

## High-Pressure Phase Transitions in the 6H Perovskites $Ba_3MSb_2O_9$ ( $M = Mg, Ni, Zn$ )

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The 6H perovskites  $Ba_3MSb_2O_9$  ( $M = Mg, Ni, Zn$ ) have been subjected to pressures of up to 5.5 GPa. No structural phase transitions were observed in  $Ba_3MgSb_2O_9$ ,  $Ba_3NiSb_2O_9$  transformed from a phase containing  $Sb_2O_9$  dimers formed by face-sharing octahedra into a phase containing  $NiSbO_6$  dimers. This was confirmed by a combination of X-ray powder diffraction and EXAFS.  $Ba_3ZnSb_2O_9$  transformed into a cubic perovskite with a partial ordering of zinc and antimony over the octahedral sites. © 1990 Academic Press, Inc.

### Introduction

Compounds having the general formula  $ABO_3$  often adopt a perovskite structure when  $A$  is a relatively large cation (usually an alkaline earth or lanthanide) and  $B$  is a transition metal. These structures can be considered to consist of an array of close packed sheets, each with the stoichiometry  $AO_3$ ; the  $B$  cations occupy the octahedral holes between the sheets. The close packed layers can themselves be stacked in either a

cubic or a hexagonal sequence, or in any mixed, but periodic, sequence. The exact stacking sequence adopted determines the way in which the octahedral  $B$  sites are linked together. If the  $AO_3$  layers are stacked in an hcp manner, then neighboring  $B$  sites have three oxygen atoms in common and the  $BO_6$  octahedra are said to share faces. If the layers are arranged in a ccp manner, then neighboring  $B$  sites have only one common oxygen atom and the  $BO_6$  octahedra are described as corner sharing. Mixed stacking sequences lead to mixtures of corner- and face-sharing octahedra, as illustrated (1) in Fig. 1 for the phase 6H- $BaTiO_3$  (2). Goldschmidt (3) showed that hexagonal stacking is favored by a large cation radius ratio  $r_A/r_B$ , and Goodenough and Kafalas (4) have subsequently pointed out that the application of pressure will

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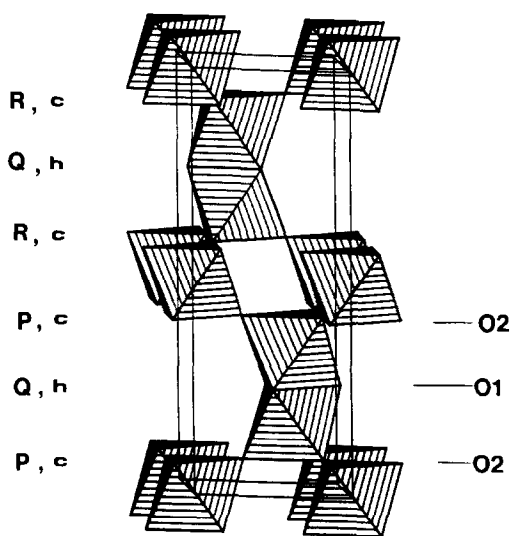


FIG. 1. The 6H- $ABO_3$  perovskite structure, showing the connectivity of the  $BO_6$  octahedra. The A atoms are omitted. Each  $AO_3$  layer is labeled P, Q, or R and is classified as hcp (h) if it has two identical neighboring layers and ccp (c) if it has two different neighboring layers.

therefore increase the relative stability of cubic stacking because A–O bonds are more compressible than B–O bonds. They also pointed out that pentavalent cations are unlikely to occupy face-sharing octahedra because of the strong electrostatic repulsion that would occur between two highly charged species only  $\sim 2.60$  Å apart, although they recognized that this repulsion could be overcome in cases where an aspherical distribution of charge in the  $d$ -orbitals provides some B–B bonding. A single crystal X-ray diffraction study of  $Ba_3NiSb_2O_9$  by Köhl and Reinen (5) was consistent with the ideas of Goodenough and Kafalas. The former authors reported that this compound adopts the 6H structure shown in Fig. 1 with the corner-sharing octahedra occupied by half the antimony and the  $B_2O_9$  face-sharing dimers occupied in an ordered manner by the nickel and the remaining antimony, thus avoiding a short

$Sb^{5+}$ – $Sb^{5+}$  distance. However, a neutron diffraction study performed on a polycrystalline sample of the same compound by Jacobson and Calvert (6) showed that the face-sharing octahedra are entirely occupied by  $Sb^{5+}$ , with the  $Ni^{2+}$  ions taking the corner sharing sites. In order to reduce the  $Sb^{5+}$ – $Sb^{5+}$  repulsion, the cations move off their ideal sites in opposite directions to give an Sb–Sb distance of 2.844 Å and the oxide ions (O1) in the common octahedral face close in to shield the positive charge, resulting in an O1–O1 distance of only 2.588 Å. The corresponding distances in Köhl and Reinen's structure, where the cation–cation repulsion was weaker, were 2.68 and 2.67 Å. Thus it appears that the cation distribution in  $Ba_3NiSb_2O_9$  is sensitive to preparation conditions, and that it is possible to prepare metastable phases. Subsequently Treiber and Kemmler-Sack (7) have described the preparation of  $Ba_3MgSb_2O_9$  and  $Ba_3ZnSb_2O_9$ , both of which contain  $Sb_2O_9$  dimers. In view of the fact that the hexagonal stacking of  $BaO_3$  layers in these compounds leads to strong, repulsive electrostatic cation–cation interactions, which are not, for a  $d^{10}$  ion, mediated by any Sb–Sb bonding, and encouraged by the fact that the structure is clearly sensitive to small perturbations, we have applied pressure to these compounds in an attempt to prepare cubic phases containing only corner-shared octahedra. The results of our experiments are described below.

## Experimental

Polycrystalline samples of  $Ba_3NiSb_2O_9$ ,  $Ba_3ZnSb_2O_9$ , and  $Ba_3MgSb_2O_9$  were prepared from stoichiometric mixtures of  $BaCO_3$ ,  $Sb_2O_3$ ,  $NiO$ ,  $ZnO$ , and  $MgO$  (Johnson Matthey "Specpure" Reagents). The mixtures were thoroughly ground, pelleted, and fired in platinum crucibles, initially at 500°C for 15 hr and then at 1100 (Ni), 1300 (Zn), and 1400°C (Mg) for several days. X-

ray powder diffraction patterns of the products could be indexed as  $6H$ - $BaTiO_3$ -like phases. A small amount of unidentifiable impurity was observed in the case of  $Ba_3MgSb_2O_9$ . High-pressure experiments were carried out in a conical double-piston apparatus (8). Approximately  $50 \text{ mm}^3$  of sample were packed in a thin-walled platinum tube fitted with platinum end plugs and subjected to pressures of 3.5–5.5 GPa at  $600^\circ\text{C}$  for 1 hr, before being allowed to cool to room temperature under pressure. All products were characterized at ambient pressure by X-ray powder diffraction using  $\text{CuK}\alpha$  radiation.

Room temperature EXAFS spectra were recorded using the Daresbury synchrotron radiation source operating at an energy of 2 GeV and a beam current of 170 mA. Data were recorded in the transmission mode on station 7.1, with the finely ground, undiluted samples held between strips of adhesive tape. A Si(111) double-crystal order sorting monochromator was used to reduce substantially the harmonic content of the monochromatic beam. Established procedures were used to extract the EXAFS oscillations from the absorption data (9). The background-subtracted EXAFS was then converted into  $k$ -space and weighted by  $k^3$  in order to compensate for the diminishing amplitude at high  $k$  due to the decay of the photoelectron wave. The data were Fourier filtered to include only the first four (or six) shells, a cutoff which can be made without introducing large truncation errors and which is not complicated by overlapping Fourier transform shells. Analysis of the Fourier-filtered EXAFS was carried out using the nonlinear least-squares program EXCURV88 (10). An ab initio approach was used to calculate initial values for the atomic phase shifts, as previously described (11, 12). We estimate the following levels of accuracy in our refinements: Debye-Waller factor  $\pm 50\%$  and radii  $\pm 0.02 \text{ \AA}$ . These are estimates arising from imperfect

transferability of phase shifts and the fitting procedure described below. Statistical fitting errors are far smaller.

## Results

### (i) $Ba_3MgSb_2O_9$

The X-ray powder diffraction pattern of  $Ba_3MgSb_2O_9$  could be indexed in a hexagonal unit cell with  $a = 5.849(3)$ ,  $c = 14.422(6) \text{ \AA}$ , in reasonable agreement with the values reported previously (7). The relative intensities of the Bragg peaks were also in good accord, and we therefore conclude that our sample contains corner-sharing  $MgO_6$  octahedra and  $Sb_2O_9$  dimers. This material did not show any phase transformation after the application of 4.5 GPa pressure.

### (ii) $Ba_3NiSb_2O_9$

The X-ray powder diffraction pattern of  $Ba_3NiSb_2O_9$ -I, the phase produced during ambient pressure synthesis, could be indexed in a hexagonal unit cell with  $a = 5.840(2)$ ,  $c = 14.400(5) \text{ \AA}$ .  $Ba_3NiSb_2O_9$ -II, produced during experiments at both 4.5 and 5.5 GPa, also gave an X-ray diffraction pattern showing hexagonal symmetry but with the somewhat smaller unit cell parameters  $a = 5.795(3)$ ,  $c = 14.287(5) \text{ \AA}$ . The intensities of the observed Bragg peaks are listed in Table I, where they are compared with those calculated (13) using the atomic coordinates and cation ordering schemes of the Jacobson and Calvert model (JC), the Köhl and Reinen model (KR), and a third model in which the  $B_2O_9$  dimers are occupied by a disordered arrangement of Sb and Ni. These data suggest that our sample of  $Ba_3NiSb_2O_9$ -I is isostructural with the polycrystalline material studied by Jacobson and Calvert, whereas  $Ba_3NiSb_2O_9$ -II apparently shows the same type of cation ordering that Köhl and Reinen found in their single crystal study. In order to confirm these tentative conclusions we collected Ni K-

TABLE I  
OBSERVED AND CALCULATED X-RAY POWDER  
DIFFRACTION INTENSITIES FOR Ba<sub>3</sub>NiSb<sub>2</sub>O<sub>9</sub>

h	k	l	<i>I</i> <sub>obsd</sub>	<i>I</i> <sub>obsd</sub>	<i>I</i> <sub>calcd</sub>	<i>I</i> <sub>calcd</sub>	<i>I</i> <sub>calcd</sub>
			Ba <sub>3</sub> NiSb <sub>2</sub> O <sub>9</sub> -I	Ba <sub>3</sub> NiSb <sub>2</sub> O <sub>9</sub> -II	(JC)	(KR)	(Model 3)
0	0	2	12	<10	9	22	16
1	0	0	35	20	41	12	9
1	0	1	85	20	102	27	21
1	0	2	47	<10	51	18	3
0	0	4	37	10	39	8	4
1	0	3	133	183	152	236	189
1	0	4	691	810	564	753	702
1	1	0	1000	1000	1000	1000	1000
1	1	2	<10	<10	6	13	8
2	0	0	12	<10	8	2	2
1	0	5	198	67	220	63	136
2	0	1			0	9	4
0	0	6	37	24	34	20	31
2	0	2	72	30	72	25	31
1	1	4	62	18	65	19	5
2	0	3	128	176	134	171	153
1	0	6	<10	<10	5	1	4
2	0	4	298	430	321	402	384
2	1	0	0	0	6	1	2
1	0	7	70	122	60	111	49
2	0	5	146	109	140	58	95

edge ( $\lambda = 1.48802 \text{ \AA}$ ,  $E = 8.332 \text{ keV}$ ) EXAFS data, in the manner described above, for phases I and II of Ba<sub>3</sub>NiSb<sub>2</sub>O<sub>9</sub>. We have previously shown (12, 14) that EXAFS is an excellent technique to use in order to determine whether a cation is in face- or corner-sharing coordination geometry; it was particularly suitable in this case

when only a small quantity of the high-pressure phase was available.

The qualitative appearance of the EXAFS data collected on Ba<sub>3</sub>NiSb<sub>2</sub>O<sub>9</sub>-I was consistent with our conclusion, based on X-ray diffraction data, that our ambient pressure sample is isostructural with that prepared by Jacobson and Calvert (6). The reliability of the calculated EXAFS phaseshifts was therefore examined by comparing the observed spectrum with that calculated from the crystallographic data of Jacobson and Calvert. It was found that the calculated backscattering phaseshifts for both the barium and the antimony atoms were unable to reproduce the experimental spectrum, particularly at low *k*. The barium and antimony phaseshifts were then refined, while the radial distribution about the central nickel atom was held fixed. The refinement method involved varying the  $\Delta E_0$  shift of the barium and antimony shells (15) consecutively until good agreement with the experimental data was obtained. The observed and calculated spectra and their Fourier transforms are shown in Fig. 2. The refined radial distances and Debye-Waller factors are presented in Table II. It can be seen that after refinement of the phaseshifts, the observed

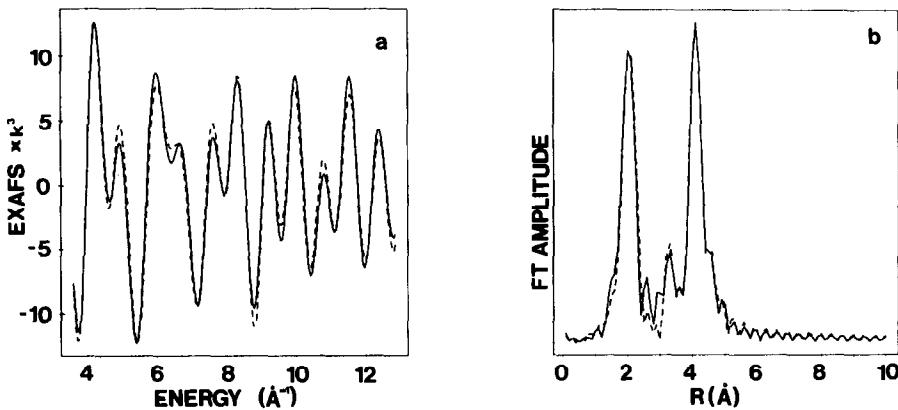


FIG. 2. (a) Observed (—) and calculated (---) Fourier-filtered EXAFS data and (b) the corresponding Fourier transforms for Ba<sub>3</sub>NiSb<sub>2</sub>O<sub>9</sub>-I.

TABLE II  
RADIAL DISTRIBUTION OF ATOMS ABOUT Ni  
IN Ba<sub>3</sub>NiSb<sub>2</sub>O<sub>9</sub>-I

Atom type	Coordination no.	2σ <sup>2</sup> (Å <sup>2</sup> )	Radial distance (Å)	
			EXAFS	JC
O	6	0.010	2.09	2.08
Ba	8	0.019	3.61	3.59
Sb	6	0.010	4.01	4.00
O	12	0.015	4.56	4.59

TABLE III  
RADIAL DISTRIBUTION OF ATOMS ABOUT Ni  
IN Ba<sub>3</sub>NiSb<sub>2</sub>O<sub>9</sub>-II

Atom type	Coordination no.	2σ <sup>2</sup> (Å <sup>2</sup> )	Radial distance (Å)	
			EXAFS	KR
O	3	0.008	2.03	2.04
O	3	0.008	2.14	2.06
Sb	1	0.008	2.68	2.68
Ba	3	0.012	3.40	3.47
Ba	4	0.012	3.59	3.63
Sb	3	0.007	4.00	4.06

and calculated EXAFS spectra are in quite good agreement. The refined phaseshifts were then used, without further refinement, to analyze the EXAFS data collected on Ba<sub>3</sub>NiSb<sub>2</sub>O<sub>9</sub>-II. These data are very different in appearance to those collected on the ambient pressure sample and so, in the light of our X-ray diffraction results, we analyzed them using a model based on the Köhl and Reinen structure, which includes a short contact between nickel and antimony atoms in face-sharing octahedra. Refinement of the radial distances and Debye-Waller factors led to a very satisfactory level of agreement between the observed and calculated EXAFS patterns, as illustrated in Fig. 3. The values of the refined

parameters are listed in Table III. These results thus confirm our view that Ba<sub>3</sub>NiSb<sub>2</sub>O<sub>9</sub>-II contains NiSbO<sub>9</sub> dimers.

(iii) Ba<sub>3</sub>ZnSb<sub>2</sub>O<sub>9</sub>

The X-ray diffraction pattern of Ba<sub>3</sub>ZnSb<sub>2</sub>O<sub>9</sub>-I, synthesized at ambient pressure, could be indexed in a hexagonal unit cell with  $a = 5.858(2)$ ,  $c = 14.456(3)$  Å, in good agreement with the values reported previously (7). The distribution of intensity among the Bragg peaks again suggested that the low pressure phase contains corner-sharing ZnO<sub>6</sub> octahedra and Sb<sub>2</sub>O<sub>9</sub> dimers. Ba<sub>3</sub>ZnSb<sub>2</sub>O<sub>9</sub>-II, produced during syn-

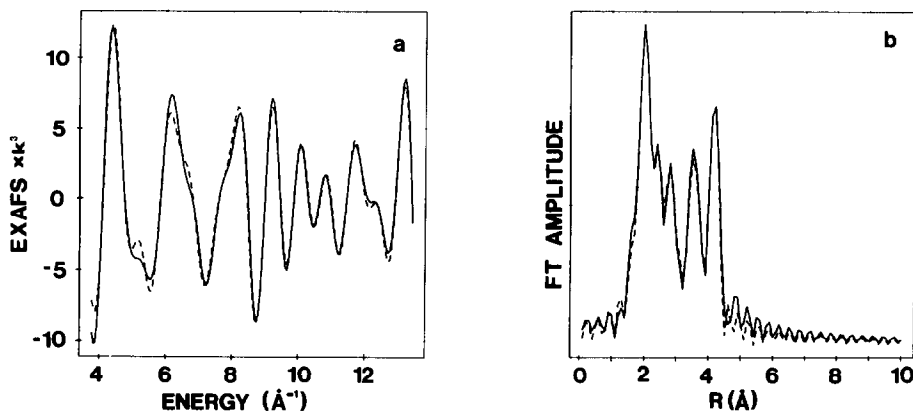


FIG. 3. (a) Observed (—) and calculated (---) Fourier-filtered EXAFS data and (b) the corresponding Fourier transforms for Ba<sub>3</sub>NiSb<sub>2</sub>O<sub>9</sub>-II.

thesis at pressures of 3.5 and 4.5 GPa, gave rise to a face-centered cubic X-ray diffraction pattern,  $a = 8.182(1)$  Å. This result indicates a transition to a phase containing only corner-sharing octahedra with some ordering among the 6-coordinate cations. However, the intensities of the  $(hkl)$  reflections having  $h + k + l = 2n + 1$  were too weak to permit a reliable structure analysis, for example  $I_{111}/I_{200} < 0.005$ .

### Discussion

There is clear correlation between the sensitivity of the hexagonal perovskite structure to pressure and the polarizability of the divalent ion.  $\text{Ba}_3\text{MgSb}_2\text{O}_9$ , containing the relatively "hard"  $\text{Mg}^{2+}$  species, shows no phase transition whereas  $\text{Ba}_3\text{ZnSb}_2\text{O}_9$ , containing "soft"  $\text{Zn}^{2+}$ , undergoes a major structural rearrangement to an apparently cubic phase. The high symmetry of the product is perhaps surprising. The phase  $\text{Ba}_3\text{ZnSb}_2\text{O}_9$  contains a highly ordered arrangement of zinc and antimony, in effect in a 1:2 layer sequence perpendicular to the  $z$  axis of the hexagonal cell (see Fig. 1). It is possible (16, 17) for this 6H structure to transform to a structure in space group  $P\bar{3}m1$  which contains only corner-sharing octahedra but retains the 1:2 sequence of the 6-coordinate cations. The transition observed in  $\text{Ba}_3\text{ZnSb}_2\text{O}_9$  is not consistent with the full retention of cation ordering, but it suggests an ordering consistent with the formulation  $\text{Ba}_2\text{Sb}(\text{Sb}_{1/3}\text{Zn}_{2/3})\text{O}_6$ , that is the cations order in sheets perpendicular to the [111] axis of the cubic crystal with zinc atoms present only in alternate sheets. A study by electron microscopy would be valuable in determining whether this is the true structure or merely the average, long-range ( $\sim 200$  Å) structure detected in an X-ray diffraction experiment (18).

The transition observed in  $\text{Ba}_3\text{NiSb}_2\text{O}_9$  can be considered as a displacement of half

the  $\text{BaO}_3$  layers with respect to the other half. In this way the cubic/hexagonal stacking sequence is modified so as to leave antimony atoms between ccp layers, that is in corner-sharing octahedral sites. There are similarities between the structure of  $\text{Ba}_3\text{NiSb}_2\text{O}_9$ -II and that described by Köhl and Reinen, but there are also significant differences. Most striking among the latter are the 2.2% reduction in unit-cell volume which is found in the sample produced under high pressure and the difference in the first coordination shell about the  $\text{Ni}^{2+}$  ions. Köhl and Reinen found Ni–O bond lengths of 2.04 and 2.06 Å whereas our EXAFS experiments lead to values of 2.03 and 2.14 Å, indicating a much less regular environment around the  $\text{Ni}^{2+}$  cations. It is interesting to note that the average of these two values is very close to the Ni–O bond length found in  $\text{Ba}_3\text{NiSb}_2\text{O}_9$ -I. The radial distances deduced for the more distant coordination shells about  $\text{Ni}^{2+}$  in  $\text{Ba}_3\text{NiSb}_2\text{O}_9$ -II are in good agreement with those found in the single crystal X-ray diffraction experiment. The Ni–Sb distance (2.68 Å) in the  $\text{NiSbO}_9$  unit is considerably shorter than the Sb–Sb distance reported (6) in  $\text{Ba}_3\text{NiSb}_2\text{O}_9$ -I. In conclusion, we have shown that the compounds  $\text{Ba}_3\text{MSb}_2\text{O}_9$  ( $M = \text{Ni}$  and  $\text{Zn}$ ) undergo phase transitions under high pressures, and that the nature of the transition is such as to eliminate the short  $\text{Sb}^{5+}$ – $\text{Sb}^{5+}$  contact which is present in the ambient pressure phase. In the compound  $\text{Ba}_3\text{ZnSb}_2\text{O}_9$  this is achieved by the total elimination of face-sharing octahedra, whereas in  $\text{Ba}_3\text{NiSb}_2\text{O}_9$  the strong electrostatic repulsion is moderated by the change from  $\text{Sb}_2\text{O}_9$  face-sharing dimers to  $\text{NiSbO}_9$  units.  $\text{Ba}_3\text{MgSb}_2\text{O}_9$  shows no transition when pressure is applied, indicating the importance of the cation polarizability. Finally we note that we were unable to induce any high pressure phase transition in  $\text{Ba}_3\text{NiRu}_2\text{O}_9$ , a compound in which the  $\text{M}_2^{5+}\text{O}_9$  dimers are stabilized by the chemi-

cal bonds formed using the partially filled ( $t_{2g}^3$ )  $d$ -orbitals of the ruthenium atoms.

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