Journal of the European Ceramic Society 21 (2001) 1303–1306
www.elsevier.com/locate/jeurceramsoc

Relaxor properties of Ba-based layered perovskites

C. Miranda, M.E.V. Costa *, M. Avdeev, A.L. Kholkin, J.L. Baptista

Department of Ceramic and Glass Engineering, University of Aveiro, 3810-193 Aveiro, Portugal

Received 4 September 2000; received in revised form 23 October 2000; accepted 30 October 2000

Abstract

Ferroelectric materials with Bi-layered structure such as SrBi$_2$Ta$_2$O$_9$ (SBT) and SrBi$_2$Nb$_2$O$_9$ (SBN) are now intensively investigated in view of their applications in non-volatile computer memories and high-temperature piezoelectric transducers. When Sr is substituted with Ba, significant disorder is induced and material exhibits broadening of the phase transition. In this work, BaBi$_2$Ta$_2$O$_9$ (BBT) and Ba$_2$Bi$_2$Nb$_2$O$_9$ (BBN) ceramics were sintered using mixed oxide route. Dielectric properties were investigated in the temperature range 20–600°C at frequencies 25 Hz to 1 MHz. Strong dispersion of the dielectric permittivity is found indicating relaxor nature of the phase transition. It is shown that the dielectric relaxation in BBN ceramics is different from that of conventional relaxors such as PbMg$_{1/3}$Nb$_{2/3}$O$_3$ (PMN). Fitting with Vögel–Fulcher relationship is used to evaluate parameters of the dielectric relaxation such as freezing temperature and attempt frequency. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Dielectric properties; Perovskites; Relaxor ferroelectrics

1. Introduction

At the beginning of 1960s Smolenskii et al.[1] reported a considerable diffuseness of the phase transformation in Ba-based ferroelectrics with Bi-layered structure, BaBi$_2$Ta$_2$O$_9$ (BBT) and BaBi$_2$Nb$_2$O$_9$ (BBN). They also found that in solid solutions of Ba$_{1-x}$ Sr$_x$Bi$_2$Nb$_2$O$_9$ (BSBN) the degree of diffuseness gradually decreases with the substitution Ba^{2+} by Sr^{2+} [2] thus leading to a sharp phase transition in SrBi$_2$Nb$_2$O$_9$ (SBN). In this family of ferroelectrics, first discovered by Aurivillius, the oxygen octahedra blocks responsible for ferroelectric behaviour are interleaved with (Bi$_2$O$_2$)$^{2+}$ layers resulting in a highly anisotropic crystallographic structure where *c*-parameter [normal to (Bi$_2$O$_2$)$^{2+}$ layers] is much greater than *a* and *b* parameters of the orthorhombic cell. Later, it was observed that, along with the large crystallographic anisotropy, Bi-layered perovskites demonstrate highly anisotropic electrical properties,[3] In particular, ferroelectric switching occurs predominantly in the (*a*,*b*) plane leading to a low switchable polarisation and poor piezoelectric properties of ceramic samples.[3,4] It was originally suggested by Smolenskii et al.[1] that large Ba ions ($R = 1.61$ Å) not only substitute Sr in perovskite blocks but enter Bi$_2$O$_2$ layers leading to inhomogeneous distribution of Ba and local charge imbalance in layered structure. This was recently confirmed by detailed X-ray and neutron diffraction investigations.[5,6] Ba-induced disorder is a probable source of the diffuseness of the phase transformation and apparent relaxor behaviour in these materials. Recently, the interest in Bi-layered perovskites (especially in a thin layer form) was raised due to their excellent stability against repetitive switching (fatigue endurance).[7] and useful piezoelectric properties.[8] Sr-based layered perovskites, SrBi$_2$Ta$_2$O$_9$ (SBT) and SrBi$_2$Nb$_2$O$_9$ (SBN), are currently the major candidates for new generation of non-volatile ferroelectric memories.[9] In this regard, their Ba-based counterparts, BBN and BBT, are of great interest in view of tailoring the mechanism of polarisation switching and controlling the degree of diffuseness of the phase transitions in these technologically important materials. Another motivation of this work was to study the mechanism of the relaxor behaviour in highly anisotropic (layered) structure and compare it with the relaxation mechanism in conventional relaxors such as Pb(Mg,Nb)O$_3$ (PMN) or Pb(La,Zr,Ti)O$_3$ (PLZT) with almost isotropic crystallographic structure.

---

* Corresponding author. Tel.: +351-234-370354; fax: +351-234-25300.

E-mail address: elisabete@cv.ua.pt (M.E.V. Costa).

0955-2219/01/$ - see front matter
PII: S0955-2219(01)00006-1

2. Experimental

BBN and BBT ceramics were prepared by mixed oxide method using $BaCO_3$, Bi_2O_3, Nb_2O_5 and Ta_2O_5 as starting reagents (all from Aldrich, 99% pure). The stoichiometric mixtures of oxides were thoroughly milled, calcined at 950°C for 2 h, uniaxially pressed at 190 MPa and sintered at temperatures varied from 1000 to 1150°C. Table 1 summarises sintering conditions, relative densities of sintered pellets and some selected electrical properties. Some of the samples were quenched from the temperature 1000°C by direct withdrawal of the sample to the room temperature. Sintering conditions were varied in order to obtain pure phase samples with high density and minimum porosity. In BBT samples quenching resulted in a large increase of the dielectric permittivity maximum, however in BBN specimens properties practically did not change. Sintered pellets were polished and Au electrodes were sputtered on their major surfaces for the electrical measurements.

Calcined and sintered specimens were analysed by X-ray diffraction (Rigaku, D/Max-B, CuK_α radiation). Scanning electron micrographs (Hitachi S4100) were taken from polished surfaces that were used for grain size and morphology determination. Dielectric properties were measured with a HP4284A LCR-meter in a frequency range 25 Hz to 1 MHz at applied ac electric field of about 1 V/cm. Samples were heated and cooled in a tube furnace with the heating and cooling rates of 1°C/min.

3. Results and discussion

Dense BBN ceramic samples were obtained after sintering at temperatures of 1100–1150°C. No second phases were found according to XRD results, and the relative density of the pellets was above 98%. The ceramic samples presented a homogeneous microstructure as illustrated in Fig. 1. For BBT composition, 1000°C was the optimum sintering temperature leading to single phase ceramics with a relative density of ~95%. In ceramics sintered at 1050°C, XRD revealed the presence of second phases. Fig. 2 shows the real (ε') and imaginary (ε'') parts of the dielectric permittivity vs. temperature in BBN ceramics at different frequencies. The measurements were done on cooling. Strong relaxation is observed in the radio frequency range where the maximum of ε' (T_{max}) shifts to higher temperature with increasing frequency. Simultaneously, ε'' demonstrates behaviour characteristic for relaxor ferroelectrics with the maximum shifted to lower temperature as compared to the real part of the permittivity. At high temperatures, both ε' and ε'' start to increase most probably due to electrical conductivity. This behaviour is similar to conventional relaxor ferroelectrics such as PMN and PLZT[10] except of much lower values of the real part of the permittivity which range up to 700. This might be explained by the reduced polarisability of the host ions and smaller interaction between dipole moments in the layered structure. It should be noted that the T_{max} shift with frequency is much stronger than in PMN ceramics in the same frequency range. For example, ΔT_{max} is over 100°C between 1 kHz and 1 MHz in BBN while it is only ~20°C in PMN. Another distinct feature of the ε'' (T) plot is a significant dispersion at low temperatures (below T_{max}) where ε'' decreases

Table 1
Characteristics of $BaBi_2Ta_2O_9$ (BBT) and $BaBi_2Nb_2O_9$ (BBN) sintered ceramic samples

Composition	Sintering temperature T_s (°C)	Relative density (%)	Dielectric permittivity maximum, ε_{max} (at 1 kHz)	Temperature of ε_{max} (T_{max},°C)
BBN	1100	~98	~700	108
BBT	1000	~95	~260	⩽25

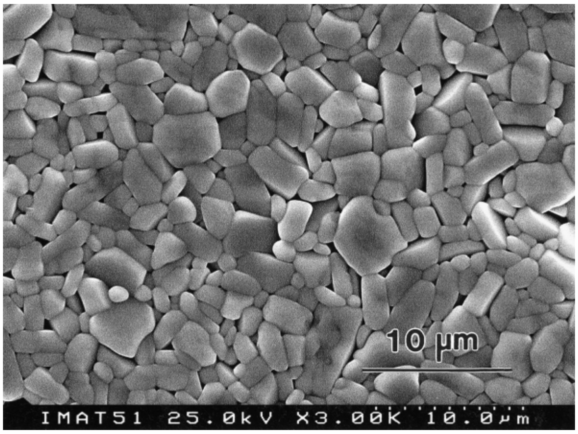

Fig. 1. SEM microstructure of $BaBi_2Nb_2O_9$ ceramics sintered at 1100°C.

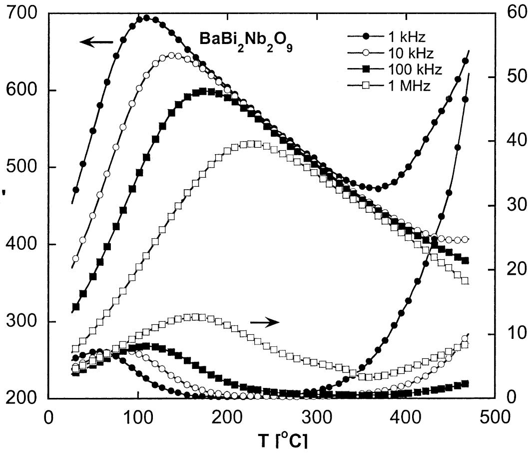

Fig. 2. Temperature dependence of the real (ε') and imaginary parts (ε'') of the dielectric permittivity in $BaBi_2Nb_2O_9$ ceramics at different frequencies.

with frequency. At higher temperature ($T > 70°C$), the relaxation behaviour is inversed and ε'' increases with increasing frequency. This implies that the inverse mean relaxation time shifts to low frequencies below this temperature while the distribution of the relaxation times becomes broader than at high temperatures. Fig. 3 shows the frequency dispersion of the real and imaginary parts of the permittivity at different temperatures. Obviously, no distinct Debye behaviour can be found even at high temperatures where the relaxation time spectrum should be relatively narrow. Below $T_{\max}$ a maximum in $\varepsilon''(\omega)$ is observed indicating that the mean relaxation time is in the radio frequency range. Since simple Debye relaxation usually fails in explaining the dielectric behaviour of relaxor ferroelectrics, Vögel–Fulcher relationship was applied to fit the dielectric data. This type of equation is interpreted as the Debye mechanism with the temperature-dependent activation energy:

$$\omega = \tau_o^{-1}\exp[-E_a/k(T_{\max} - T_f)] \tag{1}$$

where $\omega = 2\pi f$ is the measuring frequency, τ_o^{-1} is the pre-exponential factor (attempt frequency) which has a meaning of the inverse minimum relaxation time, E_a is the activation energy and T_f is the so-called freezing temperature where the spectrum of the relaxation times becomes infinitely broad. The Vögel–Fulcher plot for one of the BBN samples relating $T_{\max}$ with the logarithm of the inverse frequency is shown in Fig. 4. It is seen that the fit is sufficiently good with reasonable standard deviations of fitting parameters. Table 2 summarises the fitting parameters obtained for five BBN samples sintered at the same temperature (1100°C). Comparison with conventional relaxors like PMN or PLZT[10] indicates that the freezing temperature is very low, much lower than the temperature of the dielectric permittivity maximum. This is a natural consequence of the relatively strong shift of $T_{\max}$ with measuring frequency. It seems that the relaxation spectrum maximum moves to lower frequencies as the temperature decreases without significant broadening. In comparison, for PMN type relaxors the $T_{\max}$–T_f difference is much smaller being less than 100°C.[10] The low freezing temperature is possibly responsible for the inability to detect ferroelectric hysteresis below the temperature of the dielectric maximum in Ba-based Bi-layered perovskites.[6] It should be also mentioned that the attempt frequency is unusually high being of the order of phonon frequencies ($\sim 10^{12}$ s^{-1} in PMN). It means that dynamics of the polarisation clusters in BBN should be different from that of conventional relaxors such as PMN or PLZT. It is hypothesised that the reason of the drastic differences in Vögel–Fulcher parameters between Bi-layered perovskites and other (more isotropic) relaxor ferroelectrics can be due to the quite different structure of polarisation clusters in both cases. For PMN and other conventional relaxors, the clusters are nearly isotropic, i.e., their surface is close to sphere. As for Bi-layered materials, which are characterised by the strong crystal anisotropy, the ellipsoid is flattened in the *c*-direction of the orthorhombic cell. Allowable polarisation directions lie almost in the (*a*, *b*) plane. Recent investigations.[5,6] showed that the macroscopic

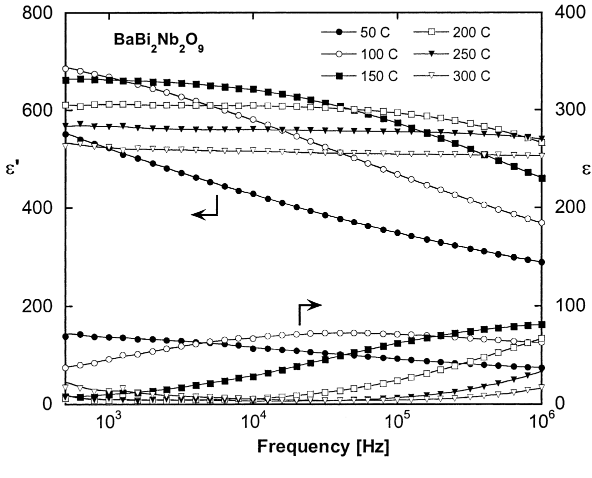

Fig. 3. Frequency dispersion of the real (ε') and imaginary parts (ε'') of the dielectric permittivity in BaBi$_2$Nb$_2$O$_9$ at different temperatures.

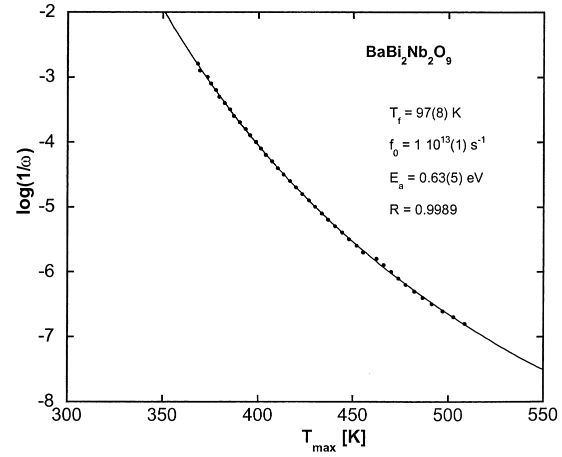

Fig. 4. Vögel–Fulcher plot relating $T_{\max}$ with logarithm of the measurement frequency in BaBi$_2$Nb$_2$O$_9$ ceramics.

Table 2
Vögel–Fulcher fitting parameters obtained for five different BaBi$_2$Nb$_2$O$_9$ samples sintered at 1100°C

Sample	T_f (K)	τ_0 $^{-1}$(s^{-1})	E_a (eV)
1	98.72	5.27×10^{13}	0.625
2	83.46	3.35×10^{14}	0.711
3	98.97	4.44×10^{13}	0.623
4	99.88	2.27×10^{13}	0.602
5	104.79	3.39×10^{13}	0.602
Average value	97.16	9.77×10^{13}	0.633
Standard deviation	8.05	1.33×10^{13}	0.044

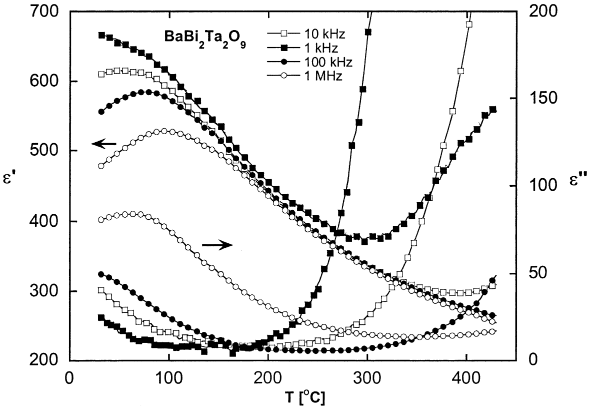

Fig. 5. Temperature dependence of the real (ε') and imaginary part (ε'') of the dielectric permittivity in $BaBi_2Ta_2O_9$ ceramics at different frequencies.

symmetry of Ba-based relaxors is actually tetragonal (space group *I4/mmm*). The difference between the macroscopic and microscopic symmetry (orthorhombic $A2_1am$) might be due to the polarisation fluctuations between allowable directions within (*a, b*) plane. Weak interaction of polarisation clusters between perovskite-like layers can be responsible for the observed unusual dielectric behaviour. Further investigations at low temperatures are obviously needed for the understanding of the nature of the dielectric relaxation and phase transition in BBN.

Fig. 5 shows the temperature measurements of the real and imaginary parts of the dielectric permittivity in BBT ceramics. Since measurements were limited to temperatures above 20°C, it was difficult to evaluate the dielectric relaxation parameters in a way it was done for BBN. However, it can be seen that the frequency dispersion is similar to that of BBN ceramics and the temperatures of the maximum of the real and imaginary parts of the permittivity are shifted to lower temperatures. This is consistent with the common notion that ferroelectric niobates have higher transition temperatures than tantalates.[11] Due to the narrow temperature range the analysis of dielectric relaxation and Vögel–Fulcher parameters was difficult to perform for BBT. Further measurements are required to compare the dielectric relaxation in BBN and BBT ceramics.

4. Conclusions

In conclusion, ceramics of Ba-based Bi-based relaxors were sintered using mixed oxide route. Calcination and sintering conditions were optimised in order to achieve single-phase and dense ceramics with good microstructure. Dielectric behaviour was investigated in the temperature range above 20°C. The results show that the dielectric relaxation is difficult to describe using Debye formalism. Instead, dielectric properties of BBN ceramics were fitted with Vögel–Fulcher type relationship. The results indicate that parameters, which characterise changes of the dielectric relaxation spectrum with temperature, are different from those of conventional relaxors. Anomalously low freezing temperature and high attempt frequency distinguish Ba-based relaxors with Bi-layered structure from other relaxor systems like PMN or PLZT.

Acknowledgements

This work was funded through the project SAPIENS/35444/99 of the Ministry of Science and Technology of Portugal.

References

1. Smolenskii, G. A., Isupov, V. A. and Agranovskaya, A. I., Ferroelectrics of the oxygen-octahedral type with layered structure. *Sov. Phys.-Sol. State*, 1961, **3**, 651–655.
2. Smolenskii, G. A., Bokov, V. A., Isupov, V. A., Krainik, N. N., Pasynkov, R. E., Sokolov, A. I. and Yushin, N. K., *Ferroelectrics and Related Phenomena*. Gordon and Breach, NY, 1981.
3. Cummins, S. E. and Cross, L. E., Electrical and optical properties of ferroelectric $Bi_4Ti_3O_{12}$ single crystals. *J. Appl. Phys.*, 1968, **39**, 2268–2274.
4. Takenaka, T. and Sakata, K., Grain orientation and electrical properties of hot-forged $Bi_4Ti_3O_{12}$ ceramics. *Jpn. J. Appl. Phys.*, 1980, **19**, 31–39.
5. Blake, S. M., Falconer, M. J., McGreedy, M. and Lightfoot, P., Cation disorder in ferroelectric Aurivillius phases of the type $Bi_2ANb_2O_9$ (A = Ba, Sr, Ca). *J. Mater. Chem.*, 1997, **7**, 1609–1613.
6. Shimakawa, Y., Kubo, Y., Nakagawa, Y., Goto, S., Kamiyama, T., Asano, H. and Izumi, F., Crystal structure and ferroelectric properties of $ABi_2Ta_2O_9$ (A = Ca, Sr, and Ba). *Phys. Rev. B*, 2000, **61**, 6559–6564.
7. Scott, J. F., Ross, F. M., Paz de Araujo, C. A., Scott, M. C. and Huffman, M., Structure and device characteristics of $SrBi_2Ta_2O_9$-based nonvolatile random-access memories. *MRS Bull.*, 1996, **21** (7), 33–39.
8. Kholkin, A. L., Brooks, K. G. and Setter, N., Electromechanical properties of $SrBi_2Ta_2O_9$. *Appl. Phys. Lett.*, 1997, **71**, 2044–2046.
9. Scott, J. F., The physics of ferroelectric ceramic thin films for memory applications. *Ferroelectrics Reviews*, 1998, **1**, 1–115.
10. Cross, L. E., Relaxor ferroelectrics. *Ferroelectrics*, 76, **987**, 241–267.
11. Lines, M. E. and Glass, A. M., *Principles and Application of Ferroelectrics and Related Materials*. Clarendon Press, Oxford, 1977.