Structural disorder in BZN-based pyrochlores

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Abstract Careful structural investigations have been carried out on the $Bi_{1.5}ZnNb_{1.5}O_7$ based dielectric system (of $A_2B_2O_7$ pyrochlore structure type) in an attempt to understand the origin and tolerance of relaxor behavior in such materials. A highly structured, characteristic diffuse intensity distribution was observed in electron diffraction patterns, which arises from static disordering caused by local short range ordering of Bi and Zn ions on the pyrochlore A sites and associated structural relaxation of the $O'A_2$ sub-structure. This structural disordering is not affected by B site substitution of the Nb^{5+} ions by Sn^{4+} or Ti^{4+} ions. The result is of significance for optimizing the dielectric properties of bismuth-based advanced ceramics.

Keywords $Bi_{1.5}ZnNb_{1.5}O_7$ · Relaxation · Disorder ·
Monte Carlo

1 Introduction

With a high (as well as tunable) dielectric constant and low dielectric loss in the RF/microwave range coupled with an ability to be fired at relatively low-temperatures, Bi-containing $A_2B_2O_6O'$ pyrochlore ceramics such as the A and B site disordered pyrochlore $(Bi_{1.5}Zn_{0.5})(Zn_{0.5}Nb_{1.5})O_7$

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(BZN) have become important candidate materials for future wireless communications technology. Polarization in the microwave frequency range is dominated by electronic and ionic polarization contributions that are strongly dependent upon local crystal structure. It is therefore critical to understand local A and B site ordering rules and associated structural relaxation in $Bi_{1.5}ZnNb_{1.5}O_7$ and related materials. Although several average structural analyses have been carried out, the mechanism underlying polarization on the local scale as well as the structural origin of the dielectric loss are still far from fully understood. In particular, the structural origin of a strong relaxation feature apparent in the frequency and temperature-dependent dielectric properties of BZN [1–3, 5] is not well understood. Although various possibilities as regards the local disordered structure of $(Bi_{1.5}Zn_{0.5})(Zn_{0.5}Nb_{1.5})O_7$ have been proposed, most lack direct experimental support. Nino et al. [6] used electron diffraction to investigate the reciprocal space of BZN. The results, however, simply revealed ".. a conventional cubic pyrochlore structure with space group symmetry of Fd-3m .." and ".. no evidence for unusual microstructural features ..." A more recent average structure refinement based on neutron diffraction data (Levin et al. [4]) reported ".. significant local deviations from the ideal pyrochlore arrangement, and substantial displacive disorder ...," particularly on the $O'A_2$ sub-structure. This paper predicted that displacements of the A-cations and of the seventh O' anion are ".. likely responsible for both the high dielectric constant and low temperature dielectric relaxation ..." The electron diffraction patterns (EDPs) presented therein, however, were very clean without any trace of the additional diffuse scattering that should accompany correlated disorder. Given that electron diffraction is ideally suited to the detection of weak features of reciprocal space such as structured diffuse scattering as a

result of the strong interaction of electrons with matter, we decided recently to carefully investigate the microstructure of this pyrochlore family of phases via XRD, TEM and Monte Carlo stimulation.

2 Experimental

$(Bi_{1.5}Zn_{0.5})(Zn_{0.5-x/3}Sn_xNb_{1.5-2x/3})O_7$ (BZSN, $0 \leq x \leq 1.5$) and $(Bi_{1.5}Zn_{0.5})(Zn_{0.5-y/3}Ti_yNb_{1.5-2y/3})O_7$ (BZTN, $0 \leq y \leq 1.5$) samples were synthesized by solid state reaction following synthesis procedures reported in the literature [2, 6, 7].

XRD data was collected using a Guinier–Hägg camera and Cu $K\alpha_1$ radiation with Si as an internal standard in order to accurately determine unit cell parameters. Samples suitable for the Transmission Electron Microscope (TEM) were prepared by the dispersion of finely ground material onto a holey carbon film. EDPs were obtained with a Philips EM 430 TEM.

3 Results and discussion

Figure 1(a) and (b) show (a) <118> and (b) ~<551> zone axis EDP's typical of BZN. The EDP's were obtained by
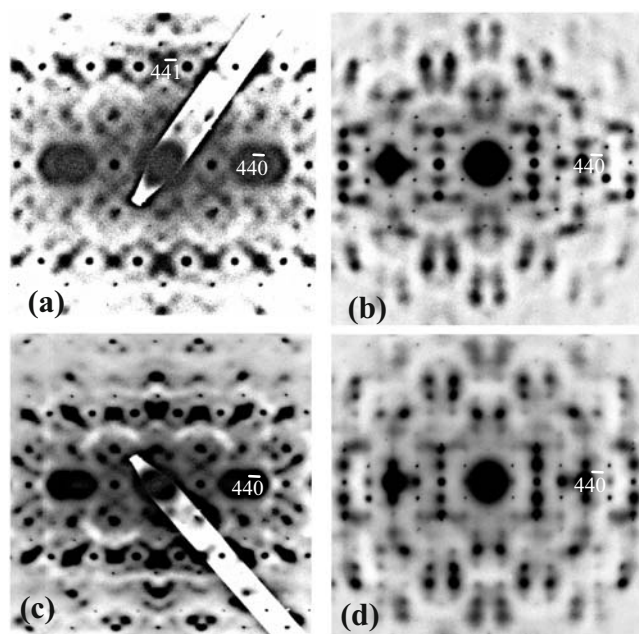
Fig. 1 Typical <118> zone axis EDPs obtained from (**a**) BZN and (**c**) BZSN ($x=1.0$), by tilting ~10° away from the <001> orientation keeping the <2,−2,0>* systematic row excited and ~<511> zone axis EDPs obtained from (**b**) BZN and (**d**) BZTN ($y=1.5$) by tilting ~8° away from the exact <110> zone axis orientation again keeping the <2,−2,0>* systematic row excited
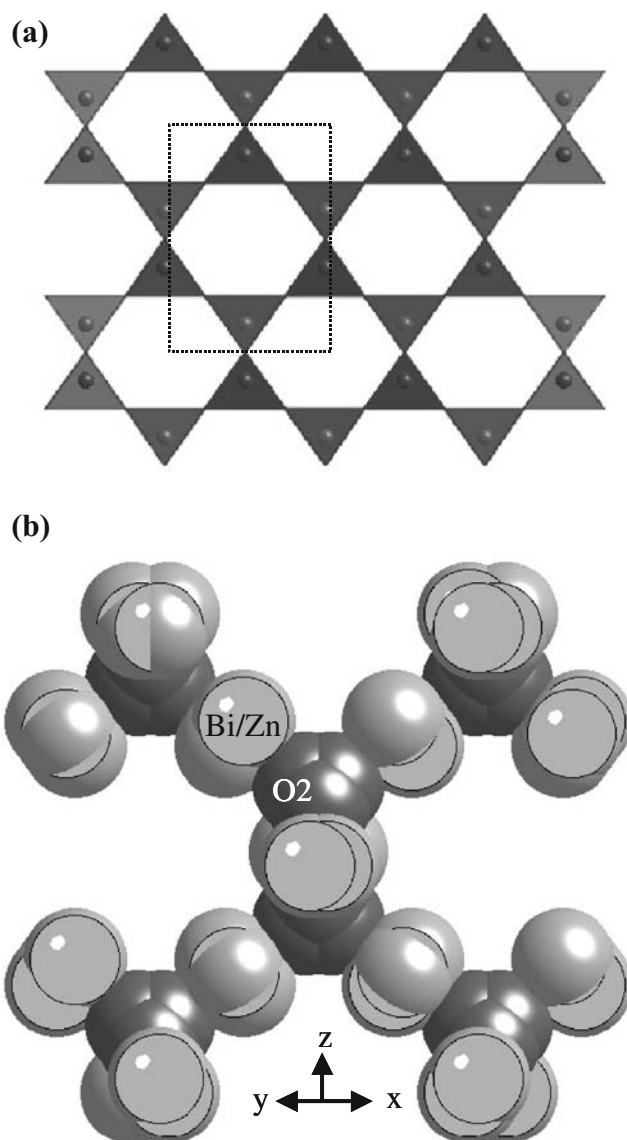
Fig. 2 (**a**) The ideal anti-β cristobalite O'A_2 substructure (the balls centreing the tetrahedra are O' ions while the A ions are at the *corners* of the tetrahedra) and (**b**) the distribution of atomic positions obtained from the Monte Carlo simulation (see *below*) via plotting the positions of the Bi, Zn and O' ions from all of the unit cells in the simulation superposed onto a single unit cell

tilting only a few degrees away from close by <110> and <001> zone axis orientations, respectively. A characteristic, highly structured and quite reproducible diffuse intensity distribution is apparent. Figure 1(c) and (d) show virtually identical zone axis EDPs obtained from Sn, *B* site doped (BZSN) and Ti, *B* site doped BZTN samples. The similarity of these EDP's strongly suggests that the observed diffuse distribution arises almost entirely from disorder associated with Bi/Zn ordering and induced relaxation associated with the O'A_2 tetrahedral corner-connected sub-structure (see Fig. 2).

Monte Carlo modeling was therefore carried out on this basis. It was assumed that Zn ions were separated as far as possible from one another (giving rise to local O'Bi$_3$Zn tetrahedra) on the A sub-lattice and that the centering O' oxygen ion in each tetrahedron would always move away from the Bi ions and towards the Zn ion in each local tetrahedron. In addition, the A site positions were relaxed such that Bi–Bi separation distances were 6% larger and the Bi–Zn distances 6% shorter than the average separation distances (see [8] for the details). Figure 3 shows a simulated <551> zone axis EDP of the resultant distribution for comparison with Fig. 1(b) and (d).

A rather good qualitative fit shows that the observed diffuse distribution arises from local Bi/Zn ordering on the A site and associated displacive relaxation in the O'A_2 substructure. The Monte Carlo simulation results show that the Bi, Zn and O' ions, while clustered around their ideal anti-β cristobalite positions, never actually stay there—see e.g. Fig. 2(b). The Bi ions move perpendicular to the local O'-A-O' direction while the O' ions move ~0.39 Å [8] towards the local Zn ion in each O'Bi$_3$Zn tetrahedra. This local Bi/Zn ordering and associated displacive relaxation is presumably static, thus contributing only to the frequency-independent part of the dielectric loss.

The existence of a reasonably close to ideal anti-β cristobalite O'A_2 substructure (even taking the structural disorder described above into account; see Fig. 2) suggests a possible relatively low energy, dynamic relaxation mechanism involving coupled tetrahedral rotation modes known as Rigid Unit Modes or RUM's. Dynamically disordered RUM modes of this type have been observed in β-cristobalite itself as well as in the O'A_2 sub-structures of a range of pyrochlore phases [9, 10]. Such RUM modes provide a low energy mechanism to enable the disordered A site ions to hop from one disordered position to another (see Fig. 2(b)). This suggested dynamical disorder might well contribute to the frequency-dependent part of the dielectric loss. The characteristic signature of the existence of such RUM

Fig. 3 ~<551> zone axis diffraction pattern obtained from MC simulation

modes of distortion is the presence of {110} sheets of transverse polarized diffuse intensity [9]. While such a diffuse distribution has not been observed in the current case, this need not necessarily rule out such a dynamic relaxation mechanism. The diffuse intensity arising from the local short range order of the Bi/Zn ions and the associated induced structural relaxation is extremely strong so that the existence of RUM modes may be swamped. Experimentally, the reported dielectric properties of BZN [11] appear to be largely frequency independent at room temperature. This suggests that static, rather than dynamic, disorder makes the largest contribution to the observed dielectric loss. When the Nb ions on the B site of BZN were substituted by Sn and Ti ions without altering the A site composition, the cubic Fd-3m pyrochlore lattice parameter was found to vary from a=10.5465 Å for pure BZN to 10.3528 Å for BZTN, y=1.5, to 10.5895 Å for BZSN, x=1.5. This lattice parameter variation has a much stronger effect upon the dielectric constant and its temperature dependence than upon the dielectric loss [2] suggesting that the latter is primarily associated with disorder in the O'A_2 sub-structure. As a result, the dielectric losses of the substituted materials do not apparently change upon B site substitution. This suggests a possible mechanism to improve or tune dielectric properties other than the dielectric loss in the RF/microwave frequency range without degrading the latter.

4 Conclusions

Local short range ordering of Bi and Zn ions on the A sites of the pyrochlore average structure of BZN coupled with the associated induced displacive relaxation of the O'A_2 substructure are responsible for an observed highly structured, diffuse intensity distribution. This disordering remains unchanged upon substitution of Sn^{4+} or Ti^{4+} ions for Nb^{5+} ions on the pyrochlore B sites. Consequently, the dielectric constant as well as the temperature dependence of the dielectric constant can be improved or tuned without degradation of dielectric loss. This result is of significance from both the fundamental as well as the practical applications points of view.
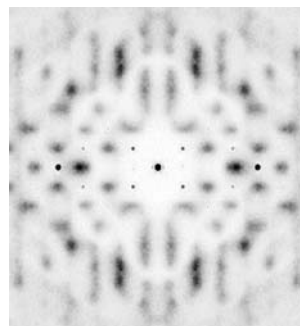
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