Local Structure of Displacively Disordered Pyrochlore Dielectrics

Victor Krayzman, Igor Levin,* and Joseph C. Woicik

Ceramics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

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Local cation environments in the pyrochlore dielectrics $A_2B_2O_6O' = (Bi,M)_2(M,Nb)_2O_6O'$ (M = Zn, Fe) were determined from the extended X-ray absorption fine structure. The A cations and O′ ions are displaced from their ideal positions, yielding the effective (4 + 2 + 2) coordination for the A cations. The A-cation displacements are directed toward a pair of the framework O atoms; the specific displacement directions are determined by the nature of the A cations (i.e., Bi, Zn, Fe) and the local Nb/Zn (or Nb/Fe) B-site configurations. Local correlations among the atomic displacements and both $[A_4O']$ and $[A_2B_2O]$ configurations provide near-ideal bond valence sums for all constituent species in these pyrochlore structures.

Introduction

Ceramics based on the pyrochlore system $(Bi,Zn)_2(Zn,Nb)_2O_7$ (BZN) exhibit low processing temperatures (<950 °C) and high relative permittivities ($\epsilon \approx 120$), which renders them attractive for temperature-stable capacitors and filters embedded in multilayer systems.[1,2] In addition, recent work on BZN thin films has shown that their dielectric properties are tunable with applied voltage.[2−4] The exploitable properties of this compound are intimately connected to the disordered static displacements which occur to satisfy the bonding requirements on the mixed Bi/Zn sites.[5−7]

The $A_2B_2O_7$ pyrochlore structure can be described by the formula $B_2O_6{\cdot}A_2O'$, which emphasizes that the structure is built of two interpenetrating networks: vertex-sharing $[BO_6]$ octahedra form a three-dimensional network based on a diamond net, resulting in large cavities which contain the O′ and A atoms forming a second anti-crystobalite-like A_2O' tetrahedral net[8] (Figure 1a). The B_2O_6 network consists of {111} layers of octahedra, which share corners to form six- and three-membered rings. The relatively large A cations are 8-fold coordinated by six O atoms in the octahedral framework, which form a puckered hexagonal ring, and two O′ atoms, located so that the O′−A−O′ link is perpendicular to the ring. The overall atomic arrangement results in a cubic unit cell with $a \approx 10$ Å and $Fd\bar{3}m$ symmetry; in the ideal arrangement the atoms occupy four special positions: A-16c, B-16d, O-48f, and O′-8b.

As discussed previously,[9] the pyrochlore phase in the Bi−Zn−Nb−O system *does not* occur at traditional pyrochlore compositions with A and B sites being occupied by the relatively large (Bi) and small (Zn/Nb) cations, respectively. Instead, these pyrochlores crystallize with compositions (e.g., $Bi_{1.5}Zn_{0.91}Nb_{1.54}O_7$) that require the presence of relatively small Zn cations on both the A and B sites. Recently, similar behavior has been reported in several other Bi−M−Nb−O systems with small B-type M cations (e.g., Fe, Mn, Co, Ni, Cu, etc) being present on the A sites.[9−12]

According to crystallographic refinements, the BZN pyrochlore, while retaining average cubic $Fd\bar{3}m$ symmetry, exhibits static displacive disorder with the A cations (Bi/Zn) displaced in the {111} planes by 0.39 Å and the O′ ions displaced isotropically by 0.46 Å.[7] The models which assumed disordered A-cation displacements along the six either ⟨112⟩[7,13,14] or ⟨110⟩[13] directions in the {111} planes generated comparable fitting statistics; that is, the powder diffraction data were consistent with a toroidal distribution of the A-cation displacements.[13] Hopping of the ions among the displaced sites has been proposed as the major origin of the dielectric relaxation observed for the BZN compound.[3,5−6] Electron diffraction has revealed the presence of well-structured diffuse scattering which suggests local correlations, such as preferential $[Bi_3Zn]$ tetrahedral configurations on the A sites, among the disordered ions.[13,15] However, the details

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* Corresponding author. E-mail: igor.levin@nist.gov.

(1) Nino, J. C.; Lanagan, M. T.; Randall, C. A. *J. Appl. Phys.* **2001**, *89* (8), 4512−4516.
(2) Ren, W.; Trolier-McKinstry, S.; Randall, C. A.; Shrout, T. R. *J. Appl. Phys.* **2001**, *89* (1), 767−774.
(3) Tagantsev, A. K.; Lu, J. W.; Stemmer, S. *Appl. Phys. Lett.* **2005**, *86* (3), article no. 032901.
(4) Park, J.; Lu, J. W.; Stemmer, S.; York, R. A. *Integr. Ferroelectr.* **2005**, *77*, 21−26.
(5) Nino, J. C.; Lanagan, M. T.; Randall, C. A.; Kamba, S. *Appl. Phys. Lett.* **2002**, *81* (23), 4404−4406.
(6) Kamba, S.; Porokhonsky, V.; Pashkin, A.; Bovtun, V.; Petzelt, J.; Nino, J. C.; Trolier-McKinstry, S.; Lanagan, S, M. T.; Randall, C. A. *Phys. Rev. B* **2002**, *66* (5), article no. 054106.
(7) Levin, I.; Amos, T. G.; Nino, J. C.; Vanderah, T. A.; Randall, C. A.; Lanagan, M. T. *J. Solid State Chem.* **2002**, *168*, 69.
(8) Subramanian, M. A.; Aravamudan, G.; Subba, Rao, G. V. *Prog. Solid State Chem.* **1983**, *15* (2), 55−143.
(9) Vanderah, T. A.; Levin, I.; Lufaso, M. W. *Eur. J. Inorg. Chem.* **2005**, *14*, 2895−2901.
(10) Lufaso, M. W.; Vanderah, T. A.; Pazos, I. M.; Levin, I.; Nino, J. C.; Provenzano, V.; Schenck, P. K. *J. Solid State Chem.* **2006**, *179* (12), 3874−3884.
(11) Vanderah, T. A.; Lufaso, M. W.; Adler, A. U.; Levin, I.; Nino, J. C.; Provenzano, V.; Schenck, P. K. *J. Solid State Chem.* **2006**, *179* (11), 3467.
(12) Vanderah, T. A.; Siegrist, T.; Lufaso, M. W.; Yeager, M. C.; Nino, J. C.; Yates, S. *J. Eur. Inorg. Chem.* **2006**, in press.
(13) Withers, R. L.; Welberry, T. R.; Larsson, A.-K.; Liu, Y.; Norén, L.; Rundlöf, H.; Brink, F. J. *J. Solid State Chem.* **2004**, *177*, 231.
(14) Melot, B.; Rodriguez, E.; Proffen, T.; Hayward, M. A.; Seshadri, R. *Mater. Res. Bull.* **2006**, *41* (5), 961−966.

10.1021/cm062429g

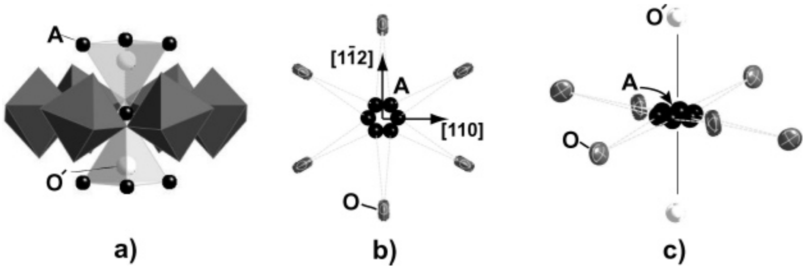

Figure 1. Coordination environment of the A cations in the ideal (a) and displacively disordered (b, c) pyrochlore structures. (b) and (c) provide different views of this environment in the disordered structure. The A cations occupy statistically one of the sites (indicated using black spheres) that are displaced from the ideal central position. Thermal ellipsoids (50% probability) for the O atoms are shown as determined from the neutron powder diffraction for the BZN sample at 12 K.[7]

of the positional disorder, the associated local correlations, and their effects on dielectric properties are not yet known. Clearly, any single measurement technique is insufficient to obtain an accurate description of local atomic arrangements in these complex structures, and a combination of several complimentary methods is needed. Successful examples of such combined analyses have been reported previously.[16] In the present study, we employed extended X-ray absorption fine structure (EXAFS) to determine the local cation coordination environments in the pyrochlore compounds Bi−M−Nb−O (M = Zn, Fe). Further, the results of EXAFS measurements were combined with those from neutron diffraction studies[7,13] to develop an improved understanding of local structures in these materials.

Experimental Section

The EXAFS measurements were conducted on the same $Bi_{1.5}Zn_{0.91}Nb_{1.54}O_7$ ($Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$) and $Bi_{1.72}Fe_{1.056}Nb_{1.134}O_7$ (BFN) samples used previously in neutron diffraction structural refinements.[7,10] EXAFS data were collected at room temperature in transmission for the Bi L_3 edge, Zn K edge, Fe K edge, and Nb K edge using the National Institute of Standards and Technology X23A2 beamline at the National Synchrotron Light Source. The double-crystal monochromator was operated with a pair of Si(311) crystals, and detuning was used to minimize the effect of harmonics. Five to ten spectra were collected for each absorption edge. All data were processed using the Athena code.[17] The Bi L_3 absorption spectra were corrected to remove the effects of double-electron excitations.[18] Normalized *k*-weighted EXAFS signals and the corresponding Fourier transform (FT) magnitudes for the BZN and BFN pyrochlores are shown in Figures 2 and 3, respectively. The exploitable EXAFS signal for all elements in the present samples was limited to $k \approx 12$ Å^{-1}. This limited range is caused by the rapid fall of EXAFS oscillations due to (1) a weak scattering by oxygen and (2) a strong displacive disorder in both BZN and BFN pyrochlore structures. As a result, for $k > 10$ Å^{-1}, the data are affected by the systematic noise.

Structural parameters were obtained by fitting the EXAFS FT calculated with the FEFF6 code[19] to the experimental data. The fit was accomplished using Artemis software.[17] The nonstructural parameters (i.e., energy shifts, E_o, and passive electron reduction factors, S_o^2) entering the EXAFS equation[19] were determined using well-characterized specimens of zirconolite $Bi_2Zn_{2/3}Nb_{4/3}O_7$ (for Bi and Nb)[20] and columbite $ZnNb_2O_6$ (for Zn).[21] Additionally, these two compounds were used as references for the Nb pre-edge structure, which is sensitive to off-center Nb displacements.[22]

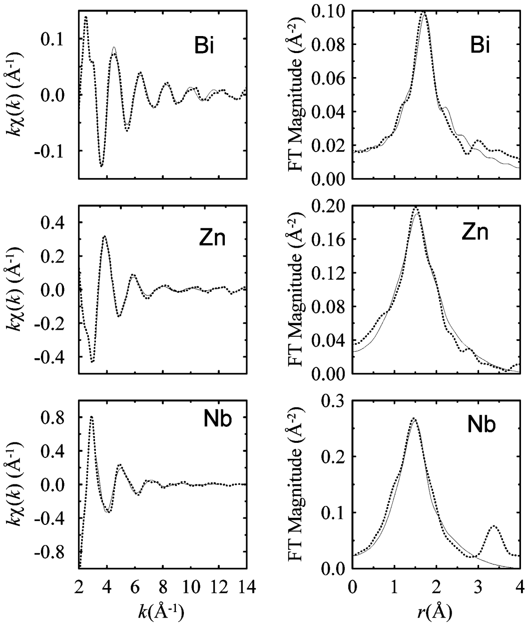

Figure 2. (left) Experimental (dotted line) and fitted (solid line) *k*-weighted EXAFS signals for Bi L_3 edge, Zn K edge, and Nb K edge in the BZN pyrochlore. The fit was conducted in *R*-space and displayed in *k*-space for the *k*-ranges used in the Fourier transform. (right) Experimental (dotted line) and fitted (solid line) magnitudes of EXAFS Fourier transform. The *k*-ranges used in the Fourier transform for Bi, Zn, and Nb were 3.1−12.0, 3.4−12.0, and 3.3−12.0 Å^{-1}, respectively. Prior to a Fourier transform, the EXAFS signal was multiplied by the Hanning window with $dk = 2$ Å^{-1}. The *R*-space fitting ranges were 1.0−2.6 Å for Bi, 1.0−2.5 Å for Zn, and 1.0−2.3 Å for Nb.

Results and Discussion

For the BZN compound, two models (Figure 1b) describing the A-site (Bi/Zn) off-center displacements along the ⟨110⟩ directions toward a pair of the framework O atoms and along the ⟨112⟩ directions toward a single O atom were tested; however, the latter displacement model was rejected

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(15) Liu, Y.; Withers, R. L.; Welberry, T. R.; Wang, H.; Du, H. *J. Solid State Chem.* **2006**, *179*, 2141−2149.

(16) Binsted, N.; Stange, M.; Owens, C.; Fjellvag, H.; Weller, M. T. *J. Synchrotron Rad.* **2001**, *8*, 305−307.

(17) Ravel, B.; Newville, M. *J. Synchrotron Radiat.* **2005**, *12*, 537.

(18) Di Cicco, A.; Filipponi, A. *Phys. Rev. B* **1994**, *49*, 12564−12571.

(19) Zabinsky, S. I.; Rehr, J. J.; Ankudinov, A.; Albers, R. C.; Eller, M. J. *Phys. Rev. B* **1995**, *52*, 2995.

(20) Levin, I.; Amos, T. G.; Nino, J. C.; Vanderah, T. A.; Reaney, I. M.; Randall, C. A.; Lanagan, M. T. *J. Mater. Res.* **2002**, *17*, 1406.

(21) Waburg, M.; Mueller-Buschbaum, H. *Anorg. Z. Allgem. Chem.* **1984**, *508*, 55−60.

(22) Shuvaeva, V. A.; Pirog, I.; Azuma, Y.; Yagi, K.; Sakaue, K.; Terauchi, H.; Raevsky, I. P.; Zhuchkov, K.; Antipin, M. Yu. *J. Phys.: Condens. Matter* **2003**, *15*, 2413−2421.

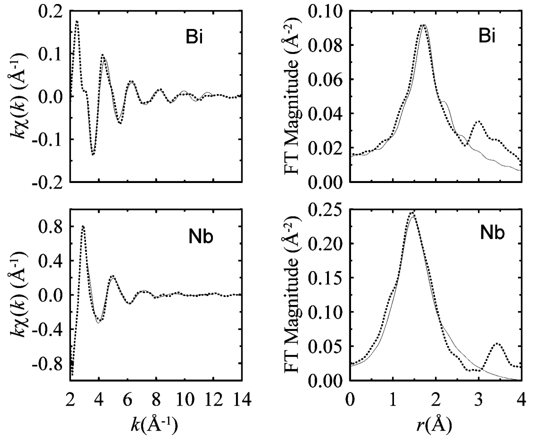

Figure 3. (left) Experimental (dotted line) and fitted (solid line) *k*-weighted EXAFS signals for Bi L_3 edge and Nb K edge in the BFN pyrochlore. The fit was conducted in *R*-space and displayed in *k*-space for the *k*-ranges used in the Fourier transform. (right) Experimental (dotted line) and fitted (solid line) magnitudes of EXAFS Fourier transform. The *k*-ranges used in the Fourier transform for Bi and Nb were 3.2−12.0 and 3.3−12.0 Å^{-1}, respectively. Prior to a Fourier transform, the EXAFS signal was multiplied by the Hanning window with dk = 2 Å^{-1}. The *R*-space fitting ranges were 1.0−2.6 Å for Bi and 1.0−2.3 Å for Nb.

Table 1. Results of the EXAFS Fits for the BZN and BFN Compounds[a]

absorber	scatterer	N	r (Å)	σ^2 (Å^2)	N_{ind}	R factor
			BZN			
Bi	O (rings)	2	2.18 (1)	0.001 (1)	9	0.011
	O′	2	2.37 (2)	0.013 (5)	9	0.011
Nb	O (octahedra)	6	1.975 (4)	0.008 (1)	7.6	0.01
Zn	O (octahedra)	6	2.11 (1)	0.018 (3)	8	0.009
	O′	2	2.11 (1)	0.018 (3)	8	0.009
	O (rings)	2	1.98 (3)	0.002[b]	8	0.009
			BFN			
Bi	O (ring)	2	2.20 (1)	0.002 (1)	9	0.012
	O′	2	2.39 (1)	0.009 (4)	9	0.012
Nb	O (octahedra)	2	1.90 (1)	0.003[b]	7.6	0.007
	O (octahedra)	2	1.99 (1)	0.003[b]	7.6	0.007
	O (octahedra)	2	2.09 (1)	0.003[b]	7.6	0.007

[a] N is the coordination number. N_{ind} refers to the number of independent data points used in the fit.[17] R factor describes the quality of the fit. Values in parentheses are the parameter uncertainties.[17] [b] For these D−W parameters varied independently, the uncertainties were greater than the refined values. Therefore, in the final fit these D−W parameters were fixed at the values corresponding to the upper limits of their respective uncertainty ranges; the constraint had little effect on the refined values of other variables and the quality of the fit.

because of a poor fit to the experimental data. For the first model a satisfactory fit (Figure 2) required a two-shell model ($2 \times R_1 + 2 \times R_2$) with the distances $R_1 = 2.18$ Å and $R_2 = 2.37$ Å (Table 1). These R_1 and R_2 values correspond to the Bi−O and Bi−O′ distances, respectively, with Bi being displaced toward a pair of the framework O atoms and O′ ions being displaced away from Bi. These Bi displacements create two equal well-defined ($\sigma_1^2 = 0.001$ Å^2) distances to the nearest O atoms, whereas the distances from Bi to the remaining four O atoms in the hexagonal rings exhibit a broad distribution which smears their contribution to EXAFS.

The Bi−O distance of $R_1 = 2.18$ Å is smaller than the value of 2.27 Å expected from the neutron-derived A-cation displacements of ≈0.4 Å. This discrepancy is caused, at least in part, by static displacements of the framework O atoms which are manifested by their strongly anisotropic displacement parameters (Figure 1b,c) in the diffraction refinement.[7] These additional O displacements (≈0.15 Å at 12 K), which are associated with local tilting/bending of the [BO_6] octahedra and directed toward/away the A cations, have to be accounted for when calculating the interatomic distances from the neutron data. A relatively small value of σ_1^2 suggests that the static displacements of Bi and the nearest framework O atoms are strongly correlated (the two O atoms are displaced toward the approaching Bi cation). The static O displacements also explain the relatively broad distribution of distances between Bi and the four more distant O atoms in the ring estimated as $R_3 \approx 2.70$ Å (×2) and $R_4 \approx 3.00$ Å (×2). The resulting Bi coordination can be described as (4 + 2 + 2).

The Zn cations, unlike Bi, occupy both A and B sites. An accurate description of the total radial distribution function around Zn therefore requires at least a three-shell model to account for the Zn(A)−O, Zn(A)−O′, and Zn(B)−O distances (Zn(A) and Zn(B) denote the Zn cations on the A and B sites, respectively). However, fitting this three-shell model to the Zn data generated large uncertainties in the structural parameters because of the large correlations among the variables. Therefore, we simplified the model for Zn coordination by using bond valence considerations and the results of neutron diffraction studies as discussed below.

In BZN, both Bi and Zn are strongly under-bonded on the A sites of the ideal pyrochlore arrangement, with bond valence[23] sums of 2.46 v.u. (valence units) and 0.86 (!) v.u., respectively ($6 \times R_{A-O} \approx 2.67$ Å, $2 \times R_{A-O'} \approx 2.29$ Å). The off-center A-cation displacements reduce the effective coordination of Bi while increasing its bond valence sum (BVS) from 2.46 to 3.15 v.u.[7,13] (This bond valence sum was calculated using the EXAFS-derived Bi−O bond distances with the O′ atoms located on the ideal 8b sites and Bi cations displaced by 0.4 Å.) Withers et al.[13] postulated that Zn atoms remain on the ideal 16c A sites so that their bond valence requirements are satisfied exclusively by the O′ displacements. As a part of the present study, we analyzed this structural model with the Zn cations located on the 16c[13] using the neutron powder diffraction data reported previously.[7] The refinements yielded abnormally large anisotropic displacement parameters for the Zn atoms, thus providing clear evidence for their off-center displacements in the hexagonal ring planes. The magnitude of the Zn(A) displacements appeared to be comparable to that of the Bi atoms. However, in contrast to Bi, the Zn displacements increase its BVS only to 1.1 v.u. Therefore, O′ displacements directed toward Zn are mandatory to achieve a reasonable BVS value around Zn. The O′ displacements of 0.46 Å determined by neutron diffraction result in Zn−O′ distances of 1.85 ± 0.05 Å. Concurrently, the Zn(A)−O distances must be similar to the Bi−O distances of 2.18 Å, which is relatively close to the expected Zn(B)−O distances of ≈2.1 Å.

As a first approximation for the Zn coordination, we therefore considered a two-shell model with a shorter distance

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(23) Brown, I. D.; Altermatt, D. *Acta Crystallogr., Sect. B* **1985**, 244−247.

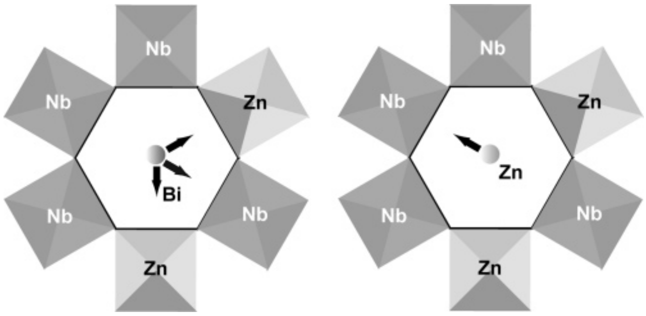

Figure 4. Schematic drawings illustrating the correlations among the directions of the A-site Bi/Zn displacements (indicated using arrows) and the B-site Nb/Zn configurations. The correlations are aimed at satisfying the bond valence sum requirements for the framework O atoms.

having a multiplicity of 2 (as expected for Zn−O′) and a longer distance having a multiplicity of 8, which corresponds to the six Zn(B)−O bonds in the $[ZnO_6]$ octahedra and the two Zn(A)−O distances resulting from the ⟨110⟩ A-site displacements in the hexagonal ring. [The ⟨112⟩ displacements of ≈0.7 Å ($R_{Zn-O} = 1.95$ Å) would be required to produce the BVS equivalent to that due to ⟨110⟩ displacements of only ≈0.4 Å ($R_{Zn-O} = 2.18$ Å); that is, the ⟨110⟩ Zn displacements are more consistent with the displacement magnitude determined from the neutron studies.] The remaining four Zn(A)−O distances in the ring were assumed to exhibit a broad distribution for reasons analogous to those discussed for Bi. The fitting parameters included the two distances and the associated Debye−Waller (D−W) factors. This double-shell model provided a satisfactory fit to the experimental data (Figure 2), yielding $R_1 = 1.98$ Å ($\sigma^2 = 0.002$ Å^2) and $R_2 = 2.11$ Å ($\sigma^2 = 0.018$ Å^2) (Table 1). A relatively broad distribution of R_2 was expected since this shell represents the Zn−O distances both in the octahedra and in the rings. Alternatively, we considered a two-shell model ($2 \times R_1 + 6 \times R_2$) that assumed a broad distribution of *all* Zn(A)−O distances in the rings so that their contribution to the EXAFS FT was negligible (for example, this could occur for the Zn(A) displacements exhibiting a toroidal distribution). However, fitting the ($2 \times R_1 + 6 \times R_2$) model to the experimental data produced a negative D−W factor for the R_2, thus suggesting that the contribution of the Zn(A)−O distances is significant. Further studies using alternative techniques are necessary to elucidate the details of Zn displacements in the hexagonal rings.

The total BVS values, calculated from the EXAFS-derived distances, around the Bi and A-site Zn are 3.08 and 1.78 v.u., being reasonably close to their ideal values. (Note that the major contribution to the BVS of both cations is coming from the nearest two framework O and two O′ ions.) The BVS value for the B-site Zn is 1.92 v.u. Analyses of the BVS values for the framework O atoms in various possible $[B_2A_2O]$ configurations suggests that (1) only one A cation can be displaced toward a given O ion in the $[BO_6]$ octahedron, and (2) the Bi cations are displaced preferentially toward those O pairs which exhibit a mixed B-site coordination Nb−O−Zn(B) for each O atom, whereas the Zn(A) cations are displaced toward the O pairs with the Nb−O−Nb environment (Figure 4). Under these conditions, the O ions acquire near-ideal BVS values ranging from 2.02 to 2.05 v.u. For comparison, the displacements of Bi toward the O pairs with the Nb−O−Nb coordination would produce the O BVS value of 2.53 v.u.

According to neutron refinements,[7,13,14] the probability density distribution for the O′ atoms can be represented by a spherical shell having a radius of ≈0.46 Å and a thickness of ≈0.2 Å; that is, the probability density around the ideal 8b sites is zero. In fact, these crystallographic refinements suggest that $[Bi_3ZnO']$ is the predominant $[A_4O']$ configuration; otherwise, the presence of $[Bi_4O']$ tetrahedra would result in a nonzero probability density around the ideal 8b sites, as was indeed observed for $Bi_2Ti_2O_7$[24] and $(Bi_{1.72}Fe_{0.19})(Fe_{0.866}Nb_{1.134})O_7$[10] compounds. As discussed previously,[7,13,15] the $[Bi_3ZnO']$ arrangement is expected to minimize the bond strain around the A sites and O′ ions. The BVS for O′ calculated for the $[Bi_3ZnO']$ configuration using the EXAFS-derived distances is 1.91 v.u.

Finally, the Nb EXAFS in the BZN pyrochlore was fitted (Figure 2) using a single-shell model with $R_{Nb-O} = 1.98$ Å ($\sigma^2 = 0.008$ Å^2) (Table 1). This distance corresponds to a BVS of 4.86 v.u., which is within a common range for Nb in oxides. Comparison of the pre-edge[22] peak intensities from the BZN pyrochlore and zirconolite $Bi_2Zn_{2/3}Nb_{4/3}O_7$ reveals no significant deviations from the centrosymmetric environment for Nb in the BZN structure. However, minor distortion of the $[NbO_6]$ octahedra (i.e., bending) cannot be ruled out, especially given the relatively large value of the D−W factor. These results are reminiscent of the studies of the $Bi_2Ru_2O_7$ pyrochlore,[25] where Ru was confirmed to reside in the centrosymmetric positions even though the $[RuO_6]$ octahedra were distorted to the trigonal antiprisms.

For the Bi−Fe−Nb−O (BFN) pyrochlore, a reliable separation of the contributions from the A- and B-site Fe to the EXAFS was precluded by the relatively small fraction of A-site Fe (18% of the total Fe content). Therefore, for this compound the analyses were limited to the Bi and Nb environments. In particular, the Bi EXAFS in the BFN was fitted (Figure 3) using a two-shell model ($2 \times R_1 + 2 \times R_2$) with $R_1 = 2.20$ Å ($\sigma^2 = 0.002$ Å^2) and $R_2 = 2.39$ Å ($\sigma^2 = 0.009$ Å^2) (Table 1) attributed to the Bi−O and Bi−O′ distances, respectively. For the Nb in the BFN, a three-shell model ($2 \times R_1 + 2 \times R_2 + 2 \times R_3$) with the Nb−O distances of $R_1 = 1.90$ Å, $R_2 = 1.99$ Å, and $R_3 = 2.09$ Å (Table 1) was needed to obtain a satisfactory fit (Figure 3). The larger distortion of $[NbO_6]$ octahedra in the BFN as compared to the BZN likely originates from a more concentrated B-site mixture in the BFN compound (BFN, Fe/Nb ≈ 0.5; BZN, Zn/Nb ≈ 0.25). Despite this pronounced distortion of the $[NbO_6]$ octahedra, the Nb K pre-edge structure in the BFN phase was very close to that in the BZN, which suggests that the Nb cations still retain their centrosymmetric environments.

The Bi−O/Bi−O′ distances in the BFN compound are similar to those identified for the BZN, yielding a total Bi BVS value of 3.04 v.u. According to neutron diffraction

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(24) Hector, A. L.; Wiggin, S. B. *J. Solid State Chem.* **2004**, *177*, 139−145.
(25) Avdeev, M.; Haas, M. K.; Jorgensen, J. D.; Cava, R. J. *J. Solid State Chem.* **2002**, *169*, 24−34.

studies,[7,10] both compounds exhibit similar Bi displacements but different behaviors of the O′ atoms. In the BFN pyrochlore, the A sites are occupied primarily by Bi (A-site Fe/Bi = 0.09) so that the [Bi_4O'] is the predominant configuration. Therefore, as expected from the bond valence arguments and confirmed by the neutron diffraction refinements,[10] the O′ atoms exhibit high probability density at the ideal 8b sites. The Bi−O′ distances of 2.39 Å are longer than the 2.31 Å estimated for the Bi atoms displaced in the {111} planes and the O′ ions located in the ideal 8b sites. This difference can be attributed to the Bi displacements directed slightly out of the {111} planes due to a strong puckering of the hexagonal O rings. Clearly, common thermal ellipsoids that have been used in neutron diffraction refinements[7,13,14] cannot provide an adequate description of such off-plane static A-cation displacements. Following the bond valence arguments for the O atoms, the Bi atoms are expected to be displaced preferentially toward the B-site Fe cations.

Conclusions

In summary, we have determined the local cation coordination environments in the displacively disordered BZN and BFN pyrochlores. The combined A-cation and O′ displacements decrease the effective A-cation coordination to (4 + 2 + 2), thereby reducing the residual bond tension around these cations to acceptable levels. In BZN, both Bi and Zn are displaced toward a pair of the framework O atoms. Bond valence analyses indicate strong correlations among the local [A_2B_2O] configurations and the displacement directions for Bi and Zn(A). Similar conclusions hold for the Bi displacements in the BFN compound. For the BZN compound, the EXAFS results are consistent with [$BiZn_3O'$] as the predominant [A_4O'] configuration, with the O′ displacements directed toward the A-site Zn and away from the Bi cations.

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