



Ferroelectric versus Relaxor Behaviour in $\text{Na}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$ – $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ Solid Solutions

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Abstract. Sodium-bismuth titanate $\text{Na}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$ (NBT) and barium bismuth titanate $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ (BBT) and their solid solutions were prepared by solid state reaction of the constituent oxides. The room temperature structural characteristics were determined by X-ray diffraction and the dielectric properties investigated in a wide range of temperatures (20–750°C) and frequencies (1 kHz–1 MHz). As the barium content increases, the unit cell change from orthorhombic to pseudo-tetragonal, the paraelectric to ferroelectric phase transition decreases from 655°C to 400–420°C and a relaxor-like behaviour is observed for high barium contents. Depending on the composition, dielectric data were fitted using both classical (low Ba) and modified Curie-Weiss law for relaxors (high Ba).

Keywords: bismuth layer oxides, ferroelectrics, relaxors, permittivity, phase transitions

1. Introduction

The ferroelectric layered bismuth compounds of the so-called Aurivillius family have received increased attention as potentially interesting materials for many applications like e.g. high temperature lead-free piezoelectric devices or ferroelectric random access memories [1–5]. They are generally formulated as $\text{Bi}_2\text{A}_{m-1}\text{B}_m\text{O}_{3m+3}$, or more conveniently $(\text{Bi}_2\text{O}_2)(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})$ since the phases are built up by the regular intergrowth of $(\text{Bi}_2\text{O}_2)^{2+}$ layers and perovskite-like $(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$ slabs. A is a combination of cations adequate for 12-coordinated interstices such as Na^+ , K^+ , Ca^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+} , Bi^{3+} , etc., B is a combination of cations well suited to octahedral coordination like Fe^{3+} , Ti^{4+} , Nb^{5+} , Ta^{5+} , W^{6+} , etc., and m is an integer between 1 and 5 which represents the number of perovskite-like slabs intercalated between the $(\text{Bi}_2\text{O}_2)^{2+}$ layers.

$\text{Na}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$ (NBT) and $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ (BBT) are members of this family with $m = 4$. They have

been thoroughly investigated from the point of view of structural and electric properties [2, 3, 6–12]. At room temperature NBT is orthorhombic with $a = 0.5427$ nm, $b/a = 1.006$ and $c = 4.065$ nm and undergoes a ferro-to paraelectric (orthorhombic $\text{A}2_1\text{am}$ to tetragonal $\text{I}4/\text{mmm}$) phase transition at $T_C = 655^\circ\text{C}$ [2]. NBT is a classical ferroelectric with a sharp maximum of the thermal variation of the dielectric permittivity close to T_C . In contrast, BBT looks like a relaxor ferroelectric with a broad maximum and a significant frequency dispersion of the dielectric permittivity in addition with an increase of the temperature (T_m) of the maximum of dielectric constant ($\epsilon'_{r,\text{max}}$) and a decrease of the magnitude of the latter with increasing frequency [2, 3]. Such a relaxor behaviour has already been observed in other Ba-bearing Aurivillius phases like $\text{BaBi}_2(\text{Nb}/\text{Ta})_2\text{O}_9$, but its origin is not fully understood up to now [13].

In this paper the thermal and frequency evolutions of the dielectric properties of the $\text{Na}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$ – $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ solid solutions are presented and discussed in terms of classical versus relaxor ferroelectric behaviour.

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2. Experimental

Compounds with nominal formulae $(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{Bi}_4\text{Ti}_4\text{O}_{15}$ ($0 \leq x \leq 1$) were prepared by solid state reaction. Stoichiometric amounts of high purity Bi_2O_3 , TiO_2 , Na_2CO_3 and BaCO_3 were thoroughly mixed in an agate ball mill using acetone as liquid medium. Single Aurivillius phases were obtained by heating the mixtures at 1050°C for 12 h. Ceramic samples were prepared by natural sintering of uniaxially pressed (200 MPa) pellets at 1100°C for 2 h in closed alumina crucibles to avoid bismuth loss. The overall weight loss was estimated to be less than 1%.

The microstructure of the ceramics were observed on thermally etched surfaces using a Philips XL30 scanning electron microscope. X-ray diffraction patterns were obtained with a Siemens D5000 diffractometer (CuK α) and the cell parameters refined using CELREF V3 program [14]. Dielectric measurements were carried out from room temperature to 800°C using a HP 4194 impedance analyser between 1 kHz and 1 MHz on disk-shaped samples coated with platinum paste.

3. Results and Discussion

The structural and dielectric characteristics of the $(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{Bi}_4\text{Ti}_4\text{O}_{15}$ solid solutions with $x = 0, 0.20, 0.40, 0.60, 0.80$ and 1 were investigated. Ac-

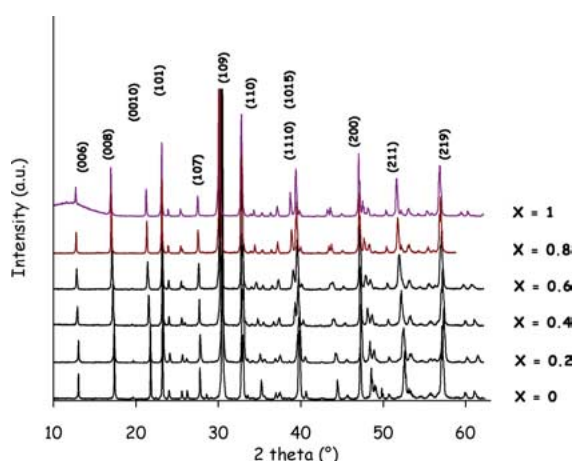


Fig. 1. X-Ray diffraction patterns of the $(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{Bi}_4\text{Ti}_4\text{O}_{15}$ solid solutions, $x = 0, 0.2, 0.4, 0.6, 0.8$ and 1 (the indexation is based on the prototype tetragonal structure).

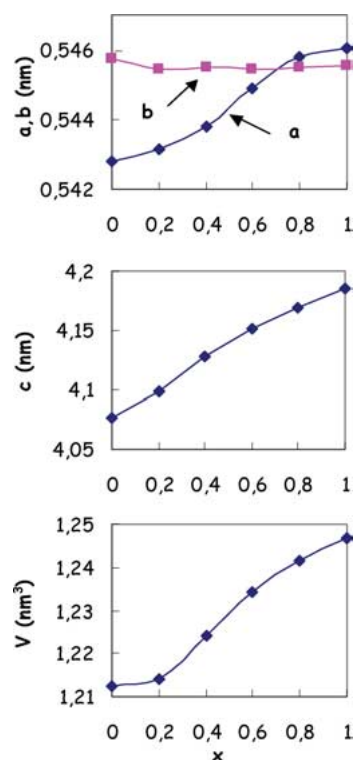


Fig. 2. Unit cell lattice parameters and volume versus composition for the $(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{Bi}_4\text{Ti}_4\text{O}_{15}$ solid solutions, $x = 0, 0.2, 0.4, 0.6, 0.8$ and 1.

ording to XRD experiments, the powder preparation conditions as well as the sintering schedule led to single phase materials with no detectable extra phase within the whole composition range (Fig. 1). The evolutions of the lattice parameters of the pseudo-tetragonal cell as a function of the barium content x are given in Fig. 2. As x changes from 0 to 1, the cell volume increases (+3.5%) as a consequence of the increase of the a and c parameters (+2.5 and 0.7% respectively). In addition, as the b parameter does not change significantly, the cell modification is strongly anisotropic in the direction of the larger parameter. Such an evolution is somewhat expected as the mean ionic radius increases from 0.128 to 0.161 nm when $(\text{Na}^+, \text{Bi}^{3+})$ is replaced by Ba^{2+} [15].

All the sintered materials show densities of about 95% of theoretical as measured by He pycnometry. Figure 3 shows that the microstructure of the surface of the ceramics gradually changes with the barium content. For no or low barium contents, the microstructure is dominated by the presence of large rounded

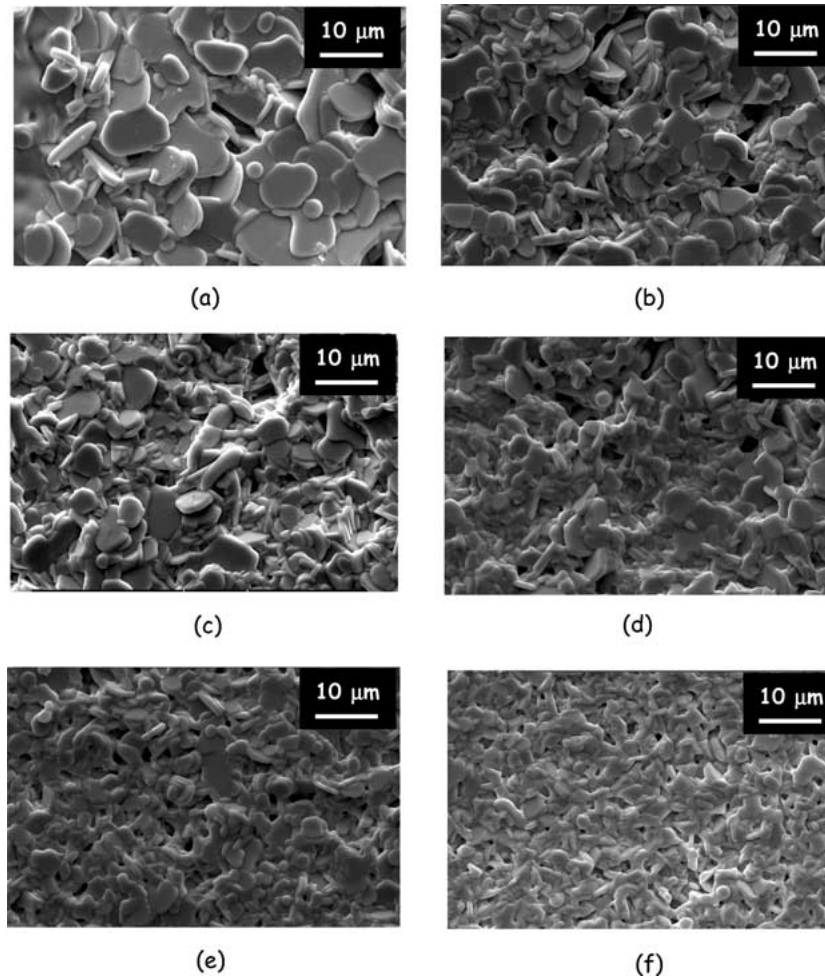


Fig. 3. SEM micrographs of sintered ceramics: (a) $x = 0$, (b) $x = 0.2$, (c) $x = 0.4$, (d) $x = 0.6$, (e) $x = 0.8$, (f) $x = 1$.

edges platelet-like grains up to $10\ \mu\text{m}$ size and $1\ \mu\text{m}$ thick. This grain shape has already been observed for many bismuth layered materials and is connected with the strong anisotropy of the crystal structure. The rounded edges are characteristic of liquid phase sintering. For high barium content, and especially for the fully substituted material, the micrographs show a significant coalescence of the grains whose size has decreased down few μm , in agreement with previous data [9].

The variations of the permittivity of the materials under investigation were measured as a function of temperature at 1, 10, 100, 500 and 10^3 kHz. Figure 4 shows the results obtained for NBT. The sharp maximum observed at 655°C —which coincides with the

minimum of the dielectric loss—is significant of the onset of a close to second order ferroelectric to paraelectric phase transition. The Curie constant C calculated from the values of the permittivity above the Curie point [$\varepsilon^{-1} = (T - \theta)/C$] is close to 0.8×10^5 K, as expected for the Aurivillius phases and the extrapolated Curie-Weiss temperature θ is about 610°C . In the case of BBT, the results shown in Fig. 5 give evidence of a diffuse phase transition accompanied by a relaxation of the permittivity. The temperature T_m of the maximum permittivity (ε_m) is shifted from 400 to 420°C as the frequency increases from 1 kHz to 1 MHz. This behaviour is typical of relaxor ferroelectrics e.g. PMN [16]. Such a phenomenon has already been observed in several Ba-bearing Aurivillius compounds [13]. The results of

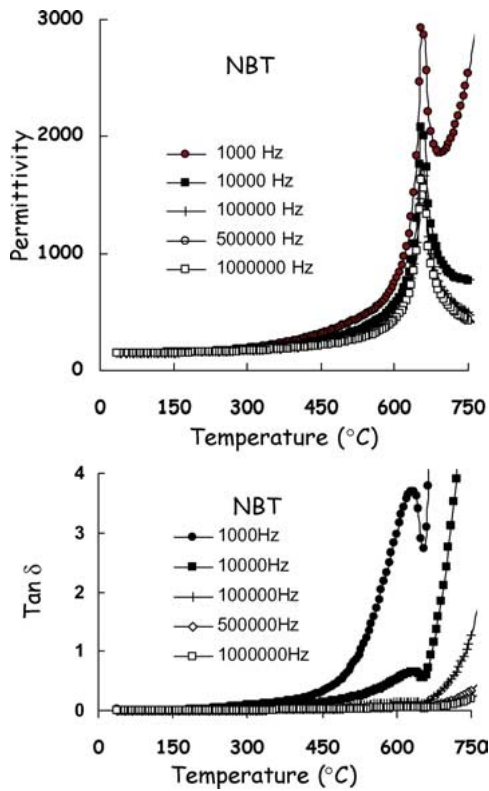


Fig. 4. Temperature dependence of the permittivity and dielectric loss of NBT ceramic at various frequencies.

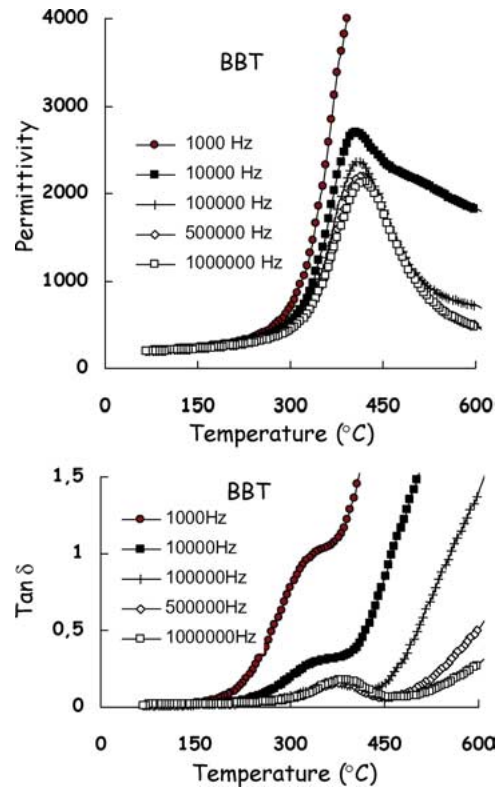


Fig. 5. Temperature dependence of the permittivity and dielectric loss of BBT ceramic at various frequencies.

the investigations of the intermediate compositions are collected in Fig. 6 (for better legibility the data are given in a narrow range around the transition temperature). They show a gradual change from second order phase transition to relaxor-like behaviour which appears as the barium content reaches 60 mol.%. In addition the Curie temperature as well as the temperature of the maximum permittivity decrease regularly as the barium concentration increases as indicated in Fig. 7. The decrease of the Curie temperature with increasing size of the 12-coordinated cations in the Aurivillius com-

pounds has been attributed to the increase of the tolerance factor (departure from the ideal perovskite-like substructure) which leads to a less distorted structure (a and b parameters becoming close to one another). Accordingly, the atomic displacements along the polar axis (a-axis) are smaller so that the energy involved to reach the prototype high temperature structure is lowered.

For materials with barium content up to 60 mol%, the Curie-Weiss (CW) law is fairly obeyed as shown in Table 1 which gathers the characteristic ferroelectric

Table 1. Characteristic ferroelectric parameters of the $(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{Bi}_4\text{Ti}_4\text{O}_{15}$ solid solutions

	$x = 0$ (NBT)	$x = 0.2$	$x = 0.4$	$x = 0.6$	$x = 0.8$	$x = 1$ (BBT)
C (K)	$0.78 \cdot 10^5$	$0.75 \cdot 10^5$	$0.75 \cdot 10^5$	$2.4 \cdot 10^6$	$8 \cdot 10^6$	$5.4 \cdot 10^6$
T_C (°C)	655	608	563	–	–	–
θ (°C)	635	592	539	450	440	400
T_m (HF)	–	–	–	499	444	420
T_m (LF)	–	–	–	495	434	400
γ	–	–	–	1.7	1.85	1.9

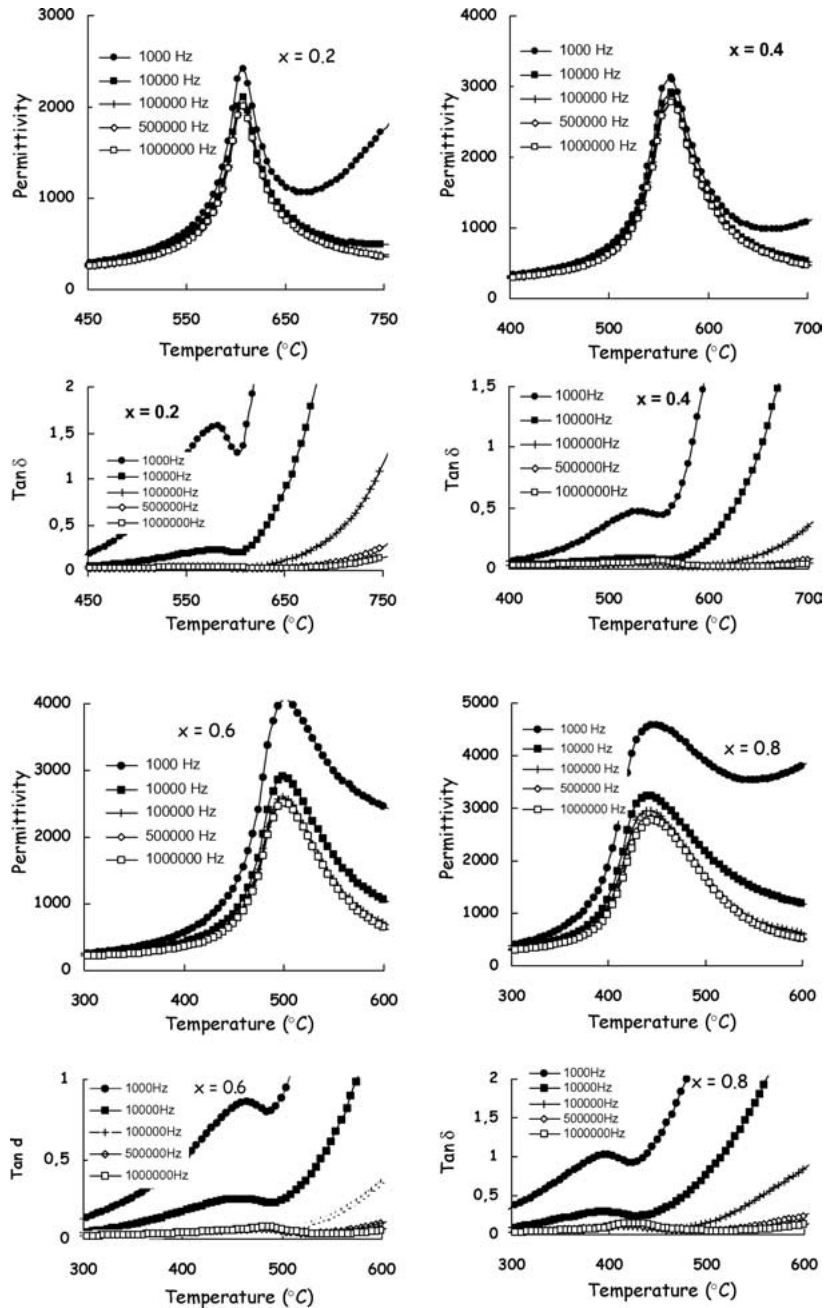


Fig. 6. Temperature dependence of the permittivity and dielectric loss of $(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{Bi}_4\text{Ti}_4\text{O}_{15}$ ($x = 0.2, 0.4, 0.6$ and 0.8) ceramics at various frequencies.

parameters. On the contrary, for richer barium compositions, it was not possible to fit the experimental data using the CW law. As they exhibit a relaxor-like behaviour, a fitting procedure was performed using the

modified CW law: $\epsilon^{-1} - \epsilon_m^{-1} = (T - T_m)^\gamma / C$, where $\gamma = 1$ for “normal” ferroelectrics and $\gamma = 2$ for relaxors which corresponds to polar domains fluctuations in the neighbourhood of the maximum permittivity [17].

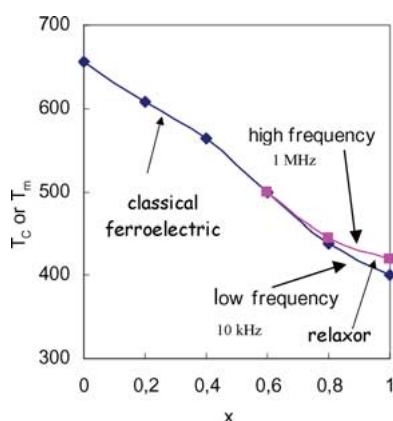


Fig. 7. Evolutions of T_C and T_m versus composition for $(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{Bi}_4\text{Ti}_4\text{O}_{15}$ solid solutions ($x = 0, 0.2, 0.4, 0.6, 0.8$ and 1).

The values obtained for γ at 1 MHz are close to 2, confirming the relaxor nature of these materials. Nevertheless, these results must be cautiously regarded as the values of the permittivity at high temperature are obviously modified by the increasing conductivity of the materials, which could result from oxygen vacancies. Experiments on samples post-annealed in pure oxygen are now in progress.

4. Conclusion

Sodium-bismuth titanate $\text{Na}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$ (NBT) and barium bismuth titanate $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ (BBT) form a complete set of solid solutions in the whole composition range. When increasing the barium content from NBT, the ferroelectric to paraelectric phase transition

gradually changes from a normal, second order type to a relaxor-like behaviour above 60 mol.% barium. The T_C or T_m temperatures decreases from 655°C (NBT) to 400–420°C (BBT) as a consequence of the substitution of larger 12-fold coordination Ba^{2+} cations for smaller $(\text{Na}, \text{Bi}_3)^{2+}$ pseudocation. The induced symmetrization of the lattice seems to be responsible of the relaxor behaviour.

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