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Structural and dielectric studies of the $Na_{0.5}Bi_{0.5}TiO_3$–$BiFeO_3$ system

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Abstract

Solid solutions $(1-x)$NBT–xBF, between rhombohedral compounds $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) and $BiFeO_3$ (BF) were studied and a continuous $R3c$ solid solution was evidenced. Lattice parameters and rhombohedral distortion evolution with BF content were studied. The "a" pseudo-cubic parameter (a_p) increases linearly with BF rate, as the "α" pseudo-cubic one (α_p) presents a more complex behaviour. The study of the dielectric properties evidenced two different ranges, with a limit composition around 50% of BF. TEM studies of the reciprocal space showed that the relaxor behaviour of NBT-rich samples is correlated both with superstructure spots and diffusion rows along some particular directions.

Keywords: Dielectric properties; Perovskite; Electron microscopy; Relaxor materials

1. Introduction

Because of environmental issues, new lead-free piezoelectric materials are the object of many studies. The $Na_{0.5}Bi_{0.5}TiO_3$ compound (NBT) is considered as a possible candidate for such applications. Moreover, it is an A-site substituted distorted perovskite compound (ABO_3) which is rarer than the B-site one. Its dielectric properties reveal two anomalies.[1] The well-known corresponds to the ferroelectric–paraelectric transition whose Curie temperature is 320 °C. The other one is frequency dependant and is not yet well-understood, since no structural transition occurs at its temperature (≈230 °C).[2] The $BiFeO_3$ compound (BF) is also a rhombohedral perovskite belonging to the same space group $R3c$ [3] and sharing the Bi^{3+} cation in the A-site with NBT. In spite of this common point with NBT, it presents very different characteristics since it has an antiferromagnetic order accounting for the Fe^{3+} (high spin) cation on the B-site,[4] within ferroelectric behaviour due to its non-centrosymetric structure. In the present study, we present results concerning the NBT–BF system. Hereafter, the structural, dielectric results and Selected Area Electron Diffraction (SAED) patterns obtained by TEM concerning this system will be reported.

2. Samples elaboration and characterization

Synthesis of ceramic materials with composition $(1-x)$ $Na_{0.5}Bi_{0.5}TiO_3$–$xBiFeO_3$ ($0<x<1$) were performed using carefully weighed and mixed stoichiometric amounts of Na_2CO_3, Bi_2O_3, Fe_2O_3 and TiO_2, which were fired between 775 and 900 °C and ground. In order to obtain pellets suitables for dielectric measurements, they were then pressed and sintered between 900 and 1130 °C, depending on the composition. The pellets were then straightened, polished and electroded using silver paint. Their dielectric properties were studied between room temperature and 750 °C (100 Hz–1 MHz). Structural investigations were carried out by X-ray diffraction (XRD) and transmission electron microscopy (TEM) using powders obtained from ground pellets. A special process was used to prepare $BiFeO_3$: a 20% Bi_2O_3 excess weight was used, in order to prevent the formation of the $Bi_2Fe_4O_9$ extra-phase. The $Bi_{25}FeO_{40}$ compound, formed during the synthesis, was eliminated by leaching the powders in concentrated nitric acid and washing them with deionised water.

3. Structural characterization

We evidenced for a continuous solid solution, with $R3c$ space group, as the characteristics superstructure peaks are presents for all the compositions (Fig. 1). The diffraction diagrams were indexed using an hexagonal cell and the parameters were then converted into the pseudo-cubic ones for sake of legibility. A linear increase of the "a" pseudo-cubic param-

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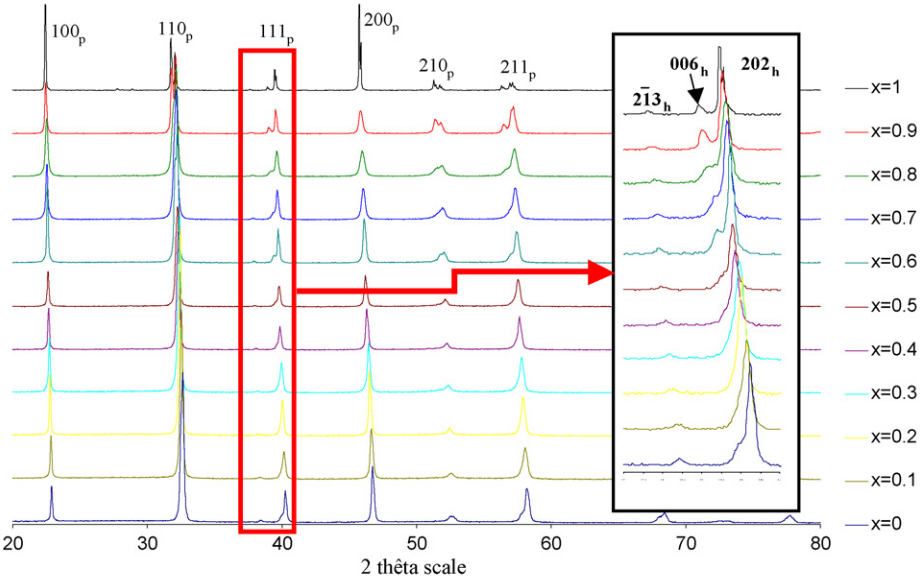

Fig. 1. XRD diagrams from $x = 0$ (NBT) to $x = 1$ (BF): (p, pseudo-cubic; h, hexagonal indexes).

eter (a_p) with the increasing BF rate was observed (Fig. 2). This evolution agree with the increase of the mean value of the ionic radius of the cations in the B-site of the perovskite, since the radius of the Fe^{3+} ion (0.645 Å) is greater than the one of Ti^{4+} one (0.605 Å), while the mean radius for the A-site remains quasi-constant (Bi^{3+} = 1.38 Å, Na$^+$ = 1.39 Å).[5] According to the decrease of the Goldsmith tolerance factor from NBT to BF (0.99–0.97), the rhombohedral distortion of the perovskite structure increases with BF content (α_p decreases). But surprisingly, this evolution is non-linear (Fig. 2): the distortion first decreases (α_p increases) up to BF contents around 10–20%, with a perovskite cell close to a cubic one ($\alpha_p \approx 89.9°$) and then regularly increases. This fact is probably correlated with the progressive replacement of the Na$^+$/Bi^{3+} pseudo-ion by the Bi^{3+} alone, since this last one presents a non-spherical shape (6s^2 lone-pair) and become quickly predominant in the A-site.

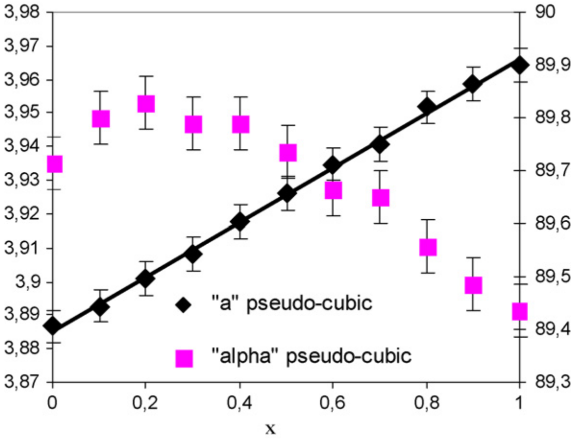

Fig. 2. Evolution of the pseudo-cubic parameters a_p and α_p.

4. Dielectric measurements

The dielectric measurements showed two different ranges for which the behaviour is similar to the one of the end-members. For $x < 0.5$, we noticed a NBT-like behaviour (Fig. 3). The hump (≈200 °C) accounting for relaxor behaviour slightly disappears until 50% of BF, and the maximum of the dielectric constant around 320 °C corresponding to the ferroelectric (rhombohedral) to paraelectric (tetragonal) phase transition evolves to high temperature as BF rate increaes. For BF contents higher than 50% BF, the electrical conductivity become quickly high and the measurements are difficults. The first anomaly of NBT (hump) is no longer visible (Fig. 3) as a result of the disappearance of the relaxor behaviour. Then, a behaviour similar to the one of others BF-rich solid solutions is observed: a diffuse phenomena around 400 °C, which is frequency and temperature dependent, and a maximum (≈650–700 °C) followed by a rapid fall of the permitivity. The first of them could be correlated to a change of the magnetic order, since the Néel temperature of BF is around 370 °C. The second phenomenon is also observed for other BF-rich solid solutions such as BaTiO$_3$–BF,[6] and will probably be also observed for pure BF. But unfortunately, no data are available for pure BF, as it starts to break up from 800 °C during sintering and so it is difficult to obtain pellets suitable for measurements. However, this last phenomenon is not well-understood at the present time, since it does not correspond to any structural transition in BF.

5. Transmission electron microscopy (TEM)

The reciprocal lattice of the samples was systematically investigated for the whole composition range. For BF-rich compounds, the observed SAED patterns fully correspond to the *R*3*c* structure. But for BF contents lower than 50%, two differ-

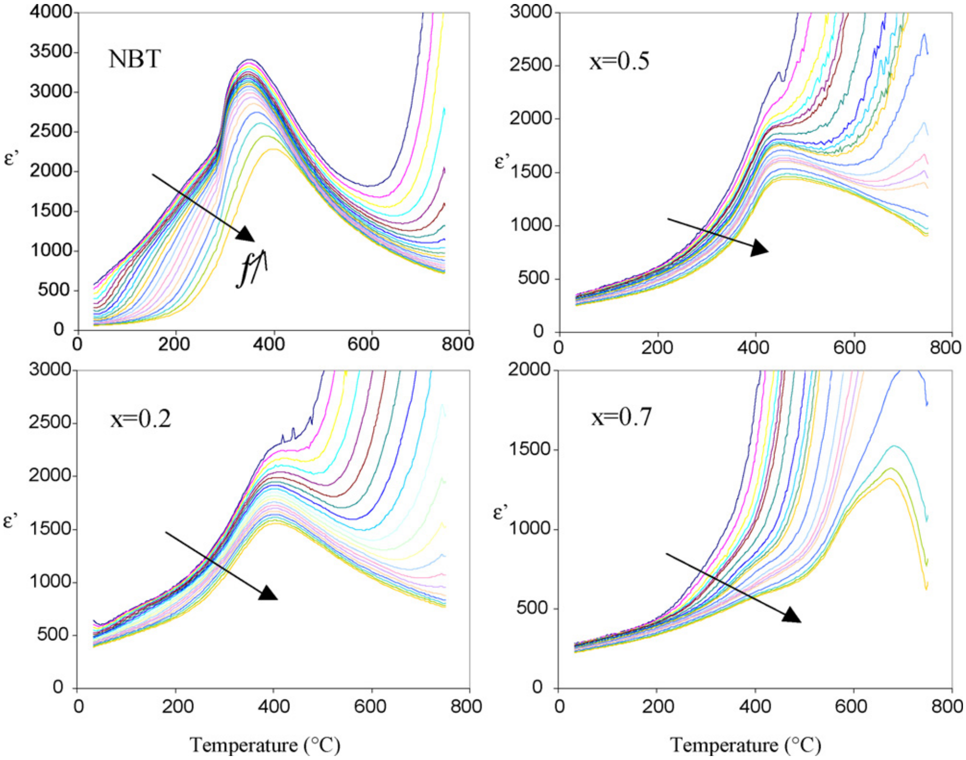

Fig. 3. Permittivity vs. temperature for $x = 0$, $x = 0.2$, $x = 0.5$ and $x = 0.7$.

ent phenomena appear: some superstructure spots (Fig. 4) for the [0 0 1] hexagonal zone axis (threefold axis of the rhombohedral one) and diffusion rows along three particular directions (Fig. 4). Both phenomena are present only for the samples possessing the NBT-like relaxor behaviour, which is, as a consequence, probably correlated with these structural observations. For the first of them, SAED patterns simulations showed that they may correspond to the occurrence of some remaining tetragonal high-temperature phase clusters inside the rhombohedral matrix, which are oriented along the three main directions of the pseudo-cubic cell. Some authors[7] have reported similar behaviour on high temperature SAED patterns, with the presence of both rhombohedral and tetragonal symmetry in tetragonal phase domain temperature of NBT. The origin of the diffusion may be attributed to partial ordering between Na^+ and Bi^{3+} on the A-site of the perovskite lattice.[8]

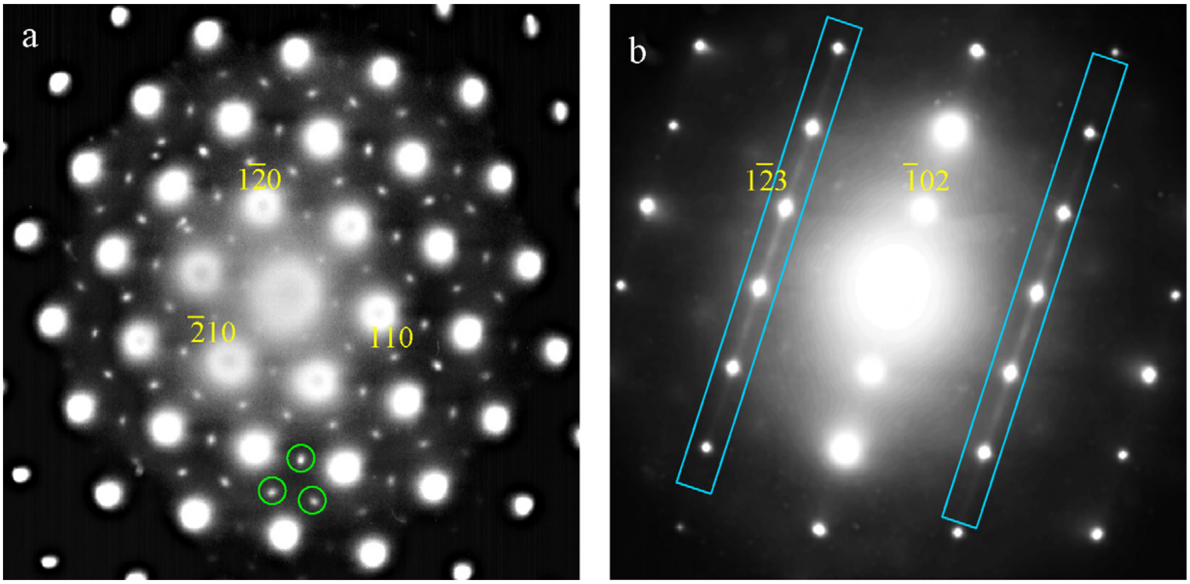

Fig. 4. SAED patterns for $x < 0.5$: (a) $[0\,0\,1]_h$ zone axis and (b) $[4\,5\,2]_h$ zone axis.

6. Conclusion

Structural investigations have shown an $R3c$ continuous solid solution. The pseudo-cubic lattice parameter a_p increases linearly with the composition, while the rhombohedral distortion angle α_p does not evolve linearly, probably because of the occurrence of cations with different shapes on the A-site.

Dielectric measurements allow us to distinguish two domains of behaviour. The first of them (NBT-rich solid solutions under 50% of BF) exhibits NBT-like behaviour and the other one seems to have a BF-like behaviour even if behaviour of pure BF is not well-known.

TEM studies for compounds exhibiting relaxor NBT-like behaviour highlighted the presence of little clusters of tetragonal symmetry inside the rhombohedral matrix and diffusion rows, probably accounting for cations partial ordering on the A-site.

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