{0.95}O_3$ composition with values of T_m near room temperature. These values make these ceramic compositions in the families of relaxors with interest properties for applications.

Keywords: Dielectric; Ferroelectric; Relaxor; Perovskite; Ceramic

1. Introduction

The relaxor ferroelectric behavior occurs mainly in the lead based perovskite type compounds and the origin of this phenomenon is still discussed. Setter and Cross proposed that the B site disorder should contribute to the diffuse phase transition behavior of the relaxor ferroelectric lead scandium titanate (PST) [1,2]. Yao et al. proved that the macro-domain to micro-domain transition dominates the dielectric behavior of relaxor ferroelectric ceramics in lanthanum doped lead zirconate titanate (PLZT) [3]. Burns and Dacol [4] and Vielhand et al. [5] treated relaxor ferroelectric as a glassy polarization phase. Cross reviewed the experimental and theoretical history of relaxor ferroelectric in perovskite compounds [6,7].

In order to develop environment-friendly materials, considerable studies have been focused on the lead-free compounds. Barium titanate ceramic is interesting because it presents a paraelectric–ferroelectric transition at about 393 K with a very high dielectric constant.

This material belongs to the perovskite family ABO_3; many investigations reported that homovalent or heterovalent substitutions of barium or titanium ions lead to remarkable changes in various characteristics [8–16]. Ravez and Simon proved that the replacement of Ti^{4+} by Zr^{4+} changes significantly the dielectric and structural properties of $BaTiO_3$:$BaTi_{1-x}Zr_xO_3$ (BTZ) is relaxor ferroelectric for substitution rate higher than about 25% [17]. In BTZ, Ba^{2+} ions in the A site are partially replaced by Ca^{2+}, the relaxor properties are increased [18,19]. In the quantum paraelectric $SrTiO_3$, the A site substitution gives $Sr_{1-x}Ca_xTiO_3$ which exhibits a relaxor dielectric behavior for low rate substitution x [20,21].

The complex perovskite oxide $Ba(Zn_{1/3}Nb_{2/3})O_3$ (BZN) ceramic is very promising for electro ceramic applications owing to their interesting dielectric properties. It can be used, for example, in applications such as ceramics capacitors of hyper frequency resonators [22,23]. The purpose of our research is to investigate the effect of the B site cations in perovskite related materials on the dielectric properties in order to elaborate new

---

* Corresponding author. Tel.: +216 74 276 484; fax: +216 74 274 437.
E-mail address: khemekhemlobna@yahoo.fr (L. Khemakhem).

0925-8388/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2007.03.056

lead-free ceramics with relaxor behavior at room temperature and with interest properties for applications.

2. Experimental

The new polycrystalline ceramics samples of $BaTi_{1-x}(Zn_{1/3}Nb_{2/3})_xO_3$ were prepared by a conventional standard solid state reaction technique. $BaCO_3$, ZnO, Nb_2O_5 and TiO_2 powder, with 99.99% purity, were used. In order to eliminate H_2O, $BaCO_3$, ZnO, Nb_2O_5 and TiO_2 were preheated at 600 °C for 1 h before use. The appropriate mixtures of powders were calcined in flowing oxygen at 1100 °C for 12 h. After carefully milling, the powders were then pressed into pellets, and finally sintered in flowing oxygen at 1320 °C for 3 h.

The relative diameter shrinkage was systematically determined as $\Delta\O/\O = (\O_{\mathrm{init}} - \O_{\mathrm{final}}/\O_{\mathrm{init}})$. $\Delta\O/\O$ of the ceramics is in the range 14–18%. The relative density of the sintered samples d_{exp}/d_X was 90–93% of the theoretical values.

X-ray diffraction analyses show that the samples are single phase only for $0.75 \leq x \leq 0.975$ with cubic structure and for $0 \leq x \leq 0.05$ with tetragonal. For $0.3 \leq x \leq 0.7$, the sample is multiphase.

The dielectric measurements were performed on ceramic discs after deposition of gold electrodes on the circular faces by cathodic sputtering. The real and imaginary relative permittivity ε_r' and ε_r'' were determined under helium as a function of both temperature and frequency using a Wayne–Kerr 6425 component analyzer. The temperature and frequency ranges were 80–600 K and 100 Hz to 100 kHz, respectively. All the dielectric data were collected while heating at a rate of 2 K min^{-1}.

3. Results and discussion

3.1. X-ray diffraction analysis

Figs. 1 and 2, show the X-ray diffraction pattern of the $BaTi_{1-x}(Zn_{1/3}Nb_{2/3})_xO_3$ sample taken at room temperature which reveals that the ceramic was single phased with compositions $x = 0.025$ and 0.1 as examples. All the reflection peaks of the X-ray profile were indexed, and lattice parameters were determined using a global profile-maching method with the Fullprof software [24]. Good agreement between the observed and calculated interplaner spacing suggests that these compositions having tetragonal and cubic structure at room temperature, respectively. These two peaks observed for $x = 0.025$ due to the tetragonal distortion of the lattice (2 0 0) and (0 0 2) reflection emerge in one peak for $x = 0.1$ indicating that the symmetry appears to be cubic. The structure and lattice parameters for $BaTi_{1-x}(Zn_{1/3}Nb_{2/3})_xO_3$ are listed in Table 1.

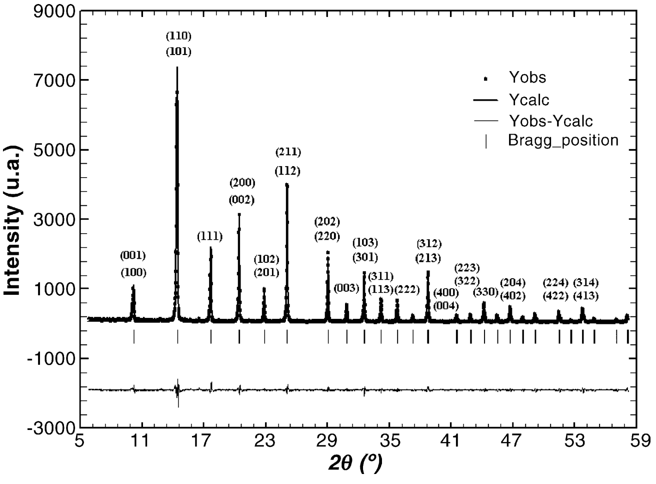

Fig. 1. X-ray diffraction pattern for $BaTi_{0.975}(Zn_{1/3}Nb_{2/3})_{0.025}O_3$ ceramic.

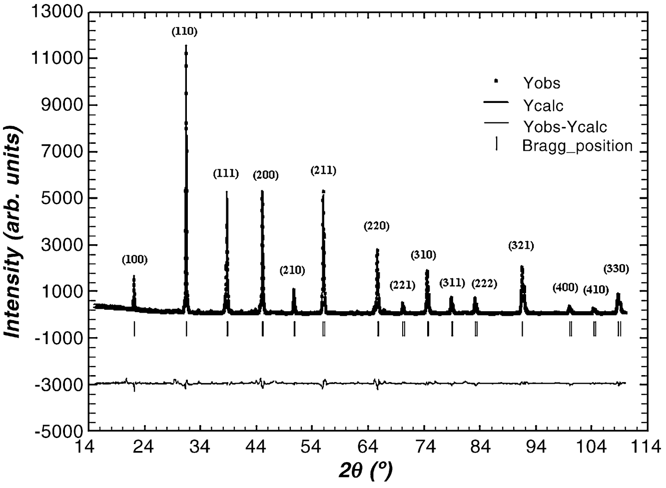

Fig. 2. X-ray diffraction pattern for $BaTi_{0.9}(Zn_{1/3}Nb_{2/3})_{0.1}O_3$ ceramic.

Table 1
Structure and lattice parameters of different compositions in the system $BaTi_{1-x}(Zn_{1/3}Nb_{2/3})_xO_3$

Composition (x)	Structure	a (Å)	c (Å)
0.025	Tetragonal	4.0062(7)	4.0091(5)
0.1	Cubic	4.0212(2)	
0.9	Cubic	4.0095(3)	

3.2. Dielectric studies

The evolution of the real (ε') part of the complex permittivity for $BaTi_{1-x}(Zn_{1/3}Nb_{2/3})_xO_3$ ceramics sample as a function of both temperature and frequency was determined. Three different dielectric behaviors were observed.

For $0 \leq x \leq 0.05$, the sample are of normal ferroelectric behavior composition. For example, Fig. 3 shows the temperature dependence of the real ε_r' parts of the permittivity at several selected measurement frequencies ($100–10^5$ Hz) for $x = 0.025$ sample. Three anomalies related to the phase transitions (rhombohedral–orthorhombic at T_2, orthorhombic–tetragonal at

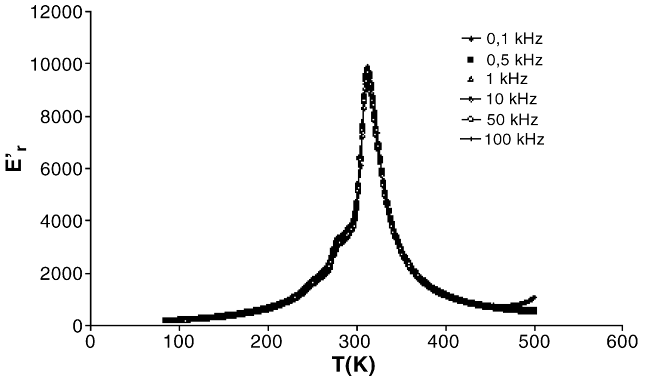

Fig. 3. Temperature dependence of the permittivity ε_r' for $BaTi_{0.975}(Zn_{1/3}Nb_{2/3})_{0.025}O_3$ ceramic.

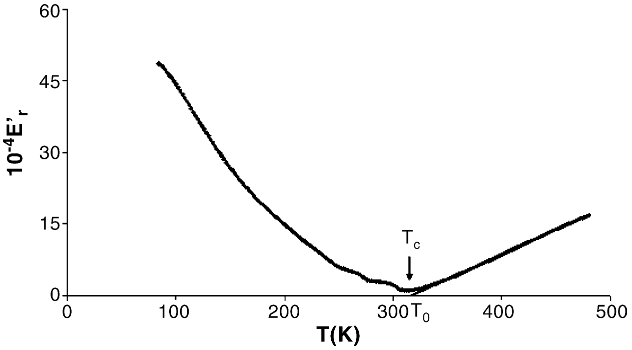

Fig. 4. the variation of $1/\varepsilon'_r$ against temperature for $x = 0.025$.

T_1 and tetragonal–cubic at T_C) for $BaTiO_3$ have been observed at $T_1 = 282$ K, $T_2 = 258$ K and $T_C = 312$ K. We note that there is no significant frequency dispersion for $T < T_C$. The values of T_1, T_2 and T_C were independent on frequency.

Fig. 4 depicts the variation of $1/\varepsilon'_r$ against temperature at 10^3 Hz for the composition $x = 0.025$. The Curie–Weiss law, $\varepsilon'_r = C/(T - T_0)$, holds for $T \geq 312$ K, where C is the Curie constant and T_0 is the Curie temperature. T_0 of 383 K and C of 1.56×10^5 K have been obtained for a pure $BaTiO_3$ crystal [25]. For $BaTi_{0.975}(Zn_{1/3}Nb_{2/3})_{0.025}O_3$, the ε'_r was fitted to the Curie–Weiss law. The fitting parameters are $C = 1.05 \times 10^5$ K and $T_0 = 314$ K nearly equal to T_C at 1 kHz. In Landau's theory of phase transition [19], a first-order transition takes place when $T_C > T_0$, and a second order transition in the case of $T_C \approx T_0$. In our case, the transition is of second order.

For $0.075 \leq x \leq 0.2$ and $0.75 \leq x \leq 0.975$, there is only one broad peak in the thermal evolution of ε'_r at T_m. A frequency dispersion occurs for $T < T_m$ with a shift of T_m with frequency. This frequency dispersion is the highest at $x = 0.95$. Figs. 5 and 6 show the temperature dependencies of the real parts of permittivity ε'_r at different frequencies of samples with compositions $x = 0.1$ and 0.95. Diffuse transition with frequency dispersion above and around the ε'_r peak were observed. The temperature and frequency variations of ε'_r were also specific: the temperature T_m of ε'_r maximum was shifted to higher values on increasing frequency. The evolution of the frequency dispersion was here characterized by an increase in ε'_r when frequency increased. This shows that these compositions are of a relaxor type.

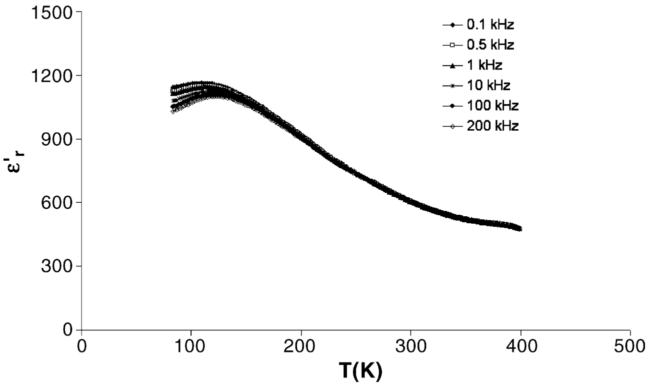

Fig. 5. Temperature dependence of the permittivity ε'_r for $x = 0.1$.

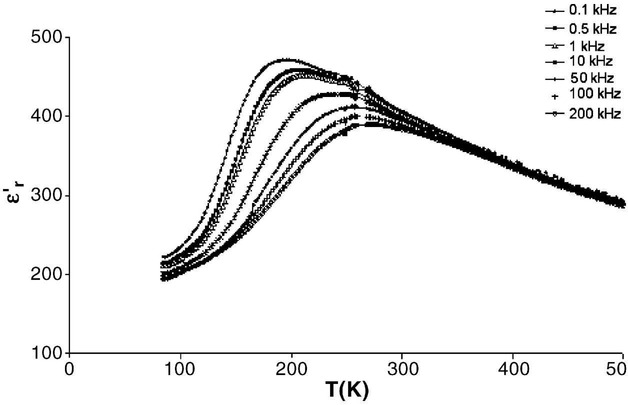

Fig. 6. Temperature dependence of the permittivity ε'_r for $x = 0.95$.

The relaxor characteristics for some compositions are reported in Table 2 as the T_m shift, $\Delta T_m = T_m(10^5\,\text{Hz}) - T_m(10^2\,\text{Hz})$ and the frequency relative dispersion $\Delta\varepsilon'_r/\varepsilon'_r = \varepsilon'_r(10^2\,\text{Hz}) - \varepsilon'_r(10^5\,\text{Hz})/\varepsilon'_r(10^2\,\text{Hz})$.

For compositions in the region $0.075 \leq x \leq 0.2$, ε'_r presents an evolution in ferroelectric phase as a function of frequency which shows a relaxor behavior but ΔT_m in this case is not very important, $\Delta T_m \approx 10$ K and T_m is lower ($T_m \approx 130$ K) so this composition cannot be considered as good relaxor for applications.

However, for compositions in the region $0.75 \leq x \leq 0.975$, the value of ΔT_m allows to 100 K for $x = 0.95$ composition, which make these compositions in the family of ferroelectrics as of very important for applications compared to PMN.

It can be noted that the partial substitution of Ba^{2+} by Zn^{2+} and Nb^{5+} in $BaTiO_3$ has considerable effects: apparition of the relaxor behavior and decrease of T_m to room temperature.

The broadened peaks indicate that the transition in all these compositions is of the diffuse type, an important characteristic of a disordered perovskite structure. In addition, there was a deviation from the Curie–Weiss law. The real part of dielectric permittivity follows the Curie–Weiss law at $T > T_{dev} = 264$ K (T_{dev} represents the temperature at which ε'_r deviates from Curie–Weiss law) (Fig. 7).

It is known that the relaxor ferroelectric behavior should be described by the Vogel–Fülcher relation [26]:

$$f = f_0 \exp\left(\frac{-E_a}{k_b(T_m - T_f)}\right)$$

where f, E_a and T_f are the applied frequency, the activation energy and the freezing temperature of the dipoles, k_b the Boltzmann

Table 2
Values of T_m, ΔT_m and $\Delta\varepsilon'_r/\varepsilon'_r$ characteristics of the relaxor behavior of some $BaTi_{1-x}(Zn_{1/3}Nb_{2/3})_xO_3$ ceramics with various compositions

x	T_m (K) at 1 kHz	ΔT_m (K)	$\Delta\varepsilon'_r/\varepsilon'_r$
0.025	312	0	0
0.1	119	10	0.0431
0.15	112	12	0.0570
0.90	197	90	0.0860
0.95	210	100	0.1512

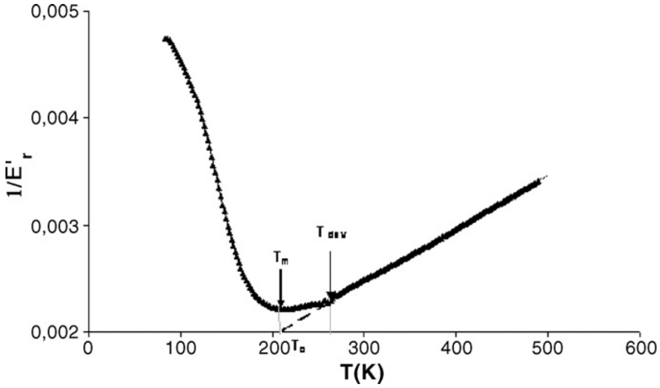

Fig. 7. the variation of $1/\varepsilon'_r$ against temperature for $x = 0.95$.

constant and f_0 the Debye frequency. In our case, the composition $x = 0.95$ is also the subject of this relation. In Fig. 8, we present the variation of $\log f$ as a function of $1/T_m$ for $x = 0.95$.

The fitting parameters of Vogel–Fülcher relation were:

$$E_a = 0.063\,\mathrm{eV}, \quad f_0 = 3.45 \times 10^4\,\mathrm{Hz} \quad \text{and} \quad T_f = 132.05\,\mathrm{K}.$$

The degree of disorder of the $BaTi_{1-x}(Zn_{1/3}Nb_{2/3})_xO_3$ was evaluated using an empirical formula developed by Uchino and Nomura [27]:

$$\frac{1}{\varepsilon'_r} - \frac{1}{\varepsilon'_{r\,max}} = \frac{(T - T\varepsilon'_{r\,max})^{\gamma}}{C'}$$

where C is a constant and γ is a measure of diffuseness; γ value is between 1 and 2. The parameters γ gives information on the character of the phase transition and only depending on the composition of the specimens. The limiting value $\gamma = 1$ and 2 reduce the equation to Curie–Weiss law for the case of normal ferroelectric and for ideal relaxor ferroelectric, respectively [28].

The logarithmic plots related to this equation for all doped compositions $x = 0.025$–0.9–0.95 are shown in Fig. 9(a and b).

The slope of the fitting is used to determine the value of γ at 10 kHz. These parameters are $\gamma = 1.1501$–1.9101, respectively, for $x = 0.025$ and 0.95. These results confirmed the diffuse phase transition for compound with $x = 0.95$.

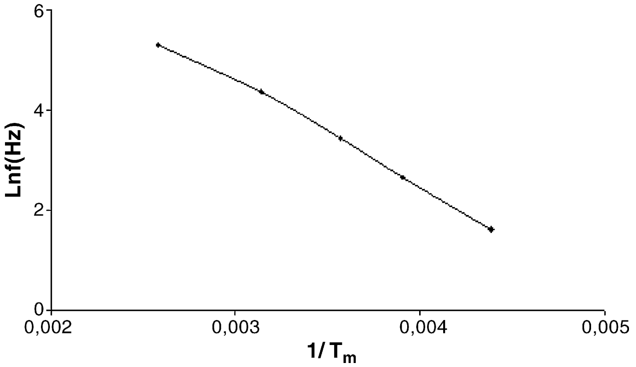

Fig. 8. Plot of ln(f) as a function of T_m for $x = 0.95$ (the symbols: experimental data; the solid curve: fitting to the Vogel–Fulcher relation).

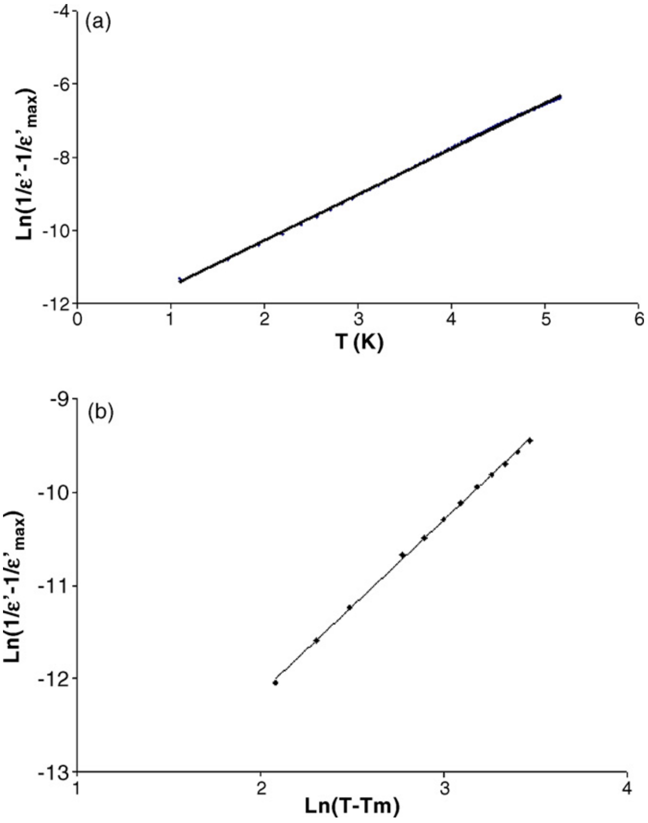

Fig. 9. (a and b): Plot of $\ln(1/\varepsilon - 1/\varepsilon_{max})$ as a function $\ln(T - T_m)$ at 10 kHz for the compositions, $x = 0.025$–0.95.

4. Conclusion

Ceramic samples of niobium (Nb) and zinc (Zn) doped barium titanate with general composition $BaTi_{1-x}(Zn_{1/3}Nb_{2/3})_xO_3$ have been elaborated by solid state reaction method. It was shown by X-ray diffraction at room temperature that the structure of the compounds is of perovskite type. Dielectric measurements shows that the permittivity peak in the compound with $x = 0.025$ composition is sharp, without frequency dependence: it is a typical ferroelectric–paraelectric phase transition.

For compositions in the regions $0.075 \le x \le 0.2$ and $0.75 \le x \le 0.975$, the phase transitions becomes diffuse and characterizes a relaxor behavior.

The relaxor character in the first region is characterized by lower values of ΔT_m ($\Delta T_m \approx 10$ K for $x = 0.1$) and low values of T_m ($T_m \approx 130$ K for $x = 0.1$).

So these relaxors are not very interesting for applications. However, for compositions in the region $0.75 \le x \le 0.975$, we consider that relaxor characteristics are very interesting for applications compared to those of PMN ($\Delta T_m \approx 100$ K for $x = 0.95$).

References

[1] N. Setter, L.E. Cross, J. Mater. Sci. 15 (1980) 2478.
[2] N. Setter, L.E. Cross, J. Appl. Phys. 51 (1980) 4356.
[3] X. Yao, Z.L. Chen, L.E. Cross, J. Appl. Phys. 54 (1984) 3399.
[4] G. Burns, F.H. Dacol, Ferroelectrics 104 (1990) 25.

[5] D. Vielhand, S.J. Jang, L.E. Cross, J. Appl. Phys. 68 (1984) 2916.
[6] L.E. Cross, Ferroelectrics 76 (1987) 241.
[7] L.E. Cross, Ferroelectrics 151 (1994) 305.
[8] J. Ravez, A. Simon, Phys. Status Solidi 159 (1997) 517.
[9] A. Outzourhit, M.A. El Idrissi Raghni, M.L. Hafid, F. Bensamka, J. Alloys Compd. 340 (2002) 214.
[10] A. Simon, J. Ravez, Ferroelectrics 240 (2000) 335.
[11] M. Lorenz, H. Hochmuth, M. Schallner, R. Heidinger, D. Spemann, M. Grundmann, Solid State Electron. 47 (2003) 2199.
[12] A. Aydi, H. Khemakhem, C. Boudaya, A. Simon, R. Von Der Mühll, Solid State Sci. 7 (2005) 249.
[13] X.G. Tang, J. Wang, X.X. Wang, H.L.W. Chan, Solid State Commun. 131 (2004) 163.
[14] P. Jha, A.K. Ganguli, Solid State Sci. 6 (2004) 663.
[15] G. Li, S. Liu, F. Liao, S. Tian, X. Jing, J. Lin, Y. Uesu, K. Kohn, K. Saitoh, M. Terauchi, N. Di, Z. Cheng, J. Solid State Chem. 177 (2004) 1695.
[16] Q. Xu, S. Chen, W. Chen, S. Wu, J. Zhou, H. Sun, Y. Li, Mater. Chem. Phys. 90 (2005) 111.
[17] J. Ravez, A. Simon, J. Kor. Phys. Soc. 32 (1998) S955.
[18] Ph. Sciau, G. Calvarin, J. Ravez, Solid State Commun. 113 (2000) 77.
[19] J. Ravez, C. Broustera, A. Simon, J. Mater. Chem. 9 (1999) 1609.
[20] J.G. Bednorz, A.K. Müller, Phys. Rev. Lett. 52 (1984) 2289.
[21] A.S. Prosandeev, W. Kleemann, J. Dec, J. Phys.: Condens. Matter 13 (2001) 5957.
[22] K. Endo, K. Fujimoto, K. Murakawa, J. Am. Ceram. Soc. 70 (9) (1987) 215.
[23] I.M. Reaney, American Ceram. Soc. Meeting, May 2002 (Abstract AMA. 1-B-01).
[24] T. Roismel (1), J. Rodriguez-Carvajal (2), Program Fullprof, Laboratoire de Chimie du Solide Inorganique et moléculaire 4MR6511, CNRS-Université de rennes (1). Laboratoire Brillouin (CEA-CNRS) (2), version 3.70, May 2004, LLB-LCSIM, March 2005.
[25] W.J. Mertz, Phys. Rev. 91 (1953) 513.
[26] H. Vogel, Z Phys. 22 (1921) 645;
G. Fulcher, J. Am. Ceram. Soc. 8 (1925) 339.
[27] K. Uchino, S. Nomura, Ferroelectrics Lett. 44 (1982) 55.
[28] D. Viehland, M. Wuttig, L.E. Cross, Ferroelectrics 120 (1991) 71.