Cation Disorder in the Ferroelectric Oxides ABi$_2$Ta$_2$O$_9$, A = Ca, Sr, Ba

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The crystal structures of the layered ferroelectric oxides ABi$_2$Ta$_2$O$_9$, (A = Ca, Sr, and Ba) have been refined using multiple-wavelength synchrotron powder diffraction data. At room temperature CaBi$_2$Ta$_2$O$_9$ and SrBi$_2$Ta$_2$O$_9$ have an orthorhombic structure with space group $A2_1am$. Bulk samples of the two oxides exhibit small, but significant amounts of disorder between the A-type and Bi atoms. BaBi$_2$Ta$_2$O$_9$ has a tetragonal structure, space group $I4/mmm$. Again significant amounts of cation disorder are detected. © 2001 Academic Press

INTRODUCTION

There has been a great deal of recent interest in developing fatigue-free, ferroelectrics for nonvolatile memory applications. SrBi$_2$Ta$_2$O$_9$ (SBT) thin-film devices display the above characteristics (1–3) and have the additional significant advantage over the more widely studied PbZr$_{1-x}$Ti$_x$O$_3$ materials that they do not contain a toxic heavy metal. While the ferroelectric properties of bulk samples of SBT were identified in the 1960s (4), it is only in recent years that detailed structural studies using techniques such as X-ray synchrotron and high-resolution neutron powder diffraction have been attempted. The spontaneous ferroelectric polarization in these oxides is dependent on the precise geometry of the constituent ions and can be moderated by chemical substitution. Obtaining precise and accurate structures of these oxides is of considerable importance in understanding the properties of these materials.

SrBi$_2$Ta$_2$O$_9$ is an example of an Aurivillius-type layered compound. The divalent Sr can be totally, or partially, replaced by other divalent cations, most commonly Pb, Ca, or Ba, without altering the key features of the structure. The crystal lattice of these ABi$_2$Ta$_2$O$_9$ Aurivillius-type oxides consists of perovskite-like layers with composition $[(A$Ta$_2$O$_7)^{2-}]_n$ interspersed between $[(Bi_2O_2)^{2+}]_n$ layers with the divalent A-type cations being located between the corner-sharing TaO$_6$ octahedra within the perovskite-like layer (Fig. 1). The thermal history of Aurivillius-type oxides of the type ABi$_2M_2$O$_9$ (A = Ca, Sr, Ba, Pb and M = Nb, Ta) is known to alter their bulk electrical properties (5). This suggests that oxygen vacancies or cation disorder within the $[(Bi_2O_2)^{2+}]_n$ layers and the perovskite A-type sites is a contributing factor in the performance of these compounds. It was long believed that, in comparison with the ease of substitution into the perovskite layers, it was not possible to substitute other cations into the Bi$_2$O$_2$ layers without destroying the structure (6, 7). The Bi$_2$O$_2$ layers are comprised of a square planar net of oxygen anions with the Bi^{3+} cations alternating above and below the plane and can be described as forming caps of the BiO$_4$ square pyramids. The asymmetrical coordination environment of the Bi cations is due to the stereochemical activity of the $6s^2$ lone pair electrons. It is this distorted environment that is thought to limit cation substitution into the Bi$_2$O$_2$ layers. Recently it has been established that other cations, especially those with stereochromically active lone pair electrons such as Sn^{2+}, Sb^{3+}, Pb^{2+}, or Te^{4+}, can be introduced, at least in part, into the Bi$_2$O$_2$ layers (8–13). Previous diffraction studies of SBT have not provided evidence of cation disorder, largely due to a preference for neutron diffraction studies that are ideally sensitive to the positions of the lighter O atoms but are relatively insensitive to cation disorder (14). Recent independent studies by Ismunandar and Kennedy (15) and Blake *et al.* (16) have demonstrated that there is a significant degree of Sr/Bi cation disorder in the isostructural ABi$_2$Nb$_2$O$_9$ compounds and that the amount of disorder is dependent on both the cation and the thermal treatment of the sample. Thus, it is possible that cation disorder also occurs in the tantalum analogues.
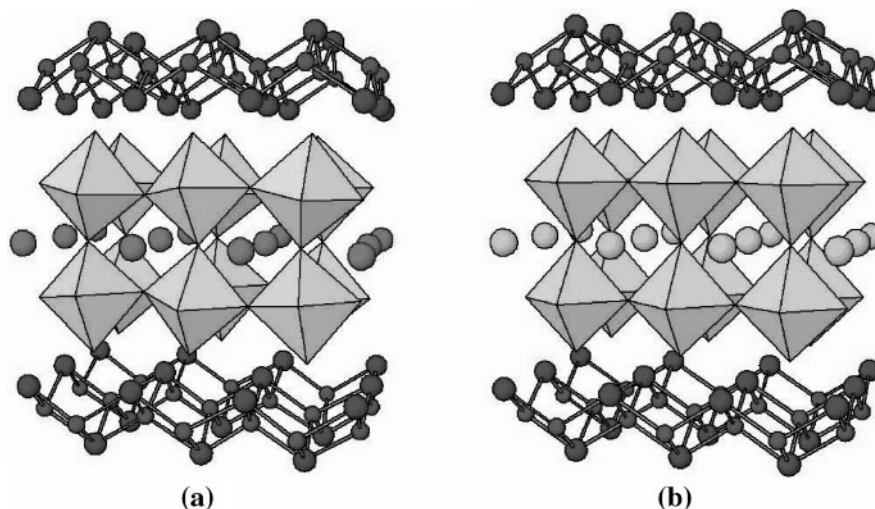
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FIG. 1. Structures of (a) $SrBi_2Ta_2O_9$ and (b) $BaBi_2Ta_2O_9$ showing $[(Bi_2O_2)^{2+}]_n$ planes and corner sharing TaO_6 octahedra with Sr/Ba cations positioned between the octahedra.

This article reports the results of structure refinements of $ABi_2Ta_2O_9$ (A = Ca, Sr, Ba), obtained from multiple-wavelength powder X-ray synchrotron diffraction measurements, aimed at determining if cation disorder exists in these oxides.

EXPERIMENTAL

Powder samples of $ABi_2Ta_2O_9$ were prepared using standard ceramic techniques, as described elsewhere (14). Powder diffraction patterns were recorded on the high-resolution powder diffractometer at beamline 20B, the Photon Factory Japan (17). The samples were contained in 0.3-mm-diameter capillaries that were rotated throughout the measurement to minimize the effects of preferred orientation. Data were collected at four wavelengths, $\lambda = 0.7407, 0.7496, 0.7565$, and 0.7657 Å, using image plates to detect the diffracted X rays. These wavelengths are above and below the Bi L1 edge and were chosen to maximize the sensitivity of the refinements to cation disorder. Due to availability of synchrotron beam time it was not possible to record data at the Bi LIII edge or to directly measure the values of f' and f'' at each wavelength. The initial wavelength was calibrated using NIST Si 640b. The Rietveld refinements (18) of the structures using the four X-ray data sets were undertaken with the PC version of the computer program LHPM (19). A pseudo-Voigt function was chosen to generate the line shape of the diffraction peaks. The Gaussian widths were given by the function $(FWHM)^2 = U \tan^2 \theta + V \tan \theta + W$, where U, V, and W are refinable parameters and the width of Lorentzian component was varied as $\eta \sec \theta$ to model particle size effect.

The values of f' and f'' were calculated using the program FPRIME (20).

RESULTS AND DISCUSSION

The synchrotron X-ray patterns for $CaBi_2Ta_2O_9$ and $SrBi_2Ta_2O_9$ were consistent with orthorhombic symmetry and the structures of these two compounds were refined in space group $A2_1am$. As found previously (14) the diffraction patterns for $BaBi_2Ta_2O_9$ can be indexed to a tetragonal cell and the structure of $BaBi_2Ta_2O_9$ was refined in space group $I4/mmm$. Attempts to refine this structure using an orthorhombic model, analogous to that employed for the Ca and Sr compounds, were unsuccessful, the refinements tending to diverge. In all cases the refinements were initiated using the model described by Shimakawa *et al.* (14) based on time-of-flight powder neutron diffraction data. These models were employed because they provide accurate oxygen positional parameters for the three oxides (15). In these refinements the oxygen positional parameters were initially fixed at the values obtained from the previous neutron diffraction study. In the case of the Ca and Sr compounds, attempts to refine the oxygen positions resulted in some instability in the refinements, and so these were not varied in the final refinements. Any small error in their positions was modelled by the atomic displacement parameters. In the case of the higher symmetry Ba compound, it was possible to refine the positions of the lighter oxygen atoms. The final refined values are given in Table 1 and are in good agreement with those determined using more accurate neutron diffraction methods.

TABLE 1
Refined Structural Parameters for BaBi$_2$Ta$_2$O$_9$

Atom	Site	x	y	z	B_{eq}	N
Ba	2a	0	0	0	1.14(6)	0.561(10)
Bi	2a	0	0	0	1.14(6)	0.439(10)
Bi	4e	0	0	0.20171(7)	1.17(3)	0.780(5)
Ba	4e	0	0	0.20171(7)	1.17(3)	0.220(5)
Ta	4e	0	0	0.41193(4)	0.56(2)	1
O1	2b	0	0	$\frac{1}{2}$	0.4(1)	1
O2	4e	0	0	0.3424(6)	0.4(1)	1
O3	4d	0	$\frac{1}{2}$	$\frac{1}{4}$	0.4(1)	1
O4	8g	0	$\frac{1}{2}$	0.4170(4)	0.4(1)	1

Note. Space group $I4/mmm$, $a = 3.9355(1)$ Å, $c = 25.5686(6)$ Å, R_p 1.94%, R_{wp} 2.66%, GOF 14.48%. The estimated standard deviations (in parentheses) refer to the last digit printed.

TABLE 2
Refined Structural Parameters for SrBi$_2$Ta$_2$O$_9$

Atom	Site	x	y	z	B_{eq}	N
Sr	4a	0	0.2643(18)	0	0.72(6)	0.850(6)
Bi	4a	0	0.2643(18)	0	0.72(6)	0.150(6)
Bi	8b	0.4675(8)	0.7679(5)	0.20066(5)	0.51(3)	0.925(3)
Sr	8b	0.4675(8)	0.7679(5)	0.20066(5)	0.51(3)	0.075(3)
Ta	8b	0.5155(9)	0.7488(7)	0.41478(3)	1.28(2)	1
O1	4a	0.5248	0.2892	0	0.16(1)	1
O2	8b	0.5219	0.6990	0.34187	0.16(1)	1
O3	8b	0.7381	0.9923	0.25076	0.16(1)	1
O4	8b	0.7554	0.9867	0.06964	0.16(1)	1
O5	8b	0.7909	0.9807	0.58359	0.16(1)	1

Note. Space group $A2_1am$, $a = 5.5272(2)$ Å, $b = 5.5218(1)$ Å, $c = 25.0275(5)$ Å, R_p 1.94%, R_{wp} 2.66%, GOF 14.48%.

Once convergence of the structural refinements had been reached using a fully ordered model, the possibility of disorder of the bismuth and A-type cations was considered. The occupancies of the two sites were constrained so that both sites were fully occupied and the A:Bi stoichiometry was maintained. It was assumed that the A-type cation and Bi occupied identical positions in the lattice and that the temperature factors of the atoms in these sites were equal. The disordered models resulted in a better agreement between the observed and calculated profiles for each of the three oxides. Figure 2 shows an example of a synchrotron diffraction profile for the three compounds, and the final refined parameters and site occupancy factors for the three compounds are given in Tables 1–3.

The most significant result from the structural refinements is the obvious disorder between the two cation sites. As observed for the analogous Nb compounds, the amount of disorder increased as the size of the cation increased (16). This is somewhat surprising since it can be imagined that the larger Ba cations should be less likely to occupy the smaller, more distorted layer positions than the smaller Ca cations. This view neglects the effects of bonding and it has been estimated, using valence bond sum calculations, that A-type cations are overbonded, with the larger Ba being most strongly effected. Conversely, the Bi atoms are underbonded. The effective valence of the A-site was estimated using bond valence sum calculations and these gave values of $A = $ Ca = 2.15, Sr = 2.40, Ba = 2.56 and for the
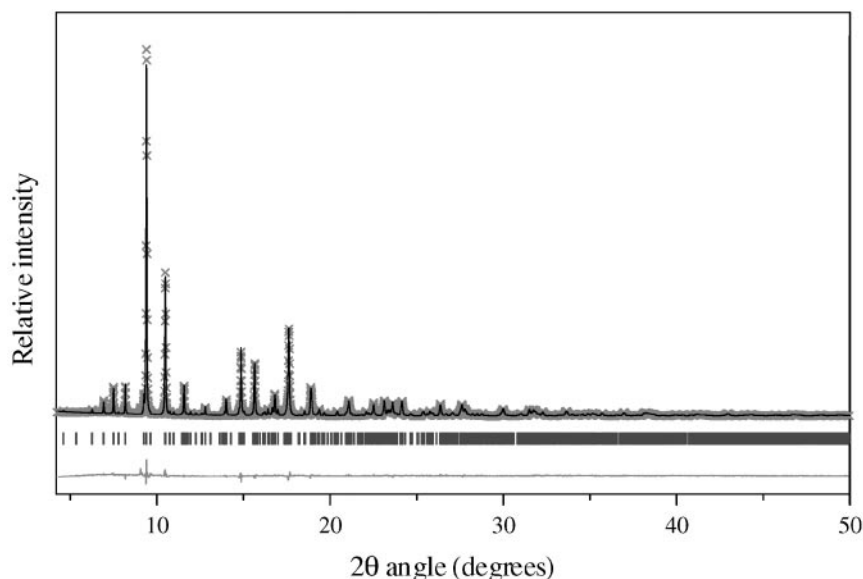

FIG. 2. Observed (crosses), calculated (solid line), and difference profiles (bottom trace) for ABi$_2$Ta$_2$O$_9$, $A = $ Ca, recorded at $\lambda = 0.7407$ Å. The short vertical lines indicate the positions of the allowed Bragg reflections.

TABLE 3
Refined Structural Parameters for CaBi$_2$Ta$_2$O$_9$

Atom	Site	x	y	z	B_{eq}	N
Ca	4a	0	0.2405(22)	0	0.76(1)	0.950(4)
Bi	4a	0	0.2405(22)	0	0.76(1)	0.050(4)
Bi	8b	0.4923(8)	0.7780(2)	0.19901(3)	0.12(2)	0.975(2)
Ca	8b	0.4923(8)	0.7780(2)	0.19901(3)	0.12(2)	0.025(2)
Ta	8b	0.5190(9)	0.7474(3)	0.41694(3)	1.00(1)	1
O1	4a	0.5575	0.3176	0	0.09(10)	1
O2	8b	0.5299	0.6801	0.34439	0.09(10)	1
O3	8b	0.7535	0.9952	0.25025	0.09(10)	1
O4	8b	0.7555	0.9639	0.06389	0.09(10)	1
O5	8b	0.8423	0.9491	0.58578	0.09(10)	1

Note. Space group $A2_1am$, $a = 5.4659(1)$ Å, $b = 5.4318(1)$ Å, $c = 24.9619(4)$ Å, R_p 1.94%, R_{wp} 2.66%, GOF 14.48%.

corresponding Bi sites the values are 2.86, 2.80, and 2.76, respectively. The effective valence of the A-site is, especially for Sr and Ba, noticeably greater than the ideal valence (2.0), suggesting the site may contain the higher valence Bi(III) cations. The introduction of the smaller Bi atoms into the perovskite-type slabs, as occurs upon disorder, acts to reduce the overbonding on this site. While the disorder of Ca, Sr, or Ba and Bi over sites stabilizes the perovskite slabs, there are two competing effects to consider for the Bi$_2$O$_2$ layers. Obviously, placing some of the larger divalent cation onto the bismuth site will increase the bonding at this site, partially overcoming the incipient underbonding. However, since the divalent cations lack lone pair electrons, local distortions, brought about by the lone pair electrons on the Bi(III), are likely to be unfavorable and may limit the extent of the disorder.

As found previously, the degree of the orthorhombic distortion, given by the deviation from unity of the ratio b/a, increased as the size of the A-type cation decreased. The less-than-optimal size of the A-type cations results in a noticeable increase in the tilting of the TaO$_6$ octahedra about the c-axis, with the Ta–O(1)–Ta angle increasing from 0° in BaBi$_2$Ta$_2$O$_9$ to 10.8° in CaBi$_2$Ta$_2$O$_9$.

CONCLUSION

In this work we have provided conclusive evidence of cation disorder in ABi$_2$Ta$_2$O$_9$, A = Ca, Ba, Sr. The extent of the disorder increases as the A-site cation size increases, apparently in response to the underbonding of the A sites.

The sterochemical activity of the Bi 6s lone pair electrons apparently limits, but does not prevent, this disorder. The less-than-optimal size of the divalent cations also results in tilting of the TaO$_6$ octahedra, this increasing as the cation size decreases. It remains to be determined if it is possible to control the extent of cation disorder in these oxides either by altering the thermal treatment of the samples or by chemical doping. Such studies are in progress.

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