

Displacive disorder in three high- k bismuth oxide pyrochlores

B. Melot^a, E. Rodriguez^a, Th. Proffen^b, M.A. Hayward^c, R. Seshadri^{a,*}

^aMaterials Department and Materials Research Laboratory, University of California, Santa Barbara, CA 93106, USA

^bLos Alamos National Laboratory, Manuel Lujan Jr. Neutron Scattering Center LANSCE-12, MS H805, Los Alamos, NM 87545, USA

^cDepartment of Chemistry, Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QR, UK

Received 12 December 2005; received in revised form 20 January 2006; accepted 6 February 2006

Available online 28 February 2006

Abstract

We use time-of-flight neutron powder diffraction to examine static displacive disorder in three different pyrochlore $A_2B_2O_6O'$ compounds with Bi on the A site. The compounds $(Bi_{1.5}Zn_{0.5})(Nb_{1.5}Zn_{0.5})O_6O'$ (BZN), $(Bi_{1.5}Zn_{0.5})(Ta_{1.5}Zn_{0.5})O_6O'$ (BZT), and $(Bi_{1.5}Zn_{0.5})(Sb_{1.5}Zn_{0.5})O_6O'$ (BZS), are of interest – particularly BZN – for their high dielectric constants in the absence of any phase transition from the cubic high temperature phase. The local structures of the three compounds is characterized by displacive disorder from the ideal pyrochlore positions for both the A and O' sites, with the precise nature of the disorder being quite similar. However the extent of displacive disorder is different, despite the B–O networks being nearly identical in the three compounds. The reported dielectric constants of the three compounds are related to the extent of local displacement, and BZN, with the largest extent of local atomic displacement of A and O' , is also reported to have the largest dielectric constant at 1 MHz. The dielectric constants are also related to the magnitudes of the thermal parameters of the different ions. The strongest correlation is found to involve the thermal parameter on the B site (Nb, Ta, or Sb).

© 2006 Elsevier Ltd. All rights reserved.

Keywords: A. Electronic materials; B. Dielectric properties

1. Introduction

In many ABO_3 perovskites, the presence of a lone-pair active A cation such as Pb^{2+} or Bi^{3+} , is often key to the development of polar behavior as these ions prefer off-centered coordination polyhedra [1,2]. In the pyrochlore [3] structure however, apart from a few exceptions, lone-pair active A cations do not necessarily lead to polar, distorted ground states. Instead, pyrochlore compounds with lone-pair active A cations frequently accommodate the off-centering through incoherent, *local* displacements. Vanderah, Levin, and Lufaso [4] have recently demonstrated that the A_2O' sublattice of the pyrochlore can tolerate a large degree of substitutional as well as displacive disorder on the A-cation site. Indeed for certain pyrochlore compositions, the phase becomes stable only when such substitutional disorder is present on the A-site [4]. Local static disorder, rather than coherent distortions of the structure can be advantageous in device applications where structural phase transitions are contraindicated. A good example of this is the system $(Bi_{1.5}Zn_{0.5})(Nb_{1.5}Zn_{0.5})O_6O'$ which displays a high dielectric constant as well as some field tunability, but

* Corresponding author. Tel.: +1 805 893 6129; fax: +1 805 893 8797.

E-mail address: seshadri@mrl.ucsb.edu (R. Seshadri).

remains paraelectric down to the lowest temperature [5–7]. Interestingly, the attractive properties of these materials are retained in thin films [8–11].

Levin et al. [12] have carried out a careful neutron structural investigation of BZN and have established that there is significant static displacement of the A and O' sites from the positions they would be expected to occupy in the ideal pyrochlore structure. This disorder is expected to be an important ingredient in the physics of BZN since the dielectric properties are believed to be closely associated with the A_2O' network [13].

In this contribution, we examine the nature of static displacive disorder in two pyrochlore oxides whose neutron structures have not previously been determined: $(Bi_{1.5}Zn_{0.5})(Ta_{1.5}Zn_{0.5})O_6O'$ (BZT) and $(Bi_{1.5}Zn_{0.5})(Sb_{1.5}Zn_{0.5})O_6O'$ (BZS) and compare their structures with that of BZN. These are compounds whose dielectric properties have been

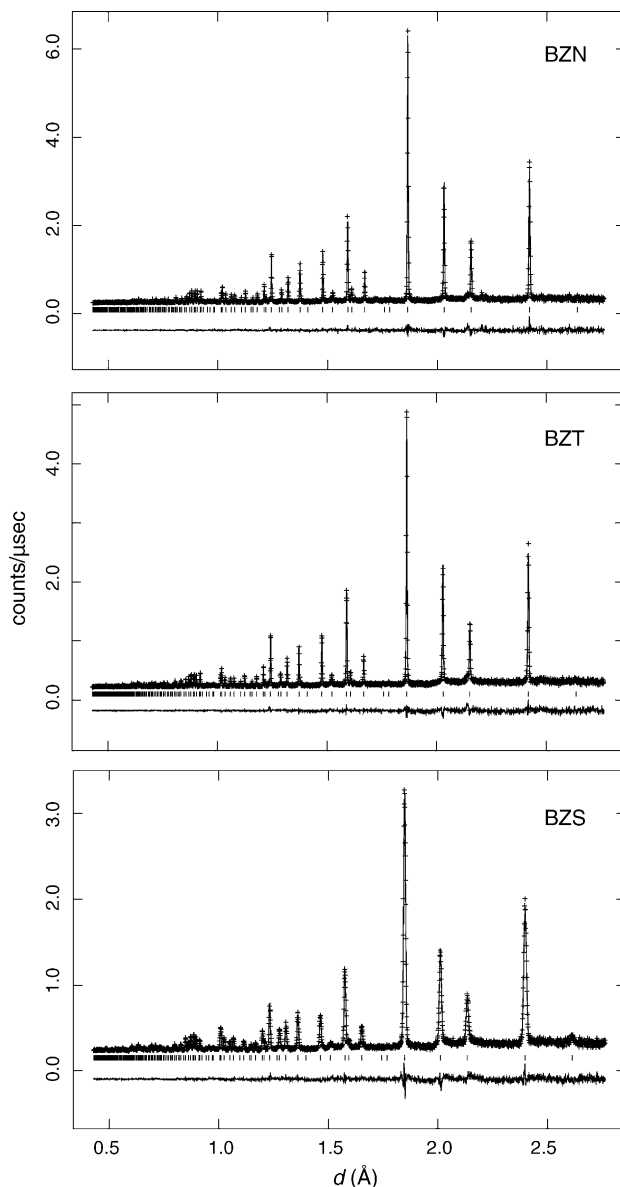


Fig. 1. Observed, calculated, and difference plots obtained by Rietveld refinement of structural models of the three oxide pyrochlores $(Bi_{1.5}Zn_{0.5})(Nb_{1.5}Zn_{0.5})O_6O'$ (BZN), $(Bi_{1.5}Zn_{0.5})(Ta_{1.5}Zn_{0.5})O_6O'$ (BZT), and $(Bi_{1.5}Zn_{0.5})(Sb_{1.5}Zn_{0.5})O_6O'$ (BZS) against time-of-flight powder neutron diffraction data.

measured, so a careful examination of the structure permits the measured displacive disorder in these three compounds to be related to their dielectric behavior.

2. Experimental

Powder samples of the three pyrochlores were prepared from oxides using the starting cation mole ratios Bi:Zn:(Nb/Ta/Sb) of 3:2:3 following standard ceramic techniques as described by Huiling and Xi. [14] Final sample heating temperatures were in the range of 1073–1273 K, and we find that thermal treatment for forming pure phases depends on the composition. Dense alumina crucibles were used to contain powders and pellets of the samples. Neutron data were collected on samples contained in vanadium cans at the neutron powder diffractometer (NPDF) [15] at the Lujan Center at Los Alamos National Laboratory.

3. Results and discussion

All three pyrochlore samples were phase pure as revealed both by laboratory powder X-ray diffraction, as well as time-of-flight powder neutron diffraction. Neutron powder diffraction data collected from the three samples were utilized to refine, using the Rietveld method as implemented in the GSAS code [16], models based on the pyrochlore structure in the space group $Fd\bar{3}m$ (No. 227, origin choice 2) with the A and O' sites displaced from their ideal positions, as described by Levin et al. [12] for BZN.

Fig. 1 displays the fit of the refined model to the highest resolution neutron powder diffraction dataset acquired on the three different samples. The BZN structure that ensues is displayed in Fig. 2 in a projection down [110]. $(\text{Nb/Zn})\text{O}_6$ octahedra form a corner connected network, and the anisotropic O ellipsoids are oblate and tangential to the octahedra. Both (Nb/Zn) and O are in their usual ideal pyrochlore positions [Tables 1–3]. The A and O' sites are split due to displacement from their ideal positions as displayed in the figure.

The precise nature of the splitting is indicated in greater detail in Fig. 3. Each O' is split into 12 different sites, through displacement from the ideal $(3/8, 3/8, 3/8)$ position to the 96 g site (x, x, y) and each A is split into six different

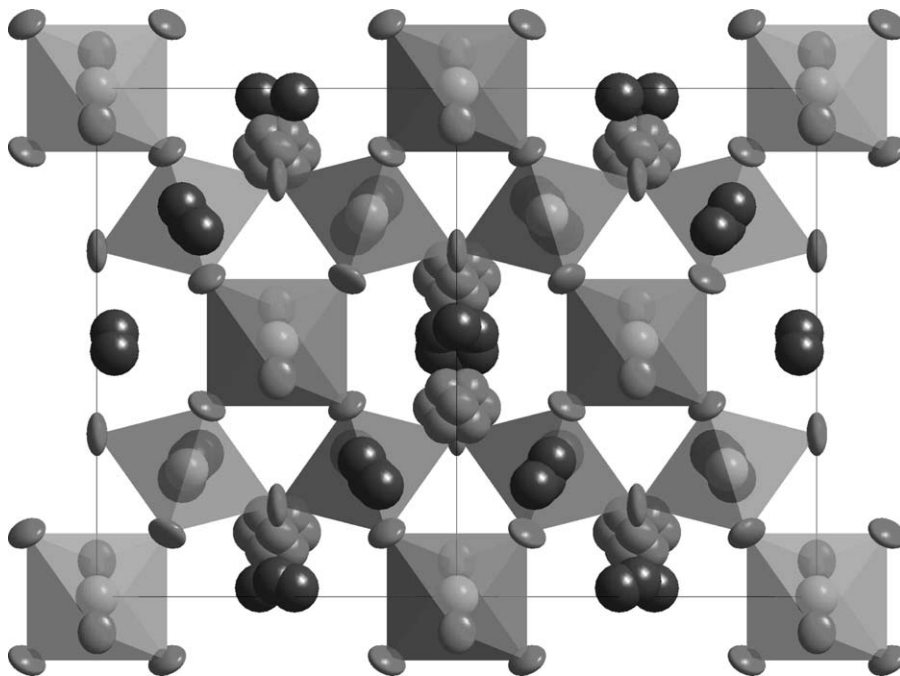


Fig. 2. Crystal structure of pyrochlore $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Nb}_{1.5}\text{Zn}_{0.5})\text{O}_6\text{O}'$ showing the ideal B(Nb/Zn)–O network of corner-connected octahedra, and the split (Bi/Zn) and O' atom positions. The projection of the structure is down [1 1 0]. For O (in the octahedra) thermal ellipsoids with 90% probability are displayed for all atoms.

Table 1
Structural parameters from the room temperature structure refinement of BZN

Atom	Wyckoff	Occ.	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
Bi/Zn	96g	0.125/0.035	0.4689 (1)	0.5174 (2)	0.5174 (2)	1.55 (3)
Nb/Zn	16c	0.750/0.250	0	0	0	1.32 (2)
O'	96g	0.0767	0.3443 (2)	0.3443 (2)	0.3770 (4)	2.2 (1)
O	48f	1	0.31996 (4)	1/8	1/8	2.20*

U_{11} , 3.30 (3); $U_{22} = U_{33}$, 1.64 (2); U_{23} , 0.90 (2). SG. $Fd\bar{3}m$ (No. 227, origin 2) $a = 10.5555(5) \text{ \AA}$ $\chi^2 = 1.872$. Anisotropic thermal parameters are presented for O.

Table 2
Structural parameters from the room temperature structure refinement of BZT

Atom	Wyckoff	Occ.	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
Bi/Zn	96g	0.125/0.035	0.4693 (2)	0.5160 (2)	0.5160 (2)	1.64 (3)
Ta/Zn	16c	0.750/0.250	0	0	0	0.90 (1)
O'	96g	0.0767	0.3443 (2)	0.3443 (2)	0.3774 (4)	2.0 (1)
O	48f	1	0.32000 (4)	1/8	1/8	2.13*

U_{11} , 3.25 (3); $U_{22} = U_{33}$, 1.56 (2); U_{23} , 0.94 (2). SG. $Fd\bar{3}m$ (No. 227, origin 2) $a = 10.5407(5) \text{ \AA}$ $\chi^2 = 1.707$. Anisotropic thermal parameters are presented for O.

sites through displacement from the ideal site (1/2, 1/2 1/2) to the 96 g site (*x*, *y*, *y*). This results in the atom positions and coordinations displayed in Fig. 3(a) around O' and in Fig. 3(b) around the A site. Each (split) A is bound to two O' and to six O.

Details of the refined structures of the three compounds are presented in Tables 1–3. The Bi:Zn ratio on the A site, as well as the occupancy of O' were fixed to the values used by Levin et al. [12] in order that comparisons between the structures would be meaningful. The actual formulas of the title compounds are therefore $(\text{Bi}_{1.5}\text{Zn}_{0.42})(\text{B}_{1.5}\text{Zn}_{0.5})\text{O}_6\text{O}'_{0.92}$ with B = Nb, Ta, or Sb. Sensible thermal parameters of all the atoms in the three compounds suggest the atom occupancies are correct within the resolution of the neutron experiments.

We use data from the structure refinements to plot in Fig. 4(a) the reported dielectric constants separately against the displacements of the A and O' sites from their ideal positions. The dielectric constant for bulk samples at 1 Mhz are reported for $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Nb}_{1.5}\text{Zn}_{0.5})\text{O}_6\text{O}'$ to be 143, [5] and 150 [14]; for $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Ta}_{1.5}\text{Zn}_{0.5})\text{O}_6\text{O}'$, they are reported to be 67, [5] 76, [14], and 71.4 [17]; for $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Sb}_{1.5}\text{Zn}_{0.5})\text{O}_6\text{O}'$ the reported value is 32. [14] While there is some tendency for a trend, the large difference in the dielectric constants of BZN and BZT do not correspond to similar large differences in the displacements of the A and O' atoms from their ideal positions. A similar trend is noted when the dielectric constants are plotted against the thermal parameters on the different sites [Fig. 4(b)]. Except for the thermal parameters on the B site (Nb, Ta, or Sb) we are unable to recognize a clear correlation, apart from that large thermal parameters are associated with large dielectric constants at 1 MHz.

Two aspects of the structural summary require remark. The first is that d^0 cations Nb^{5+} and Ta^{5+} are expected to display a tendency to so-called second-order Jahn-Teller (SOJT) distortions, [18] and indeed, this tendency should be greater for Nb^{5+} than for Ta^{5+} . Sb^{5+} , which has a filled d shell should display no such tendency. The trend of local

Table 3
Structural parameters from the room temperature structure refinement of BZS

Atom	Wyckoff	Occ.	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
Bi/Zn	96g	0.125/0.035	0.4763 (3)	0.5137 (3)	0.5137 (3)	1.45 (3)
Sb/Zn	16c	0.750/0.250	0	0	0	0.64 (1)
O'	96g	0.0767	0.3493 (2)	0.3493 (2)	0.3801 (5)	1.7 (1)
O	48f	1	0.32392 (4)	1/8	1/8	1.49*

U_{11} , 1.84 (2); $U_{22} = U_{33}$, 1.31 (1); U_{23} , 0.67 (2). SG. $Fd\bar{3}m$ (No. 227, origin 2) $a = 10.452(1) \text{ \AA}$ $\chi^2 = 1.649$. Anisotropic thermal parameters are presented for O.

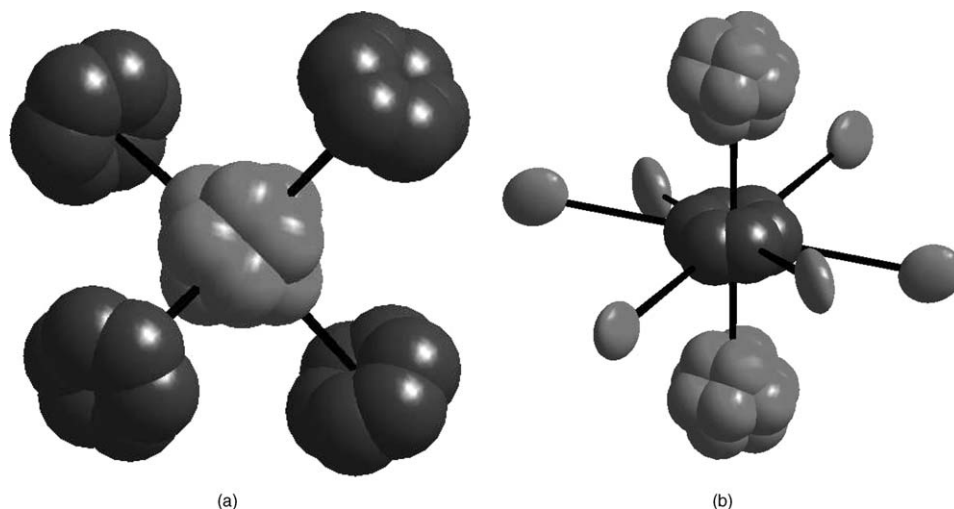


Fig. 3. (a) View of a single O' –(Bi/Zn) tetrahedron in the crystal structure of $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Nb}_{1.5}\text{Zn}_{0.5})\text{O}_6\text{O}'$ emphasizing the manner in which these atoms are split, (b) view of the (Bi/Zn)– O,O' coordination. 90% thermal ellipsoids are displayed for all atoms.

displacements and thermal parameters in the three compounds is in keeping with this chemical expectation, except that the distortions on the B site are dynamic and manifest via the thermal parameters rather than as static displacements. The B–O networks in the three compounds are nearly identical in terms of their static structures, so the only change that should influence the A and O' displacements, are the larger thermal parameters on the B site in the Ta and Nb compounds.

The second aspect concerns the very large relative magnitude of the static displacements. The Lindemann criterion [19] is often invoked in relating the extent of dynamics in crystals, as manifest in thermal displacement parameters, to the melting point; melting is often found to occur when thermal displacements in a crystal reach a magnitude near 10% of typical bond distances. In this work, we find that static displacements in the pyrochlore structure are as large as 20% or more of typical bond lengths. Using the Lindemann criterion as a guide, one would not expect crystals with such large extents of disorder to remain stable, and the disorder could be suggestive of proximity to a phase transition. The observed fact that these pyrochlore structures remain cubic till the lowest temperature is curious, and is perhaps related to the intrinsic difficulty of distorting the cubic ice-like lattice of the pyrochlore structure in a coherent fashion [20].

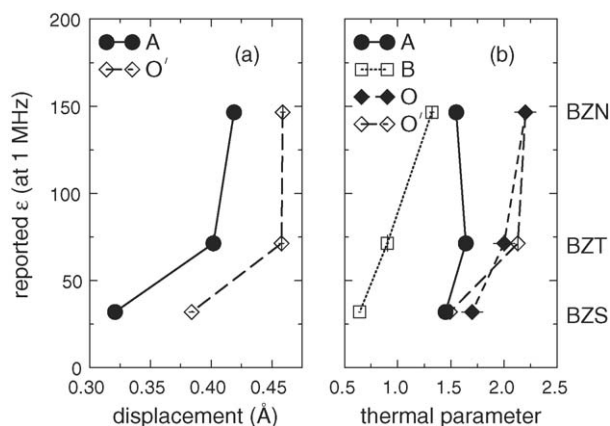


Fig. 4. (a) Reported dielectric constants of the three pyrochlore compounds plotted against the displacements of the A and O' sites from their ideal positions, (b) reported dielectric constants plotted against the refined thermal parameter of the different atoms. Error bars on ϵ indicate the range of experimental data.

Acknowledgements

We thank Susanne Stemmer for suggesting the problem and Katharine Page for help with data collection. This work was supported by the National Science Foundation through the MRL program (DMR00-80034), through a Chemical Bonding Center (CHE04-34567) and through an IGERT fellowship to ER. Measurements at the Lujan Center at Los Alamos Neutron Science Center were supported by the Department of Energy Office of Basic Energy Sciences and Los Alamos National Laboratory funded by the Department of Energy under contract W-7405-ENG-36. MAH thanks the Royal Society for funding.

References

- [1] B.G. Hyde, S. Andersson, *Inorganic Crystal Structures*, John Wiley, New York, 1989.
- [2] R. Seshadri, *Proc. Indian Acad. Sci. (Chem. Sci.)* 113 (2001) 487.
- [3] M.A. Subramanian, G. Aravamudan, G.V. Subba Rao, *Prog. Solid State Chem.* 15 (1983) 55.
- [4] T.A. Vanderah, I. Levin, M.W. Lufaso, *Eur. J. Inorg. Chem.* (2005) 2895.
- [5] D.P. Cann, C.A. Randall, T.R. Shrout, *Solid State Commun.* 100 (1996) 529.
- [6] X. Wang, H. Wang, X. Yao, *J. Am. Ceram. Soc.* 80 (1997) 2745.
- [7] M. Valant, P.K. Davies, *J. Am. Ceram. Soc.* 83 (2000) 147.
- [8] W. Ren, S. Trolier-Kinstry, C.A. Randall, T.R. Shrout, *J. Appl. Phys.* 89 (2001) 767.
- [9] Y.P. Hong, S. Ha, H.Y. Lee, Y.C. Lee, K.H. Ko, D.W. Kim, H.B. Hong, K.S. Hong, *Thin Solid Films* 419 (2002) 183.
- [10] J. Lu, S. Stemmer, *Appl. Phys. Lett.* 83 (2003) 2411.
- [11] J. Lu, D.O. Klenov, S. Stemmer, *Appl. Phys. Lett.* 84 (2004) 957.
- [12] I. Levin, T.G. Amos, J.C. Nino, T.A. Vanderah, C.A. Randall, M.T. Lanagan, *J. Solid State Chem.* 168 (2002) 69.
- [13] S. Kamba, V. Porokhonskyy, A. Pashkin, V. Bovtun, J. Petzelt, J.C. Nino, S. Trolier-McKinstry, M.T. Lanagan, C.A. Randall, *Phys. Rev. B.* 66 (2002) 054106.
- [14] D. Huiling, Y. Xi, *J. Mater. Sci. Mater. Electron.* 15 (2004) 613.
- [15] Th. Proffen, T. Egami, S.J.L. Billinge, A.K. Cheetham, D. Louca, J.B. Parise, *Appl. Phys. A* 74 (2002) 163.
- [16] A.C. Larson, R.B. Von Dreele, General structure analysis system (GSAS), Los Alamos National Laboratory Report LAUR 86–748 (2000); B.H. Toby, *J. Appl. Cryst.* 34 (2001) 210.
- [17] H.-J. Youn, C. Randall, A. Chen, T. Shrout, M.T. Lanagan, *J. Mater. Res.* 17 (2002) 1502.
- [18] P.S. Halasyamani, K. Poepplmeier, *Chem. Mater.* 10 (1998) 2753.
- [19] F.A. Lindemann, *Z. Physik* 11 (1910) 609.
- [20] R. Seshadri, *Solid State Sci.*, submitted for publication.