1716 *Inorg. Chem.* **2001,** *40,* 1716−1717

Antimony in the Sr_4PtO_6 Structure: A Neutron Diffraction Study of Sr_3NaSbO_6

Peter D. Battle,* Sonia J. Hartwell, and Caroline A. Moore

Inorganic Chemistry Laboratory, Oxford University,
South Parks Road, Oxford, OX1 3QR, U.K.

Received November 1, 2000

Introduction

There is currently a great deal of interest[1−3] in mixed-metal oxides that are structurally related to Sr_4PtO_6.[4] This rhombohedral structure (Figure 1) consists of [001] chains made up of alternating, face-sharing SrO_6 trigonal prisms and PtO_6 octahedra, with the remaining 75% of the Sr cations occupying sites between the chains. To emphasize that there are two distinct Sr environments and to fit in with what follows, it is convenient to write the chemical formula as Sr_3SrPtO_6. Recent research has involved the introduction of various magnetic d-block[5] and f-block[6] cations into one or both of the polyhedral sites, and subsequent investigations have included spin dimensionality, magnetic ordering, and magnetic frustration. Relatively few attempts have been made to introduce p-block elements into the chains, although compounds are known[7,8] that contain prismatic lead or octahedral bismuth. However, we have a long-standing interest in mixed-metal oxides containing Sb^{5+}, with a particular emphasis on their structural similarities to those that contain Ru^{5+},[9−12] and reports[13,14] of the synthesis and characterization of $A_3A'RuO_6$ (A = Ca, Sr; A′ = Li, Na) therefore prompted us to prepare and characterize the analogous diamagnetic phases $A_3A'SbO_6$. Although a number of different compositions are discussed below, our most detailed results relate to Sr_3NaSbO_6.

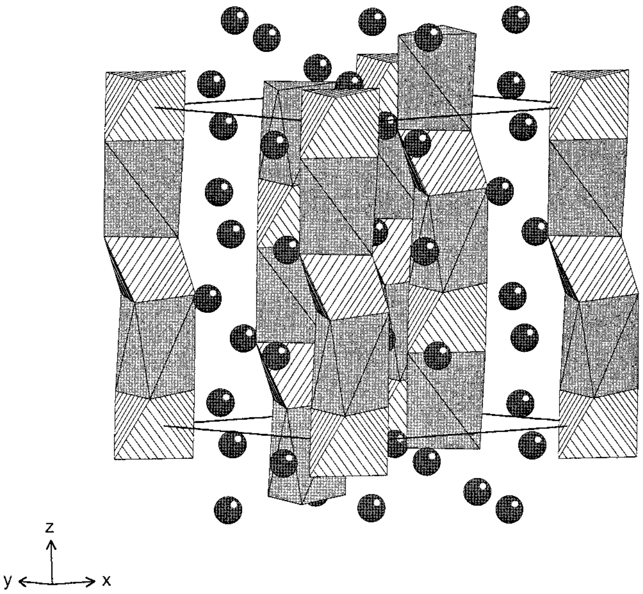

Figure 1. Crystal structure of Sr_4PtO_6. PtO_6 octahedra are hatched, SrO_6 prisms are shaded, and filled circles represent Sr cations in the interchain space.

Experimental Section

Attempts were made to prepare polycrystalline samples of $A_3A'SbO_6$ (A = Ca, Sr, Ba; A′ = Li, Na) using the standard techniques of solid-state chemistry. Stoichiometric quantities of ACO_3 and Sb_2O_3 were intimately mixed with a slight (∼10%) excess of A'_2CO_3 (to compensate for the volatility of Li and Na), loaded into alumina crucibles, and heated for a period of days until X-ray powder diffraction indicated that the reaction was complete. All reaction mixtures were initially heated at 873 K, and the temperature was then increased as necessary to a maximum of 1073 K (Ca_3LiSbO_6), 1223 K (Sr_3LiSbO_6), or 1273 K (Sr_3NaSbO_6, Ba_3LiSbO_6, Ba_3NaSbO_6); all attempts to prepare Ca_3NaSbO_6 in this way were unsuccessful. The phases with A = Ba were unstable (on a time scale of hours) under ambient conditions, and a rapid X-ray data collection was the only characterization possible. Rietveld analysis of relatively high-resolution X-ray diffraction patterns, collected over the angular range $5° \leq 2\theta \leq 120°$ on a Siemens D5000 diffractometer using Cu Kα_1 radiation, showed that Ca_3LiSbO_6, Sr_3LiSbO_6, and Sr_3NaSbO_6 had formed as stable phases isostructural with Sr_4PtO_6. One weak impurity peak was observed in the case of Ca_3LiSbO_6 ($d \approx 2.40$ Å). On the basis of the X-ray diffraction data, Sr_3NaSbO_6 was selected for study by neutron diffraction; the relatively high neutron absorption cross section of Li was also a factor in this choice. Time-of-flight neutron diffraction experiments were performed at room temperature on the General Materials (GEM) diffractometer at ISIS, Rutherford Appleton Laboratory. An amount of 6.1 g of sample was loaded in a vanadium can, and data sets covering the *d* spacing range $0.3\ \text{Å} \leq d \leq 10\ \text{Å}$ were acquired in the remarkably short time of 15 min. A Rietveld analysis[15] of the neutron data collected in the backscattering position and on the detector at $2\theta \approx 90°$ (covering the range $0.3\ \text{Å} \leq d \leq 3\ \text{Å}$) was carried out using the GSAS suite of programs.[16] Sr_3NaSbO_6 was also studied by electron diffraction. The finely ground powder was suspended in hexane and placed on lacey carbon-coated copper grids. Selected area electron diffraction (SAED) patterns were obtained by use of a double-tilting goniometer stage (±30°) to tilt the specimen in a JEOL 2000FX transmission electron microscope (TEM).

Results

The unit cell parameters of the phases successfully prepared are listed in Table 1. The structural parameters resulting from the more detailed neutron diffraction study of Sr_3NaSbO_6 are presented in Table 2, with the derived bond lengths and angles being listed in Table 3. The observed and calculated neutron diffraction patterns are presented in parts a and b of Figure 2. The former shows high-resolution data collected in the back-

---

* To whom correspondence should be addressed.

(1) Irons, S. H.; Sangrey, T. D.; Beauchamp, K. M.; Smith, M. D.; zur Loye, H. C. *Phys. Rev. B* **2000**, *61*, 11594.
(2) Layland, R. C.; zur Loye, H. C. *J. Alloys Compds.* **2000**, *299*, 118.
(3) Kawasaki, S.; Takano, M.; Inami, T. *J. Solid State Chem.* **1999**, *145*, 302.
(4) Randall, J. R.; Katz, L. *Acta Crystallogr.* **1959**, *12*, 519.
(5) Nguyen, T. N.; zur Loye, H.-C. *J. Solid State Chem.* **1995**, *117*, 300.
(6) James, M.; Attfield, J. P. *Chem. Eur. J.* **1996**, *2*, 737.
(7) Smith, M. D.; Stalick, J.; zur Loye, H. C. *Chem. Mater.* **1999**, *11*, 2984.
(8) Carlson, V. A.; Stacy, A. M. *J. Solid State Chem.* **1992**, *96*, 332.
(9) Battle, P. D.; Kim, S. H.; Powell, A. V. *J. Solid State Chem.* **1992**, *101*, 161.
(10) Almaer, S. A.; Battle, P. D.; Lightfoot, P.; Mellen, R. S.; Powell, A. V. *J. Solid State Chem.* **1993**, *102*, 375.
(11) Lightfoot, P.; Battle, P. D. *Mater. Res. Bull* **1990**, *25*, 89.
(12) Battle, P. D.; Bush, T. S.; Catlow, C. R. A. *J. Am. Chem. Soc.* **1995**, *117*, 6292.
(13) Darriet, J.; Grasset, F.; Battle, P. D. *Mater. Res. Bull.* **1997**, *32*, 139.
(14) Frenzen, S.; Müller-Buschbaum, H. *Z. Naturforsch.* **1995**, *50b*, 581.
(15) Rietveld, H. M. *J. Appl. Crystallogr.* **1969**, *2*, 65.
(16) Larson, A. C.; von-Dreele, R. B. *General Structure Analysis System (GSAS)*; Report LAUR 86-748; Los Alamos National Laboratories: Los Alamos, NM, 1990.

10.1021/ic001213s CCC: $20.00

Table 1. Unit Cell Parameters[a] of $A_3A'BSbO_6$ (A = Ca, Sr, Ba; A′ = Li, Na)

	Ca_3LiSbO_6	Sr_3LiSbO_6	Sr_3NaSbO_6	Ba_3LiSbO_6	Ba_3NaSbO_6
a/Å	9.3810(2)	9.7747(2)	9.7629(1)	10.2684(6)	10.2442(5)
c/Å	10.8574(3)	11.2171(3)	11.6019(2)	11.5739(9)	11.9549(9)
V/Å^3	827.47	928.15	957.67	1056.86	1086.51

[a] Derived from X-ray powder diffraction data.

Table 2. Atomic Parameters[a] of Sr_3NaSbO_6[b]

atom	site	*x*	*y*	*z*	U_{iso} (Å^2)
Sr	18e	0.35135(7)	0	$^1/_4$	0.0051(2)
Na	6a	0	0	$^1/_4$	0.0079(6)
Sb	6b	0	0	0	0.0019(3)
O	36f	0.17872(7)	0.02473(7)	0.09919(5)	0.0060(2)

[a] Derived from neutron diffraction data. [b] Space group $R\bar{3}c$, a = 9.75825(7) Å, c = 11.5958(1) Å. $2\theta = 91.3°$ detector: R_{wp} = 3.30%. $2\theta = 154.4°$ detector: R_{wp} = 6.69%. Combined: R_{wp} = 3.60%, χ^2 = 1.699.

Table 3. Interatomic Distances (Å) and Bond Angles (deg) for Sr_3NaSbO_6

Sr−O	2.5220(8) × 2
	2.6190(7) × 2
	2.6202(6) × 2
	2.8810(9) × 2
Na−O	2.3952(6) × 6
Sb−O	2.0005(7) × 6
O−O shortest	2.823(1)
O−S−O	89.77(3)
	90.23(3)
O−Na−O	72.57(3)
	94.66(3)
	131.03(3)
	149.47(3)

scattering position, and the latter shows data at higher *d* spacings, which were collected on the detector at $2\theta \approx 90°$. Two broad, weak impurity lines, which were not observed in the X-ray diffraction pattern, can be seen at *d* spacings of ∼2.28 and 2.36 Å; we believe that they are due to the use of excess sodium in the synthesis of this sample. The electron diffraction patterns shown in Figure 3 show no superlattice reflections and are consistent with the principal phase being isostructural with Sr_4PtO_6.

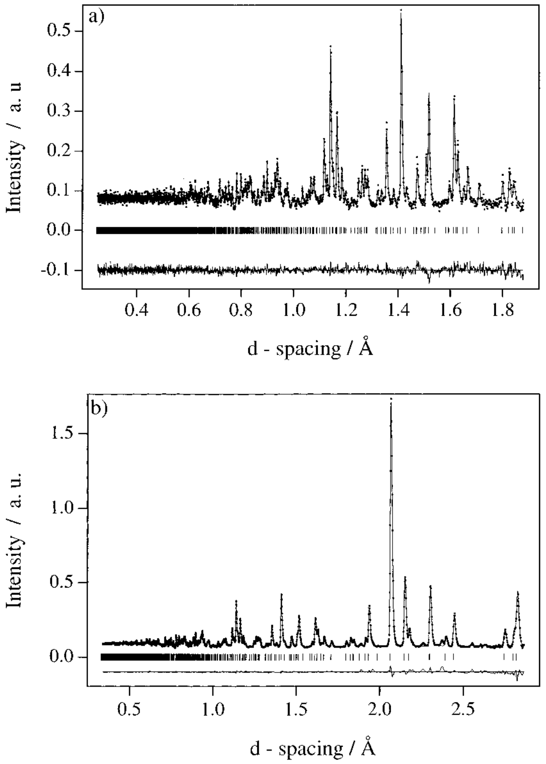

Figure 2. Observed, calculated, and difference time-of-flight neutron powder diffraction profiles of Sr_3NaSbO_6 recorded at $2\theta = 154.4°$ (a) and at $2\theta = 91.3°$ (b). Reflection positions are marked.

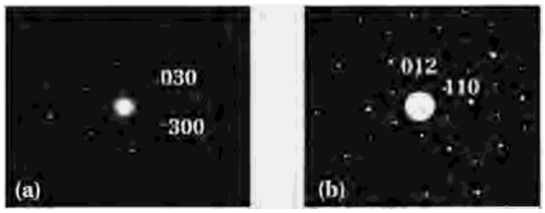

Figure 3. SAED patterns showing (a) [001] and (b) [$2\bar{2}1$] projections of Sr_3NaSbO_6.

Discussion

The successful preparation of the $A_3A'SbO_6$ phases listed in Table 1 illustrates the similarities in the structural chemistry of Sb^{5+} and Ru^{5+}. For each pair of elements (A, A′), the unit cell volume is larger in the case of the Sb analogue and the Sb−O bond length in Sr_3NaSbO_6 (2.0005(7) Å) is longer than the Ru−O distance in Sr_3NaRuO_6 (1.976(4) Å[14]). This Sb−O distance is similar to those observed in other mixed-metal oxides where Sb^{5+} is found in six coordination,[17−19] although, and in contrast to Ru^{5+}, it is somewhat unusual to find this cation in what is close to being a regular octahedron. As in the case of the Ru compounds,[13] the unit cell parameter *a* is relatively insensitive to the element in the trigonal prismatic site, actually decreasing as the size of the alkaline earth cation increases. The increase in unit cell volume is thus accounted for by an increase in the parameter *c*. The insensitivity of *a* to chemical composition is consistent with the description[20] of these phases in terms of *xy* layers of composition A_3O_6, which contain interstices large enough to accommodate the A′ cation without distortion; the B cations then occupy the octahedral interstices that are formed when the layers are stacked in an *hcp* sequence. The successful replacement of Ru by Sb in A_3NaBO_6 phases contrasts with our failure[9] to prepare isostructural Ru analogues of the pseudocubic perovskites $Sr_4A'Sb_3O_{12}$ [18] and $Ba_4A'Sb_3O_{12}$ [21] (A′ = Li, Na), although we were able to prepare hexagonal perovskites of composition $Ba_4NaRu_3O_{12}$ (8H) and $Ba_4LiRu_3O_{12}$ (6H). The results described above are thus consistent with our previous suggestion[11] that the Ru/Sb analogy holds best when the cations are located in face-sharing rather than edge-sharing polyhedra; the present work extends the former category to include trigonal prisms in addition to octahedra. The Na−O distance (2.3952 Å) within the trigonal prisms of Sr_3NaSbO_6 is significantly longer than those observed within the NaO_6 octahedra of $Sr_4NaSb_3O_{12}$ (mean is 2.17 Å) and $Ba_4NaRu_3O_{12}$ (2.24 Å). The particularly short value observed in $Sr_4NaSb_3O_{12}$ is consistent with the refusal of this compound to accept substitution of Sb^{5+} by the smaller Ru^{5+}, which would require a further compression of the Na−O bond.

Acknowledgment. We are grateful to EPSRC for financial support and to P. G. Radaelli for experimental assistance at ISIS.

IC001213S

---

(17) Groen, W. A.; Ijdo, D. J. W. *Acta Crystallogr.* **1988**, *C44*, 782.

(18) Alonso, J. A.; Mzayek, E.; Rasines, I. *J. Solid State Chem.* **1990**, *84*, 16.

(19) Jacobson, A. J.; Collins, B. M.; Fender, B. E. F. *Acta Crystallogr.* **1974**, *B30*, 1705.

(20) Darriet, J.; Subramanian, M. A. *J. Mater. Chem.* **1995**, *5*, 543.

(21) Alonso, J. A.; Mzayek, E.; Rasines, I. *Mater. Res. Bull.* **1987**, *22*, 69.