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Synthesis of $Rb_3Sc_2(AsO_4)_3$ and Its Structure Determination by Synchrotron Single Crystal Methods

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$Rb_3Sc_2(AsO_4)_3$ is a new cubic phase built up from vertex-sharing ScO_6 and AsO_4 building blocks and fused together via Sc–O–As bonds. Variously coordinated Rb^+ cations occupy lacunae in the Sc/As/O network. $Rb_3Sc_2(AsO_4)_3$ is closely related to the perovskite superstructure phase $Na_4BaCu_3F_{12}$. Synchrotron radiation methods elucidated the correct primitive unit cell for $Rb_3Sc_2(AsO_4)_3$ compared to the apparent body-centered cell resulting from laboratory data. Crystal data: $Rb_3Sc_2(AsO_4)_3$, $M_r = 763.09$, cubic, space group $Pa\bar{3}$ (No. 205), $a = 16.8749(7)$ Å, $V = 4805.3(3)$ Å^3, $Z = 16$, $R(F) = 0.0403$, $wR(F^2) = 0.0761$ (1818 reflections). © 1998 Academic Press

INTRODUCTION

In this paper we report the synthesis and synchrotron X-ray single crystal structure of $Rb_3Sc_2(AsO_4)_3$, which crystallizes in a new cubic structure type for $A_3B_2(XO_4)_3$ oxides which shows some similarity to, but is distinctly different from the garnet topology (1). Its structure also shows similarities to that of the perovskite-related fluoride $Na_4BaCu_3F_{12}$ (2). We are not aware of any previous structural studies of the Rb/Sc/As/O phase space.

EXPERIMENTAL

Synthesis and Initial Characterization

A mixture of 8.73 g Rb_2CO_3 (37.8 mmol, Alfa), 0.552 g Sc_2O_3 (4 mmol, Varlacoid Chemical Corp.), and 8.58 g $NH_4H_2AsO_4$ (54 mmol, Alfa) was heated at 300°C for 3 h, then 920°C for 2 days. Liquors were decanted into a Pt crucible which was then cooled from 930 to 850°C at a rate of 1°C/hr. The flux was decanted off, and after cooling to ambient, the residual flux was dissolved in water. A yield of 0.172 g of transparent, faceted $Rb_3Sc_2(AsO_4)_3$ crystals (maximum linear dimension 2 mm) were recovered by filtration.

Powder second harmonic generation (PSHG) (3) measurements on a thoroughly ground powder sample of $Rb_3Sc_2(AsO_4)_3$ gave a null response, indicating that this phase probably crystallizes in a centrosymmetric space group, as confirmed in the single crystal studies.

Laboratory Single Crystal Study

The initial diffraction experiment (irregular shard-like fragment, $\sim 0.2 \times 0.1 \times 0.1$ mm, room temperature) was carried out using a laboratory Enraf-Nonius CAD4 automated diffractometer (Mo$K\alpha$ radiation, $\lambda = 0.71073$ Å). The application of default-setting peak searching, centering, and indexing routines yielded a body-centered cubic cell with $a = 16.898(5)$ Å, and 2259 intensity maxima were scanned ($2° < 2\theta < 60°$, $+h$, $+k$, $\pm l$). The systematic absences in the reduced data ($0kl$, k, l; hhl, l; $00l$, l) indicated space group $Ia\bar{3}$ (No. 206). After merging to 530 reflections, 305 of these were considered observed, based on the criterion $F > 4\sigma(F)$.

Starting heavy atom positions (three Rb, two Sc, one As) were located by direct methods (4), and four oxygen atoms were located from difference Fourier maps, resulting in a chemically reasonable atomic connectivity [$R(F) \approx 10\%$]. Anisotropic refinement of the heavy atoms improved the fit to $R(F) \approx 5\%$. However, anisotropic refinement of the oxygen atoms was unsuccessful, with non-positive-definite thermal ellipsoids for the O atoms and unrealistic As–O bond distances resulting. Attempts to model the structure in other body centered cubic space groups did not lead to satisfactory solutions. A careful rescanning of the same crystal revealed a handful of very weak peaks which violated the body centering condition. An attempted refinement in space group $Pa\bar{3}$ (atomic model developed from the $Ia\bar{3}$ refinement) did not converge.

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Synchrotron Diffraction Study

An irregular crystal ($\sim 0.18 \times 0.22 \times 0.38$ mm) of $Rb_3Sc_2(AsO_4)_3$ was selected and synchrotron X-ray diffraction data [$\lambda = 0.6879$ Å as selected by a Si(111) monochromator, $T = 160(2)$ K] were collected on a Siemens SMART CCD area detector diffractometer at SRS beamline station 9.8 at Daresbury Laboratory, UK (5).

Preliminary scans clearly indicated a primitive cubic unit cell with $a \approx 16.875$ Å, and data were collected in narrow-slice ω-scan mode (6), resulting in 10561 measured intensities ($-21 \le h \le 6$, $-14 \le k \le 18$, $-7 \le l \le 20$) for $4° \le 2\theta \le 55°$. Data merging resulted in 1818 unique reflections ($R_{\mathrm{Int}} = 0.061$) of which 1492 were considered observed according to the criterion $F > 4\sigma(F)$. Absorption and incident beam decay corrections were applied on the basis of multiple and symmetry-equivalent reflections (7), with a resulting correction factor range of 0.044–0.151. X-ray scattering factors were taken from Ref. (8). The systematic absences ($0kl$, k; $h0l$, l; $hk0$, h) indicated space group $Pa\bar{3}$ (No. 205). A crystallographic model corresponding to the stoichiometry $Rb_3Sc_2(AsO_4)_3$ (anisotropic thermal factors for all atoms) was successfully refined (9) in this space group as summarized in Table 1.

RESULTS

Atomic positional and thermal parameters for $Rb_3Sc_2(AsO_4)_3$ are listed in Table 2, with selected bond distance/angle data in Table 3. $Rb_3Sc_2(AsO_4)_3$ contains four distinct rubidium cations, three scandium atoms (octahedral coordination), and two arsenic atoms (tetrahedral). Eight distinct oxygen atoms complete the structure. A fragment of the $Rb_3Sc_2(AsO_4)_3$ structure is illustrated in Fig. 1, and the complete structure is shown in Fig. 2.

The four rubidium cations occupy distinct coordination polyhedra with respect to nearby O atoms: Rb1 is 8-coordinate with $d_{\mathrm{av}}(\mathrm{Rb–O}) = 3.024$ Å (Fig. 3) and has a bond valence sum (BVS) of 1.22 (10). Rb2 and Rb4 adopt nine fold

TABLE 1
Crystallographic Parameters for $Rb_3Sc_2(AsO_4)_3$

Empirical formula	$Rb_3As_3Sc_2O_{12}$
Formula weight	763.09
Crystal system	Cubic
a (Å)	16.8749 (7)
V (Å^3)	4805.3 (3)
Z	16
Space group	$Pa\bar{3}$ (No. 205)
T (°C)	-113 (2)
Radiation	Synchrotron X rays
λ (Å)	0.6879
ρ_{calc} (g/cm^3)	4.22
μ (cm^{-1})	214.7
Total data	10561
Merged data	1818
Parameters	123
min., max. $\Delta\rho$ (e /Å^3)	-1.46, $+1.39$
$R(F)$	0.0353,[a] 0.0403[b]
w$R(F^2)$	0.0761[b,c]
S (goodness of fit on F^2)	1.028

[a] 1492 reflections with $F > 4\sigma(F)$.

[b] All data.

[c] $w_i = 1/[\sigma^2(F_o^2) + (0.0387P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

TABLE 2
Atomic Positional/Thermal Parameters for $Rb_3Sc_2(AsO_4)_3$

Atom	W[a]	x	y	z	U_{eq}
Rb1	24d	0.24511(2)	− 0.00215(3)	0.00560(2)	0.0114(2)
Rb2	8c	0.13054(2)	0.13054(2)	0.13054(2)	0.0128(2)
Rb3	8c	0.25184(2)	0.25184(2)	0.25184(2)	0.0154(2)
Rb4	8c	0.37526(2)	0.37526(2)	0.37526(2)	0.0100(2)
Sc1	24d	0.49682(4)	0.25098(4)	0.21697(5)	0.0060(2)
Sc2	4b	1/2	0	0	0.0058(4)
Sc3	4a	1/2	1/2	0	0.0061(4)
As1	24d	0.63099(2)	0.09943(3)	0.13892(2)	0.0059(2)
As2	24d	0.36935(2)	0.39584(3)	0.13462(2)	0.0057(2)
O1	24d	0.5613(2)	0.0387(2)	0.1008(2)	0.0120(6)
O2	24d	0.5929(2)	0.1747(2)	0.1923(2)	0.0116(6)
O3	24d	0.4322(2)	0.1927(2)	0.1290(2)	0.0108(6)
O4	24d	0.5425(2)	0.2932(2)	0.3229(2)	0.0122(6)
O5	24d	0.4044(2)	0.3405(2)	0.2107(2)	0.0084(6)
O6	24d	0.4339(2)	0.4647(2)	0.1010(2)	0.0094(6)
O7	24d	0.5570(2)	0.3393(2)	0.1574(2)	0.0092(6)
O8	24d	0.4462(2)	0.1696(2)	0.2913(2)	0.0122(6)

[a] Wyckoff site.

TABLE 3
Selected Geometrical Data (Å,°) for $Rb_3Sc_2(AsO_4)_3$

Rb1–O3	2.687(3)	Rb1–O6	2.778(3)
Rb1–O1	2.866(3)	Rb1–O8	2.966(3)
Rb1–O7	3.106(3)	Rb1–O4	3.194(3)
Rb1–O5	3.289(3)	Rb1–O7	3.305(3)
Rb2–O6 × 3	3.044(3)	Rb2–O2 × 3	3.146(3)
Rb2–O4 × 3	3.219(3)	Rb3–O5 × 3	3.057(3)
Rb3–O2 × 3	3.127(3)	Rb4–O5 × 3	2.881(3)
Rb4–O1 × 3	2.986(3)	Rb4–O4 × 3	3.265(3)
Sc1–O8	2.046(3)	Sc1–O7	2.065(3)
Sc1–O4	2.072(3)	Sc1–O3	2.088(3)
Sc1–O2	2.111(3)	Sc1–O5	2.175(3)
Sc2–O1 × 6	2.095(3)	Sc3–O6 × 6	2.123(3)
As1–O3	1.665(3)	As1–O2	1.685(3)
As1–O4	1.686(3)	As1–O1	1.687(3)
As2–O7	1.667(3)	As2–O8	1.675(3)
As2–O6	1.690(2)	As2–O5	1.693(3)
As1–O1–Sc2	147.4(2)	As1–O2–Sc1	149.1(2)
As1–O3–Sc1	152.1(2)	As1–O4–Sc1	147.6(2)
As2–O5–Sc1	132.1(2)	As2–O6–Sc3	143.2(2)
As2–O7–Sc1	150.3(2)	As2–O8–Sc1	158.5(2)

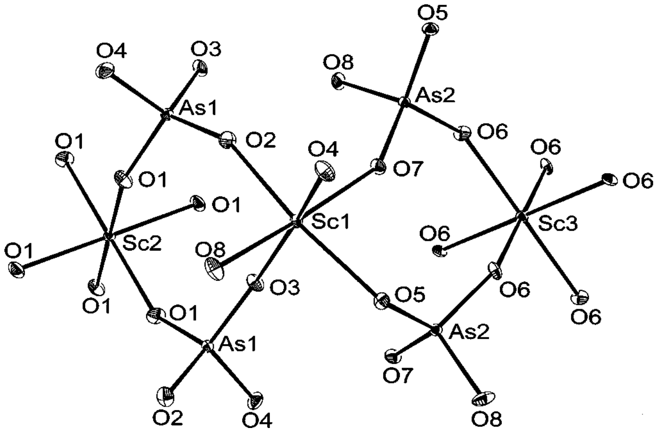

FIG. 1. ORTEP (17) view of a fragment of the $Rb_3Sc_2(AsO_4)_3$ structure, showing the connectivity of the ScO_6 and AsO_4 polyhedra (50% thermal ellipsoids).

coordination (Figs. 4 and 5) with average Rb–O contact distances of 3.136 and 3.044 Å, respectively [BVS(Rb2) = 0.87, BVS(Rb4) = 1.19]. Rb3 is octahedrally coordinated with d_{av}(Rb–O) = 3.092 Å and BVS(Rb3) = 0.64. The three distinct scandium cations show typical, regular octahedral coordination [d_{av}(Sc1–O) = 2.093 Å; BVS(Sc1) = 3.12, BVS(Sc2) = 3.09, BVS(Sc3) = 2.86]. The two arsenate tetrahedra are typical, with d_{av}(As1–O) = 1.681 Å, d_{av}(As2–O) = 1.681 Å, BVS(As1) = 5.05, and BVS(As2) = 5.04. All eight O atoms form scandium–arsenic bridges with an average Sc–O–As bond angle of 147.5°, resulting from the vertex-sharing alternation of the ScO_6 and AsO_4 polyhedra. All the O atoms also make bonds to one or more Rb^+ cations.

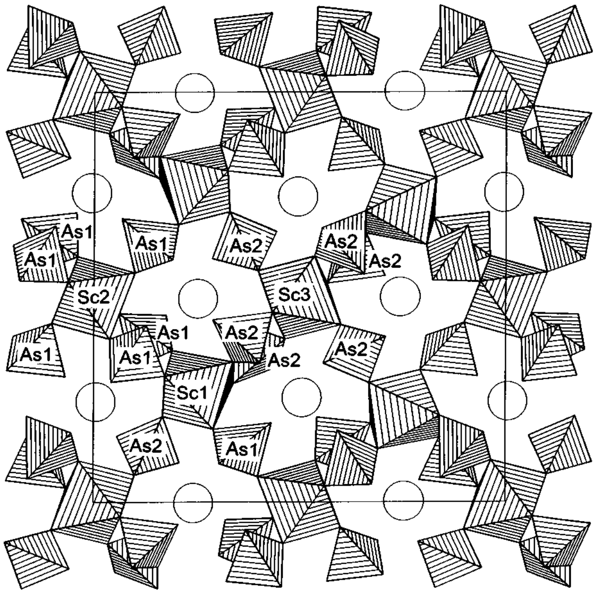

FIG. 2. Polyhedral view of the $Rb_3Sc_2(AsO_4)_3$ structure, with selected polyhedra labeled with their central atom.

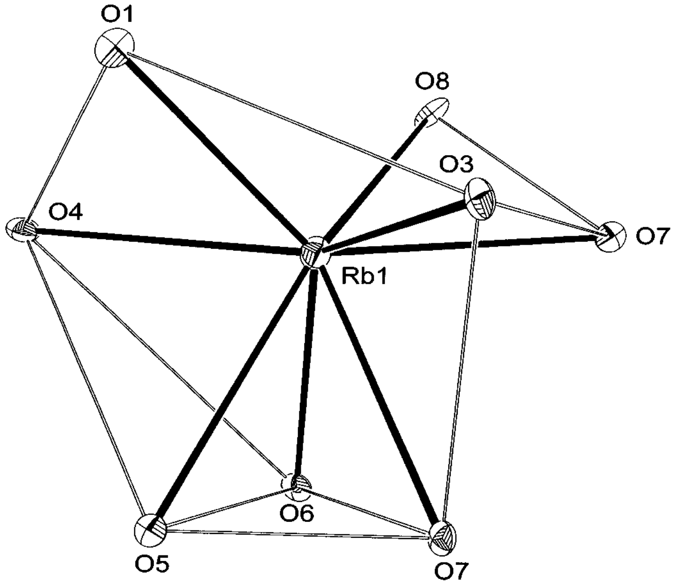

FIG. 3. Detail of the eightfold Rb1 coordination in $Rb_3Sc_2(AsO_4)_3$. O ··· O contacts of less than 4.0 Å are indicated by thin lines.

The polyhedral connectivity of the ScO_6 and AsO_4 units in $Rb_3Sc_2(AsO_4)_3$ results in a dense three-dimensional network of alternating Sc- and As-centered moieties. Rubidium cations occupy interstices in this Sc/As/O framework. A distinctive structural feature is the presence of corrugated chains of polyhedral 4-rings (two Sc and two As nodal atoms) which propagate along ⟨100⟩ (Fig. 2). In terms of Sc–As–Sc topological connectivity, both the Sc2 and Sc3

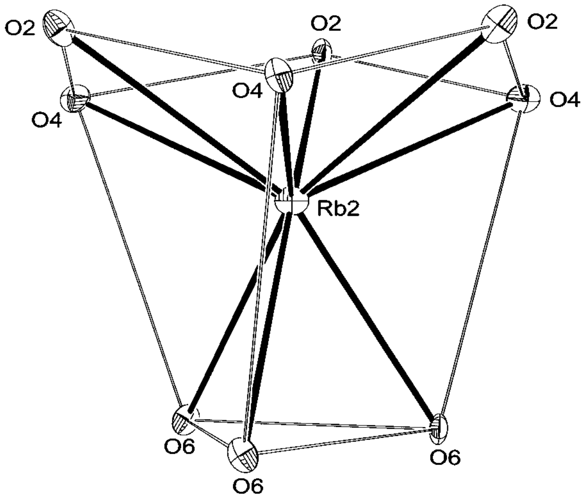

FIG. 4. Detail of the Ninefold Rb2 coordination in $Rb_3Sc_2(AsO_4)_3$. O ··· O contacts of less than 4.0 Å are indicated by thin lines.

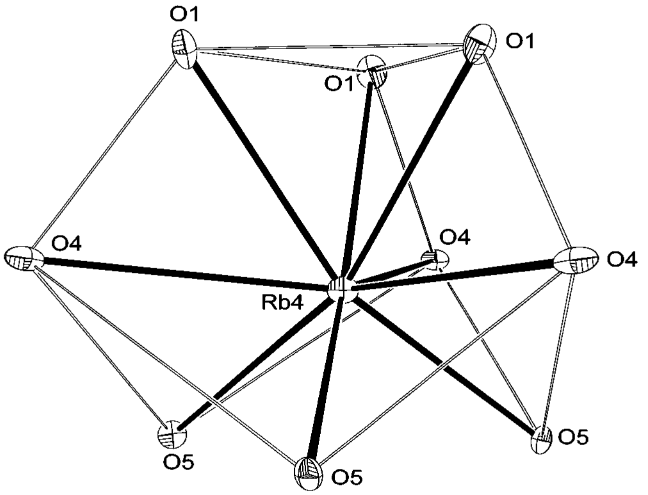

FIG. 5. Detail of the ninefold Rb4 coordination in $Rb_3Sc_2(AsO_4)_3$. O ⋯ O contacts of less than 4.0 Å are indicated by thin lines.

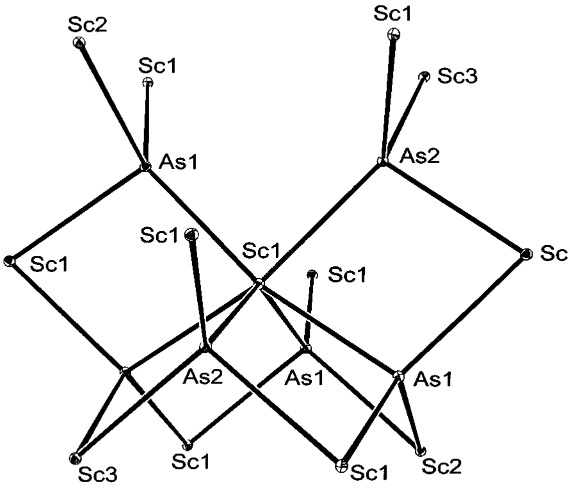

FIG. 7. Topological connectivity of the Sc1 site in $Rb_3Sc_2(AsO_4)_3$, with Sc–O–As links indicated by lines.

centers are surrounded by six As nodes which each participate in two 4-rings completed by Sc1 atoms. Each of these six As centres also bonds to a third Sc1 center (Fig. 6). This octahedral/tetrahedral/octahedral topology is identical to that found in the garnet structure (1, 11). The equivalent Sc1-centered network is distinct and consists of four equivalent As atoms participating in two 4-rings and also making a link to an additional Sc atom. The remaining two As atoms participate in one 4-ring and bond to two additional Sc atoms (Fig. 7).

DISCUSSION

$Rb_3Sc_2(AsO_4)_3$ is a new cubic phase based on a three-dimensional framework of alternating, vertex-sharing ScO_6 and AsO_4 polyhedra. It shares identifiable aspects of polyhedral architecture with the garnet $A_3B_2(XO_4)_3$-type topology (1). The $+1/+3/+5$ cation distribution over the large, octahedral, and tetrahedral cation sites, respectively, in $Rb_3Sc_2(AsO_4)_3$ is uncommon for garnet types, with one synthetic example being $Na_3Fe_2(AsO_4)_3$ (12). A significant difference between the two structure types is seen in the average Rb–O distance in $Rb_3Sc_2(AsO_4)_3$ of 3.074 Å which is much longer than the typical bond length of 2.5 Å or less for the corresponding 8-coordinate *A*-cation site in garnets (13). Some other $A_3B_2(XO_4)_3$-type phases containing a $+1/+3/+5$ cation distribution include $Na_3In_2(AsO_4)_3$ (14), which contains edge-sharing pairs of InO_6 octahedra and the NASICON-type $Na_3Fe_2(PO_4)_3$ (15) containing characteristic "lantern" like groupings of two octahedra bridged by three tetrahedra. The high temperature modification of $Na_3In_2(AsO_4)_3$ contains distinctive tetramers of edge-sharing FeO_6 octahedra (12).

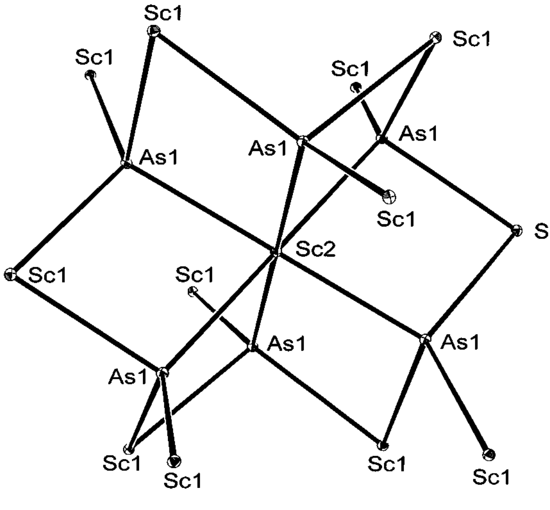

FIG. 6. Topological connectivity of the Sc2 site in $Rb_3Sc_2(AsO_4)_3$, with Sc–O–As links indicated by lines.

$Rb_3Sc_2(AsO_4)_3$ shows a striking similarity to the complex fluoride $Na_4BaCu_3F_{12}$, reported to crystallize in space group $Ia\bar{3}$ with $a = 16.135(2)$ Å by de Kozak *et al.* (2). These workers encountered problems in the modeling of the anisotropic thermal factors of the light atoms in space group $Ia\bar{3}$. There is a one-to-one correspondence in cation positions between the $Ia\bar{3}$ model for $Rb_3Sc_2(AsO_4)_3$ and that of the $Na_4BaCu_3F_{12}$ structure (Table 4). However, the O and F atoms are arranged differently in the two materials to result in two quite distinct structures. In particular, the As^V general-position site in $Rb_3Sc_2(AsO_4)_3$ has essentially regular tetrahedral coordination whilst the equivalent Cu^{II} site in $Na_4BaCu_3F_{12}$ adopts strongly Jahn–Teller distorted octahedral coordination. $Na_4BaCu_3F_{12}$ may be regarded as an ABF_3 perovskite superstructure [i.e., $(Na_3Ba)_{1/4}(NaCu_3)_{1/4}F_3$] with a novel cation ordering pattern over

TABLE 4
Comparison of the $Rb_3Sc_2(AsO_4)_3$ and $Na_4BaCu_3F_{12}$ Structures in Space Group $Ia\bar{3}$

Position	Wyckoff site	$Rb_3Sc_2(AsO_4)_3$[a]	$Na_4BaCu_3F_{12}$[b]
$0, \frac{1}{4}, \sim 0.03$	24*d*	Rb11 (6-coordinate)	Na3 (distorted octahedral)
~ 0.13, 013, 0.13	16*c*	Rb12 (9-coordinate)	Na1 (octahedral)[c]
$\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$	8*b*	Rb13 (6-coordinate)	Ba2 (12-coordinate)
$\sim 0.26, 0, \frac{1}{4}$	24*d*	Sc11 (octahedral)	Na2 (distorted octahedral)
0, 0, 0	8*a*	Sc12 (octahedral)	Ba1 (12-coordinate)
~ 0.37, 0.13, 0.12	48*e*	As11 (tetrahedral)	Cu1 (distorted octahedral)[c]

[a] Correspondence of atoms between the body centered cubic and primitive cubic (Table 2) models for $Rb_3Sc_2(AsO_4)_3$: Rb11 ≡ Rb1; Rb12 ≡ Rb2 and Rb4; Rb13 ≡ Rb3; Sc11 ≡ Sc1; Sc12 ≡ Sc2 and Sc3; As11 ≡ As1 and As2.

[b] Atom notation from Ref. (2).

[c] Na1 and Cu1 form the perovskite-type network of vertex-sharing octahedra in $Na_4BaCu_3F_{12}$.

both the *A* and *B* sites, and shows ferromagnetic ordering below 10 K (2).

The symmetry reduction from $Ia\bar{3}$ to $Pa\bar{3}$ in $Rb_3Sc_2(AsO_4)_3$, which can be visualized as slight polyhedral rotations of the ScO_6 and AsO_4 units, may arise from the optimization of rubidium coordination environments. The Rb11, Rb12, and Rb13 species (Table 4) have bond valence sums of 0.91, 0.96, and 0.63, respectively. By increasing the coordination number of Rb11/Rb1 from six ($Ia\bar{3}$ model) to eight ($Pa\bar{3}$ model), its BVS is increased significantly to 1.22 (vide supra). However, the octahedrally coordinated Rb13/Rb3 species is distinctly underbonded in both structural models for $Rb_3Sc_2(AsO_4)_3$. The average Sc–O–As bond angle changes from 154.3° ($Ia\bar{3}$) to 147.5° ($Pa\bar{3}$).

Synchrotron X-ray methods were successful in elucidating the primitive cubic structure of $Rb_3Sc_2(AsO_4)_3$, although it is strongly pseudo body centered. No particular problems of high correlations between atomic parameters related by pseudo symmetry were encountered in the refinement against the synchrotron data, contrary to the situation with laboratory data where no primitive-cubic model could be refined. Simulations indicated that the strongest primitive reflection violating the body centering condition had an intensity of $\sim 0.4\%$ that of the strongest reflection consistent with body centering. Even so, some 550 reflections with $h + k + l \neq 2n$ in the merged synchrotron data set were observable according to the criterion $F > 4\sigma(F)$, indicating the remarkable sensitivity to weak reflections of this synchrotron source/CCD detector setup.

Several synchrotron single crystal structure determinations have been performed on microcrystals that are far too small to offer any chance of data collection using a laboratory diffractometer (16). The elucidation of the $Rb_3Sc_2(AsO_4)_3$ structure by synchrotron methods indicates that this technique is also highly applicable to some classical crystallographic problems in solid state chemistry involving symmetry lowering and/or superlattices where accurate measurement of weak reflections, rather than small crystal size, is the primary issue.

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REFERENCES

1. S. Geller, *Z. Kristallogr.* **125,** 1 (1967).
2. A. de Kozak, M. Samouël, J. Renaudin, and G. Férey, *Eur. J. Solid State Inorg. Chem.* **27,** 771 (1990).
3. J. P. Dougherty and S. K. Kurtz, *J. Appl. Crystallogr.* **9,** 145 (1976).
4. G. M. Sheldrick, "SHELXS-86 User Guide." University of Göttingen, Germany.
5. R. J. Cernik, W. Clegg, C. R. A. Catlow, G. Bushnell-Wye, J. V. Flaherty, G. N. Greaves, I. Burrows, D. J. Taylor, S. J. Teat, and M. Hamichi, *J. Synchrotron Rad.* **4,** 279 (1997).
6. SMART and SAINT software for area-detector diffractometers, Siemens Analytical X-ray Systems, Madison, Wisconsin, 1994.
7. G. M. Sheldrick, "SADABS," program for scaling and correction of area detector data. University of Göttingen, Germany, 1997.
8. International Tables for Crystallography, Vol. C, Tables 4.2.6.8 and 6.1.1.4. Kluwer Academic, Dordrecht, The Netherlands, 1992.
9. G. M. Sheldrick, "SHELXL-97 User Guide." University of Göttingen, Germany, 1997.
10. I. D. Brown, *J. Appl. Crystallogr.* **29,** 479 (1996).
11. Y. Piffard, A. Verbaere, and M. Kinoshita, *J. Solid State Chem.* **71,** 121 (1987).
12. F. d'Yvoire, M. Pintard-Screpel, and E. Bretey, *Solid State Ionics* **18,** 502 (1986).
13. H. Sawada, *J. Solid State Chem.* **132,** 300 (1997) (and included references).
14. K.-H. Lii and J. Ye, *J. Solid State Chem.* **131,** 131 (1997).
15. F. d'Yvoire, M. Pintard-Screpel, E. Bretey, and M. de La Rochere, *Solid State Ionics* **9,** 851 (1983).
16. S. J. Andrews, M. Z. Papiz, R. McMeeking, A. J. Blake, B. M. Lowe, K. R. Franklin, J. R. Helliwell, and M. M. Harding, *Acta Crystallogr. Sect. B* **44,** 73 (1988); H. E. King Jr., L. A. Mundi, K. G. Strohmaier, and R. C. Haushalter, *J. Solid State Chem.* **92,** 1 (1991); M. M. Harding, B. Kariuki, R. J. Cernik, and G. Cressey, *Acta Crystallogr. Sect. B* **50,** 673 (1994); G. W. Noble, P. A. Wright, P. Lightfoot, R. E. Morris, K. J. Hudson, Å. Kvick, and H. Graafsma, *Angew. Chem. Int. Ed. Engl.* **36,** 81 (1997); M. M. Harding, *J. Synchrotron Rad.* **3,** 250 (1996).
17. L. J. Farrugia, *J. Appl. Crystallogr.* **30,** 565 (1997).