

# Dielectric study of ferroelectric or relaxor Behavior in $\text{Ba}_{1-x}\text{Na}_x(\text{Ti}_{0,8}\text{Sn}_{0,2})_{1-x}\text{NbO}_3$ ceramics

A. AYDI<sup>a\*</sup>, A. SIMON<sup>b</sup>, D. MICHAU<sup>b</sup>, R. VON DER MÜHLL<sup>b</sup>, N. ABDELMOULA<sup>a</sup>, H. KHEMAKHEM<sup>a</sup>

<sup>a</sup>Laboratoire des Matériaux Ferroélectriques, Faculté des Sciences de Sfax, 3018 Sfax, Tunisie

<sup>b</sup>CNRS, Université de Bordeaux, ICMCB, 87 Avenue Dr A. Schweitzer, Pessac, F - 33608

The ferroelectric and piezoelectric properties of  $\text{Ba}_{1-x}\text{Na}_x(\text{Ti}_{0,8}\text{Sn}_{0,2})_{1-x}\text{NbO}_3$  (BTSnNx0.2), the new lead-free ceramic, are investigated. At room temperature, X-ray diffraction (XRD) study suggests that the compositions have a single phase with cubic symmetry. The dielectric study reveals that the material has a ferroelectric or a relaxor behavior. The polarization state is checked by hysteresis and piezoelectric measurements.

(Received February 4, 2012; accepted April 11, 2012)

**Keywords:** Ceramic, Permittivity, Ferroelectric, Relaxor, Piezoelectricity

## 1. Introduction

A large number of perovskite materials exhibit a ferroelectric or relaxor behavior [1, 2, 3, 4]. These materials can be very useful for different solid-state devices [5, 6, 7]. The best known relaxor is  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ , a lead-based ceramic with a perovskite structure. Its derived compounds are also the best lead-based relaxors. In accordance with environmental concerns, we have to avoid PbO-related problems; thus, researchers have moved toward lead-free relaxors [8, 9, 10, 11].

The relaxor effect was then related to the substitution within octahedral site in lead-free perovskites which are derived from  $\text{BaTiO}_3$  [12, 13, 14]. This behavior can be related to either a cationic or anionic disorder in the A or B sites of  $\text{ABO}_3$  structure [15, 16].

The aim of the present work is to study the dielectric response temperature and frequency of BTSnNx0.2 ceramics to experimentally point out the ferroelectric behavior of these materials using dielectric, hysteresis and piezoelectric measurements.

## 2. Experimental process

The polycrystalline ceramic samples of BTSnNx0.2 were prepared via solid-state reactions at 1030°C for 15 hours under oxygen atmosphere, using  $\text{BaCO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{TiO}_2$ ,  $\text{SnO}_2$  and  $\text{Nb}_2\text{O}_5$  powders in stoichiometric amounts.

Weighed ingredients were pressed under 100 MPa into disks of 8 mm in diameter and about 1 mm in thickness. Calcination was done at 1030 °C for 15 hours, followed by a two-hour sintering period at 1250°C for  $0.60 \leq x \leq 0.90$ .

The relative diameter shrinkage,  $\frac{\Delta\Phi}{\Phi} = \frac{\Phi_{init} - \Phi_{end}}{\Phi_{init}}$

(initial diameter - final diameter / initial diameter) and the compactness (experimental density / theoretical density) were systematically determined. Their average values were in the range of 11-16 % and 91-95%, respectively depending on the composition.

XRD patterns were recorded on a Philips diffractometer using the  $\text{CuK}\alpha$  radiation, the angular range  $10 \leq 2\theta \leq 110^\circ$  (with each step =  $0.02^\circ$ ) and 10 seconds counting.

Dielectric measurements were performed on ceramic disks after deposition of gold electrodes on the circular faces by cathodic sputtering. The real and imaginary parts of relative permittivity, which are respectively  $\epsilon_r'$  and  $\epsilon_r''$ , were determined under helium atmosphere versus both temperature (80 - 600K) and frequency ( $10^2$  -  $2.10^6$  Hz) using a Wayne - Kerr 6425 frequency analyzer.

A conventional Sawyer-Tower circuit was used to measure the polarisation hysteresis (P-E) loop at 50 Hz. The electromechanical coupling factor  $k_p$  and the piezoelectric coefficient  $d_{31}$  were determined by the resonance method according to IEEE standard using an impedance analyser (HP 4194 A).

A Scanning Electronic Microscope (SEM), JEOL 6360A, was used to characterize the microstructure.

## 3. Results and discussion

The SEM micrograph of BTSnNx0.2 ceramic is shown on Fig.1. All samples were sintered at 1250°C for 2 hours. We obtain a well dense ceramic with an average grain size of about  $2\mu\text{m}$ .

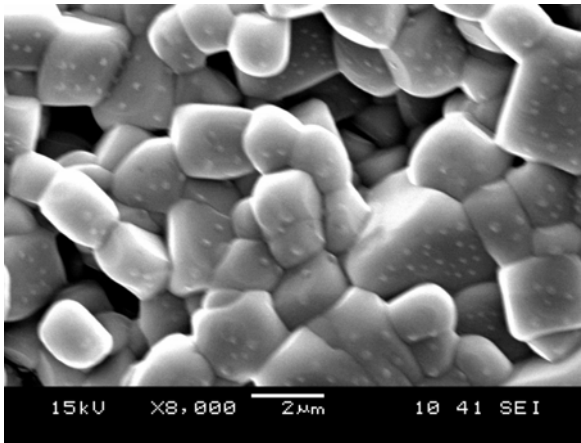


Fig.1 : SEM picture of the surface of  $BTSnNx_{0.2}$  ceramic ( $x = 0.85$ ).

XRD measurements of  $BTSnNx_{0.2}$  ( $x = 0.80$ ) powder are reported in Fig.2. The results reveal a single perovskite phase with cubic structure. The cell parameters were calculated by least-square refinement. Good agreement between the observed and the calculated interplaner spacing suggests that this composition has a cubic structure at room temperature. Final refinement with the cubic space group  $Pm\bar{3}m$  gives the estimated value of unit cell parameter  $a = 4,010 \text{ \AA}$ . The powder diffraction data are given in Table 1.

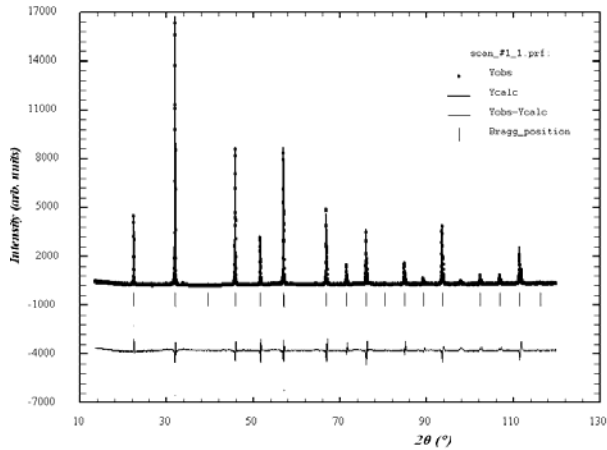


Fig. 2. XRD pattern of a  $BTSnNx_{0.2}$  ( $x = 0.8$ ) powder.

Table 1. X-ray powder diffraction data for  $BTSnNx_{0.2}$  ( $x = 0.8$ ).

Bragg	h k l
22.46	0 0 1
31.90	1 0 1
40.02	1 1 1
45.72	0 0 2
51.52	1 0 2
56.82	1 1 2
66.68	2 0 2
71.30	0 0 3
76.02	1 0 3
80.22	1 1 3
84.52	2 2 2
93.22	2 1 3
98.82	2 0 3
101.92	0 0 4
106.42	1 0 4
111.02	1 1 4

Fig. 3a; 3b; 3c; 3d; 3e and 3f show temperature dependence of the real permittivity  $\epsilon'_r$  in the frequency range 0.1 - 200 kHz for  $BTSnNx_{0.2}$  ( $x = 0,6; 0,7; 0,8; 0,825; 0,85$  and  $0,90$ ).

For  $x < 0,85$ , the samples are of relaxor behavior compositions. There is only one broad peak in temperature evolution of  $\epsilon'_r$  at  $T_m$ . A frequency dispersion occurs while  $T < T_m$  with a shift of  $T_m$  when the frequency varies. The temperature  $T_m$  of maximum  $\epsilon'_r$  ( $\epsilon'_{r,max}$ ) shifted to higher values on frequency increase.  $T_m$  is near 300 K for  $x = 0,8$ .

For  $x \geq 0,85$ , The samples reveal ferroelectric behavior compositions. Three anomalies are observed when the temperature increases gradually for  $BTSnNx_{0.2}$  ( $x = 0.90$ ). These anomalies are related to the trigonal-orthorhombic, orthorhombic-tetragonal and tetragonal-cubic phase transitions at  $T_C$ .

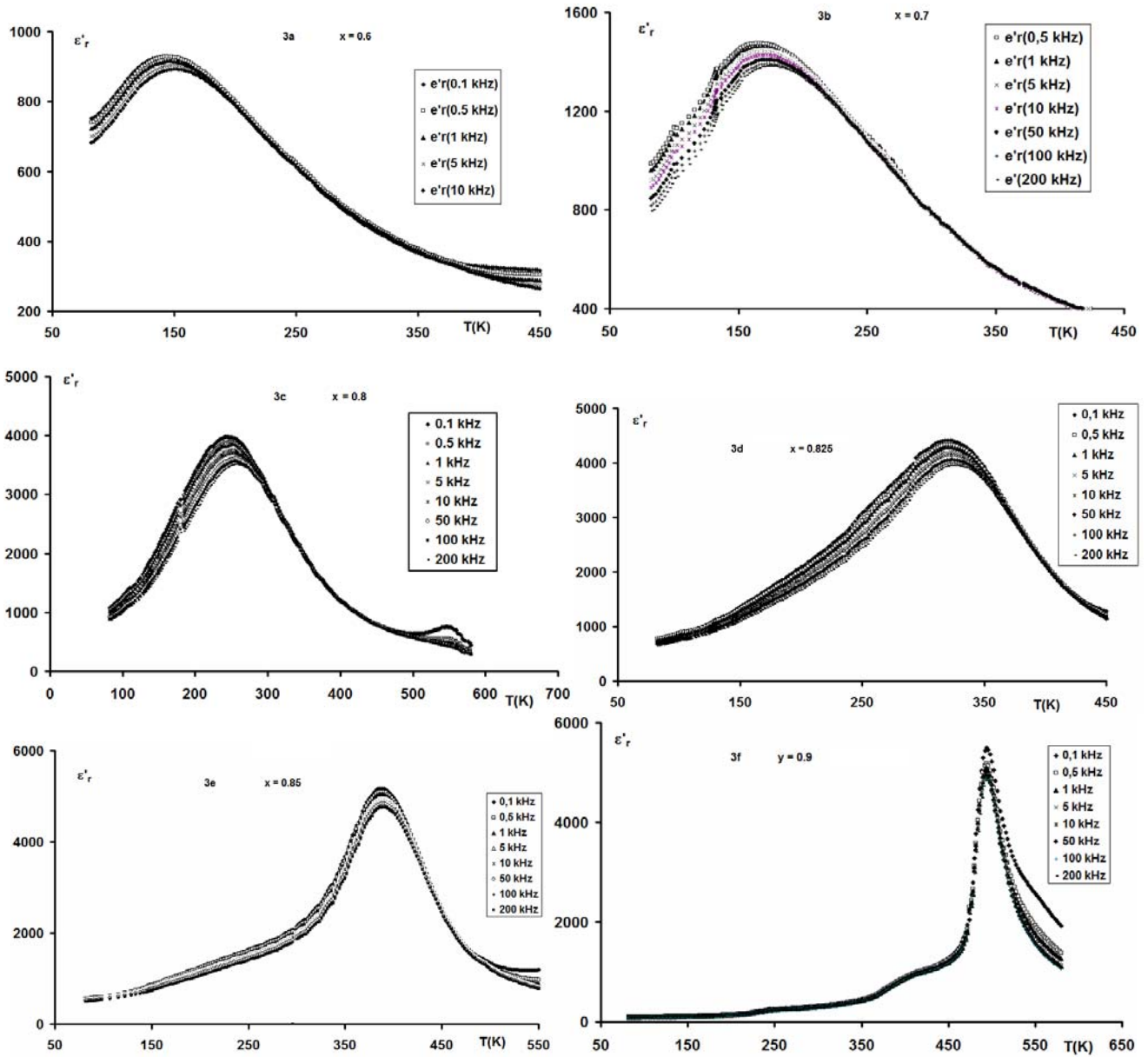


Fig 3. Thermal variation of permittivity  $\epsilon'_r$  for  $\text{BTSnN}x0.2$  ( $x = 0,6; 0,7; 0,8; 0,825; 0,85$  and  $0,90$ ).

Fig. 4a; 4b; 4c and 4d show the thermal evolution of the imaginary part of the permittivity for some ceramics. The dielectric losses are about 2 %.

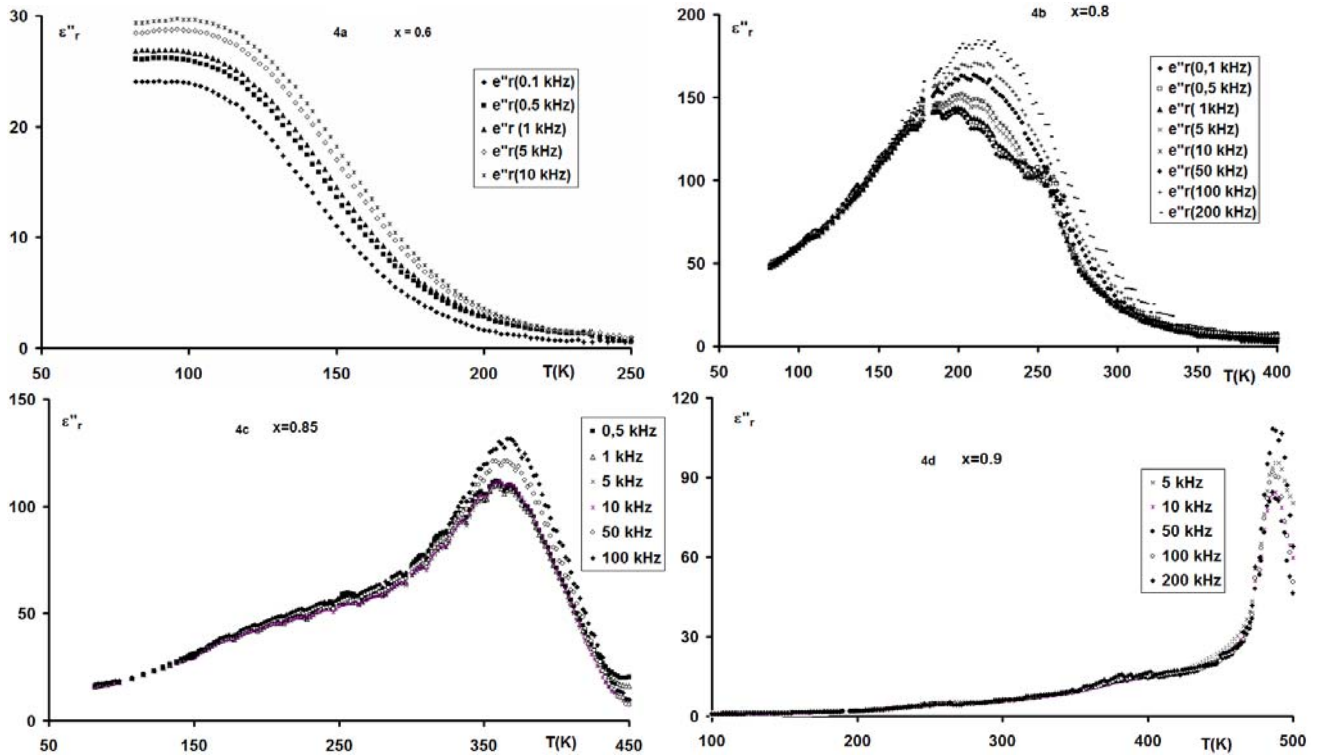


Fig 4. Thermal variation of permittivity  $\epsilon''_r$  for  $\text{BTSnN}x0.2$  ( $x = 0,6; 0,8; 0,85; \text{ and } 0,9$ ).

The dielectric measurement shows that  $\epsilon'_{r, \text{max}} = 6000$  for ceramic solution  $\text{BTSnN}x0.2$  ( $x = 0.90$ ) but for the  $\text{BSNN}0.9$  ceramic,  $\epsilon'_{r, \text{max}} = 1947$  [4]. Therefore, the addition of titanium (Ti) shows an increase of the maximum value of permittivity.

The variation of the temperature of dielectric anomalies as a function of composition  $x$  is shown in Fig.5. It can be observed that the value of  $T_m$  or  $T_c$  increases when  $x$  increases. The relaxor character becomes more important when the composition parameter  $x$  decreases. This behavior is then similar to the others reported in the literature [4].

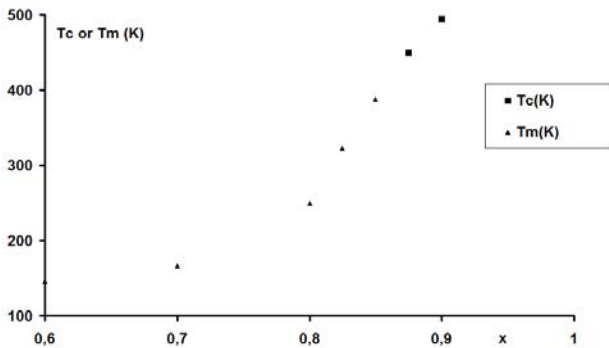


Fig. 5. Variation of  $T_c$  or  $T_m$  vs composition for  $\text{BTSnN}x0.2$  ceramics.

Fig.6a and 6b depict the temperature dependence of  $1/\epsilon'_r$  at 1 kHz for the compositions  $x = 0,8$  and  $x = 0,85$ , respectively. For  $x = 0.85$ ,  $T_c = T_0$ , where  $T_0$  and  $C$  is the

Curie-Weiss temperature and constant, respectively defined by  $1/\epsilon'_r = (T - T_0)/C$  and the phase transition was clearly of the second order. However, a deviation from the Curie-Weiss was observed for the composition  $x = 0,8$ .

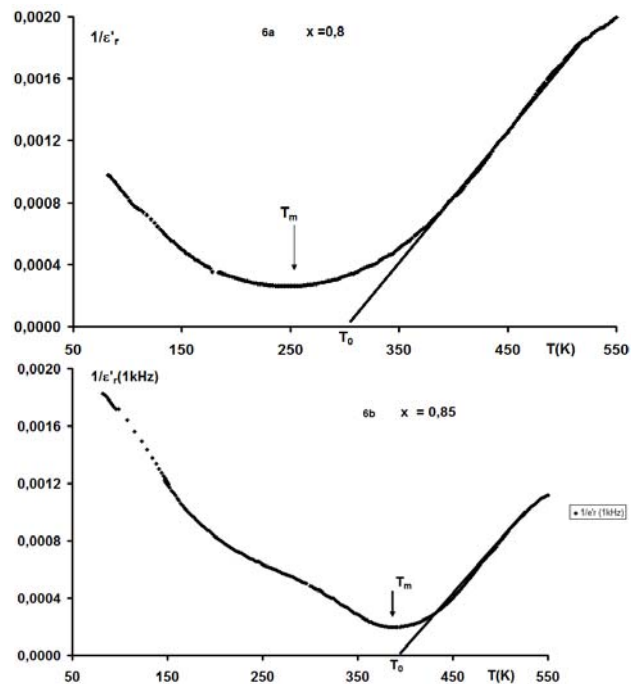


Fig 6. Thermal variation of  $1/\epsilon'_r$  (1kHz) for  $\text{BTSnN}x0.2$  ( $x = 0.8 \text{ and } 0.85$ ).

In order to demonstrate the ferroelectric character of the material, we attempt to measure the hysteresis or piezoelectric effect of polarized ceramics.

Ambient temperature ( $T = 300K$ ) which is far below  $T_C = 324; 388; 392K$  (for  $x = 0.825; 0,85; 0,875$  respectively), ferroelectric (P-E (polarisation-field)) loops are observed in Fig 7a; 7b and 7c. Spontaneous polarizations are  $P_s = 1, 92; 1.54$  and  $1,37 \mu C/cm^2$  and coercive fields  $E_c = 3,31; 4.53$  and  $5,1 kV/cm$  for compositions  $x = 0.825; 0,85$  and  $0,875$ , respectively. These figures show that the material has good ferroelectric nature. The shape of P-E loops varies with  $x$ . It can be seen that for low applied fields, the P-E loops is far from saturation. Sharp and well saturation squared P-E loops could be observed for increasing  $E$  showing full domain switching.

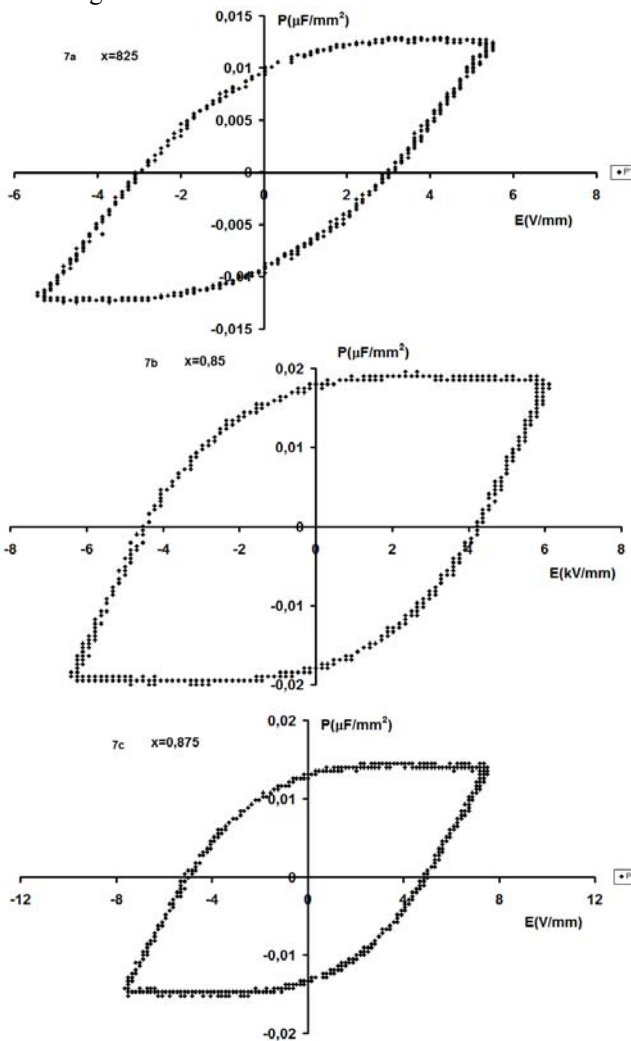


Fig. 7. P- E hysteresis loops of  $BTSnNx0.2$  ( $x = 0,825; 0,85$  and  $0,875$ )

The piezoelectric measurements were performed at room temperature on the ceramic with composition  $BTSnNx0.2$  ( $x = 0.85$ ). The admittance and susceptance of this ceramic disk were measured versus frequency around the main transverse resonance mode. The variation of the admittance ( $G$ ) and the susceptance ( $B$ ) versus frequency is shown on Fig.8 and Fig 9.

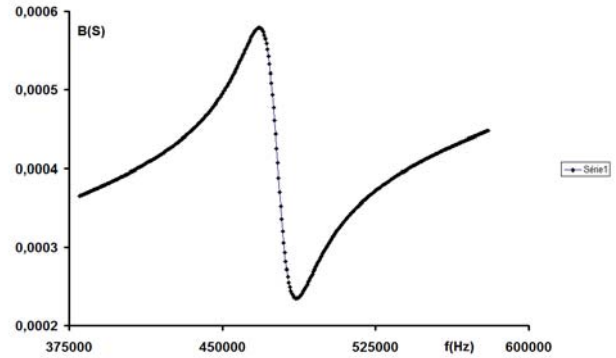


Fig. 8. Variation of the susceptance ( $B$ ) as function of frequency at  $T = 300 K$  for  $BTSnNx0.2$  ceramic with  $x = 0.85$ .

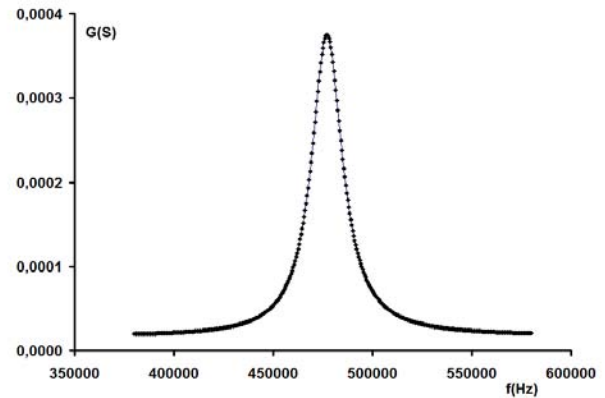


Fig. 9. Variation of the admittance ( $G$ ) as function of frequency at  $T = 300 K$  for  $BTSnNx0.2$  ceramic with  $x = 0.85$ .

The decrease of  $B$  and the increase of  $G$  as well indicate the ferroelectric- paraelectric transition.

Fig. 10 reflects the admittance circle ( $B$ - $G$ ) recorded at  $300 K$  and the calculation of the transverse piezoelectric coefficient at room temperature yields  $d_{31} = 69,5pC/N$ . This value is obtained by fitting the admittance circle  $B = f(G)$ .

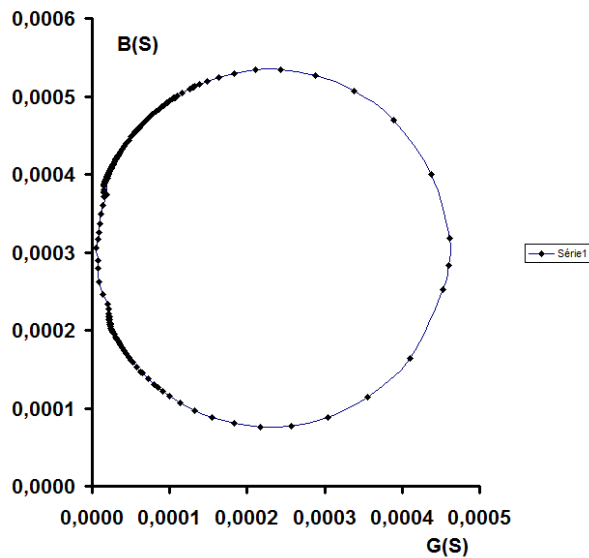


Fig. 10. Piezoelectric admittance circle at the main radial resonance for  $BTSnN_{x0.2}$  ( $x = 0.85$ ), at 300 K.

#### 4. Conclusions

$BTSnN_{x0.2}$  ceramics were prepared by a solid-state technique. The XRD study shows that the compound exists in a single phase at room temperature. Dielectric measurements reveal two kinds of behavior depending on the type of composition: classical ferroelectric or relaxor.

According to the dielectric properties, the addition of Titanium (Ti) shows the increase of the maximum value of permittivity.

The piezoelectric coefficient  $d_{31} = 69,5 \text{ pC/N}$  and the Spontaneous polarizations  $P_s = 1,92 \text{ } \mu\text{C/cm}^2$  make these lead-free ceramics suitable for diverse applications (dielectrics for capacitors, actuators...).

#### References

- [1] A. kerfah, K. Taïb, A. Guerhia-Laidoudi, A. Simon, J. Ravez., *Solid State Sci.* **8**, 613 (2006).
- [2] N. Nanakorn, P. Jaluppom, N. raneesorn, A. Thanaboonsombut., *Ceramics International.* **34**, 779 (2008).
- [3] L. Khemakhem, A. Maalej, A. Kabadou, A. Ben Salah, A. Simon, M. Maglione., *J Alloys Compd.* **452**, 441 (2008).
- [4] A. Aydi, H. Khemakhem, C. Boudaya, R. Von Der Mühl, A. Simon., *Solid State Sci.* **6**, 333 (2004).
- [5] E Cross., *Nature.* **432**, 24 (2004).
- [6] Y. Saito, H. Takoo, T. Tani et al., *Nature.* **84** (2004).
- [7] T. Takenouaka, H. Magata., *J Eur Ceram Soc.* **25**, 2693 (2005).
- [8] A. Aydi, H. Khemakhem, A. Simon, D. Michau, R. Von Der Mühl., *J. Alloys. Compounds.* **484 - 1, 2, 18**, 356 (2009).
- [9] A. Aydi, H. Khemakhem, C. Boudaya, A. Simon, R. Von Der Mühl., *Sol. State Sci.* **73**, 249 (2005).
- [10] Ravez. J and Simon. A., *Eur. J. Solid State Inorg. Chem.* **34**, 1199 (1997).
- [11] R. Von Der Mühl, A. Simon, C. Elissalde, A. Villesuzanne., *J Phys Chem Solids.* **65**, 1039 (2004).
- [12] K. Aliouane, A. Guehria-Laidoudi, A. Simon, J. Ravez., *Solid State Sci.* **7**, 1324 (2005).
- [13] F. D Morrison, D. C Sinclair, A. R West., *Int j Mat.* **3**, 1205 (2001).
- [14] M. Maglione, U. T Höchli, J. Joffrin., *Phys Rev Lett.* **57**, 436 (1987).
- [15] U. T Höchli, K. Knorr, A. Loidl., *Adv Phys.* **39**, 405 (1990).
- [16] L. E Cross., *Ferroelectrics.* **76**, 241 (1987).

\*Corresponding author: aydi\_abdelhedi@yahoo.fr