Absorption correction:
analytical
$T_{\min} = 0.061$, $T_{\max} = 0.827$
1169 measured reflections
116 independent reflections
109 observed reflections
$[I > 2\sigma(I)]$

$h = -5 \rightarrow 5$
$k = -5 \rightarrow 5$
$l = -9 \rightarrow 9$
6 standard reflections
monitored every 100 reflections
intensity variation: none

Refinement

Refinement on F^2
Final $R(F) = 0.0215$
$wR(F^2) = 0.0481$
$S = 1.094$
116 reflections
10 parameters
Calculated weights,
$w = 1/[\sigma^2(F_o^2) + 0.0016F^2]$
$(\Delta/\sigma)_{\max} = 0.113$
$\Delta\rho_{\max} = 4.59$ e Å^{-3}
$\Delta\rho_{\min} = -1.53$ e Å^{-3}

Extinction correction:
*SHELXL*92 (Sheldrick, 1992)
Extinction coefficient:
0.0341 (43)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Refinement on F^2 for all reflections; the observed threshold $I > 2\sigma(I)$ is used only for calculating $R_{\rm obs}$ *etc.* given here for comparison with refinements on F. Cell refinement: *CELREF*, local program. Data reduction: *NUPICK*, local program. Program used to solve structure: *XS* subroutine of *SHELXTL/PC* (Sheldrick, 1990). Program used to refine structure: *SHELXL*92 (Sheldrick, 1992). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL*92; *DATABL*, local program.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{\rm eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
U	$\frac{1}{4}$	$\frac{1}{4}$	0.18946 (7)	0.0034 (3)
Se	$\frac{1}{4}$	$\frac{1}{4}$	0.6328 (2)	0.0043 (4)
O	$\frac{3}{4}$	$\frac{1}{4}$	0	0.007 (2)

Table 2. *Geometric parameters* (Å, °)

U—O$^{\rm i}$	2.346 (4)	U—Se	3.080 (5)
U—Se$^{\rm ii}$	3.012 (5)		
O$^{\rm i}$—U—O$^{\rm iii}$	71.66 (9)	Se$^{\rm ii}$—U—Se$^{\rm v}$	131.60 (9)
O$^{\rm i}$—U—O$^{\rm iv}$	111.76 (9)	Se$^{\rm ii}$—U—Se$^{\rm vi}$	80.33 (9)
O$^{\rm i}$—U—Se$^{\rm ii}$	139.81 (6)	O$^{\rm i}$—U—Se	124.12 (8)
O$^{\rm iv}$—U—Se$^{\rm ii}$	72.30 (9)	Se$^{\rm ii}$—U—Se	65.80 (9)

Symmetry codes: (i) $1-x, -y, -z$; (ii) $1-x, 1-y, 1-z$; (iii) $x-1, y, z$; (iv) $1-x, 1-y, -z$; (v) $-x, -y, 1-z$; (vi) $-x, 1-y, 1-z$.

This work was supported by the US National Science Foundation through grant DMR91-14934.

Lists of structure factors, anisotropic thermal parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71186 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1058]

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Structure of $Ba_4NaSb_3O_{12}$ by Neutron Powder Diffraction

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Abstract

The structure of the ordered perovskite triantimony tetrabarium sodium dodecaoxide, $Ba_4NaSb_3O_{12}$, was determined by Rietveld analysis of powder time-of-flight neutron diffraction data. The Na and Sb atoms form a 1:3 ordered arrangement on the *B* sites similar to that observed for $Ba_4LiSb_3O_{12}$.

Comment

The ABO_3 perovskite structure can accommodate more than one cation on both the *A* and *B* sites in ordered or disordered arrangements depending on stoichiometry and on the specific *A* and *B* cations present (Galasso, 1969). Ordering of the *A* cations is quite rare for perovskite compounds though some important cases, for example $YBa_2Cu_3O_7$, are well known. Many more examples of compounds exist where two different *B* cations form an ordered structure, usually when the metal cations differ significantly in either size or charge. The most common ordered arrangements correspond to *B*/*B*′ ratios

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equal to 1:1 and 1:2 with stoichiometries $A(B_{1/2}B'_{1/2})O_3$ and $A(B_{1/3}B'_{2/3})O_3$. Compounds with a 1:3 ratio of B site cations are less common but examples include $Ba_4LiSb_3O_{12}$, $Sr_4NaSb_3O_{12}$, $Ba_{3.92}Ca_{1.08}Cu_3O_{8.85}$ and $Ba_4YCu_3O_{8.5+y}$ (Jacobson, Collins & Fender, 1974; Alonso, Mzayek & Rasines, 1990; Kubat-Martin, Kwei, Lawson & Peterson, 1992; DeLeeuw, Mutsaers, Steeman, Frikkee & Zandbergen, 1989). The structure of $Ba_4LiSb_3O_{12}$ has been determined previously by neutron diffraction (Jacobson, Collins & Fender, 1974). The ordered arrangement corresponds to a body-centered doubled-cubic unit cell (space group $Im\bar{3}m$) with no tilting of the BO_6 octahedra. The closely related phases $Ba_{3.92}Ca_{1.08}Cu_3O_{8.85}$ and $Ba_4YCu_3O_{8.5+y}$ also show a 1:3 order on the B sites and have doubled-cubic unit cells. A combined X-ray and neutron diffraction study of $Ba_{3.92}Ca_{1.08}Cu_3O_{8.85}$ indicated significant mixing of Ba and Ca atoms on both the A and B sites, disorder not observed in $Ba_4LiSb_3O_{12}$. In contrast to the cubic structures, $Sr_4NaSb_3O_{12}$ has been reported to be monoclinic (space group $P2_1/n$) with NaO_6 and SbO_6 octahedra rotated by angles ranging from 5.2 to 12.1° from the cube axes.

As part of a more detailed study of cation ordering in bismuth and antimony-containing perovskites, we decided to investigate the structure of $Ba_4NaSb_3O_{12}$ to determine the extent of B site order and also the possibility of octahedra rotations due to O-atom displacements which would lower the symmetry from $Im\bar{3}m$. An X-ray intensity calculation (Alonso, Mzayek & Rasines, 1987) indicated that the cation ordering corresponded to the body-centered 1:3 arrangement, but X-ray data are relatively insensitive to O-atom displacements. The results of the structure determination of $Ba_4NaSb_3O_{12}$ using time-of-flight powder neutron diffraction data are reported.

The neutron diffraction refinement of the structure of $Ba_4NaSb_3O_{12}$ confirms the 1:3 ordered arrangement of the NaO_6 and SbO_6 octahedra. No evidence for any deviation from cubic $Im\bar{3}m$ symmetry is observed and the compound is isostructural with the corresponding $Ba_4LiSb_3O_{12}$ phase. In the final refinement, the occupation numbers of the Sb and Na atoms were refined without constraining the composition. The results indicate complete ordering within estimated errors with no deviation from the ideal composition. In a separate refinement, the possibility of site disorder of the Na and Ba atoms between the A and B sites was also investigated but no evidence was obtained for any site mixing. Refinement of oxygen occupancies indicated no deviation from stoichiometry.

In the 3:1 ordered arrangement, each NaO_6 octahedron is surrounded by six SbO_6 octahedra and the SbO_6 octahedra are surrounded by two NaO_6 and four other SbO_6 octahedra. One O atom (O1) is located at the midpoint between two Sb atoms, while the other (O2) lies between the Na and Sb atoms but is displaced from the midpoint in order to decrease the Sb—O distance and increase the Na—O distance. The Sb1—O1 and Sb1—O2 distances of 2.068 (1) and 1.891 (1) Å, respectively, are similar to those found in $Ba_4LiSb_3O_{12}$ which are 1.89 and 2.04 Å, respectively. The Na1—O2 bond distance of 2.247 (1) Å is somewhat shorter than the expected

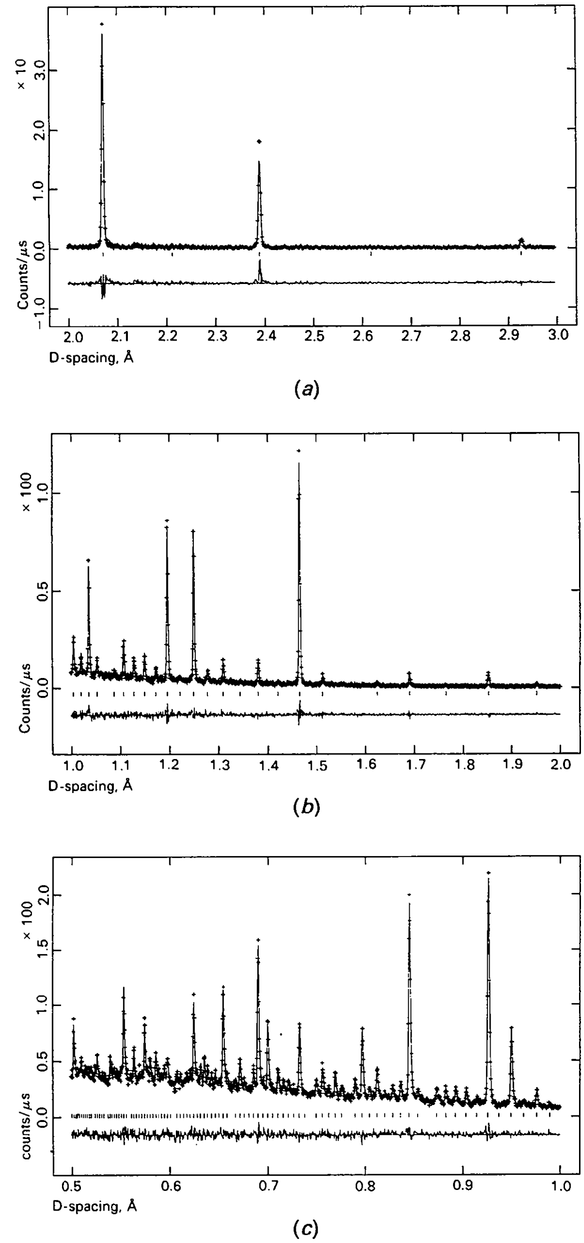

Fig. 1. Observed and calculated time-of-flight neutron diffraction data (148° detector bank). The lower curve is the difference plot and the small vertical markers are the positions of the Bragg reflections contributing to the profile.

distance of 2.35 Å calculated from the crystal radii of Shannon (1976). The values for the Sb1—O1, Sb1—O2 and Na1—O2 bond distances (2.07, 1.81 and 2.33 Å, respectively) determined from an estimate of the X-ray intensities (Alonso, Mzayek & Rasines, 1987) are in reasonable agreement with the results from the refinement of the neutron diffraction data.

Experimental

Crystal data

$Ba_4NaSb_3O_{12}$
M_r = 1129.6
Cubic
$Im\bar{3}m$
a = 8.2785 (2) Å
V = 566.22 Å^3

Z = 2
D_x = 6.62 Mg m^{-3}
Neutron TOF radiation
T = 298 K
Crystal source: powder

Data collection

TOF detector banks at ±90, ±148°

Refinement

Final R = 7.25% (profile)
wR = 10.63% (weighted profile)

303 reflections
41 parameters

Table 1. *Refined profile and structural parameters for* $Ba_4NaSb_3O_{12}$

	Site	x	y	z	Occupancy	U_{iso} (Å^2)	
Ba1	8 (*c*)	0.25	0.25	0.25	1.0	0.00964 (2)	
Sb1	6 (*b*)	0.5	0.0	0.0	0.975 (5)	0.00546 (2)	
Na1	2 (*a*)	0.0	0.0	0.0	1.04 (2)	0.01082 (9)	
						U_{11} (Å^2)	U_{22} (Å^2)
O1	12 (*d*)	0.5	0.0	0.25	1.0	0.00627 (5)	0.01418 (5)
O2	12 (*e*)	0.2714 (1)	0.0	0.0	1.0	0.00762 (6)	0.01344 (6)

	β_0	β_1	σ_0	σ_1	σ_2	R_{wp}	R_p
H1*	0.0492 (8)	0.00242 (2)	0.737 (5)	93.86 (1)	8.93 (2)	0.1153	0.0778
H2*	0.0493 (7)	0.00262 (2)	−3.893 (4)	110.6 (8)	5.02 (2)	0.1123	0.0756
H3*	0.0721 (1)	0.00484 (5)	22.68 (9)	380.8 (2)	2.63 (5)	0.0978	0.0681

* H1, H2 and H3 refer to data from the +148, −148 and −90° detector banks, respectively.

Table 2. *Interatomic distances* (Å)

Ba1—O1	2.927 (1)	Sb1—O1	2.068 (1)
Ba1—O2	2.932 (1)	Sb1—O2	1.891 (1)
Na1—O2	2.247 (1)		

A sample of $Ba_4NaSb_3O_{12}$ (10 g) was prepared by solid-state reaction of $BaCO_3$, Na_2CO_3 and Sb_2O_3 (Aldrich) in the appropriate stoichiometric amounts. The sample was ground and heated at 1023 K (12 h) and then at 1123 K (2 d) to ensure complete reaction of the sodium carbonate in order to avoid volatilization of sodium at higher temperatures. A final firing at 1273 K (3 d) resulted in a single-phase sample. X-ray powder data were collected on a Scintag XDS2000 with Cu $K\alpha$ radiation to check the sample purity. All of the peaks could be indexed on a body-centered cubic unit cell with a = 8.273 (4) Å. The lattice parameter was determined by least squares fitting of the X-ray diffraction data.

Time-of-flight neutron powder diffraction data were collected on the Neutron Powder Diffractometer at LANSCE, Los Alamos National Laboratory. The sample (10 g) was contained in a vanadium can. Data were collected at ambient temperature using four banks of detectors located at ±148 and ±90° to the incident neutron beam. The time-of-flight powder diffraction data were analyzed by Rietveld profile analysis using the *GSAS* programs (Larson & Von Dreele, 1991). After initial inspection, the data from the +90° detector bank were excluded from the refinement because of counting problems.

The time-of-flight powder neutron diffraction data showed systematic reflections $h+k+l = 2n$ indicative of the I Bravais lattice. The data are consistent with space groups $Im\bar{3}m$, $I43$ and $I\bar{4}3m$. Based on previous knowledge, $Im\bar{3}m$ was chosen and the structure was refined with the starting parameters taken from the corresponding lithium structure. Atomic positional and thermal parameters, and background and profile coefficients were refined simultaneously. Neutron scattering lengths b_i ($\times$ 10^{-12} cm) were taken as b_{Ba} = 0.525, b_{Sb} = 0.564, b_{Na} = 0.363 and b_O = 0.5805 (Koester & Yelon, 1982). The time-of-flight profile function used was a convolution of two back-to-back exponentials with a Gaussian. The profile coefficients refined were β_O, β_1, σ_0, σ_1 and σ_2 where $\beta = \beta_O + \beta_1/d^4$ is the decay coefficient for the exponential and $\sigma^2 = \sigma_O + \sigma_1^2 d^2 + \sigma_2^2 d^4$ is the Gaussian variance. The Rietveld refinement was performed on all data points with d spacings between 0.5 and 3.0 Å^{-1} (time of flight 10-50 ms). The reduced $\chi^2 = M/(N_{obs} - N_{var})$ and $R_{wp} = [M/\Sigma(wI_o^2)]^{1/2}$ where the quantity minimized is $M = \Sigma w(I_o - I_c)$, with I_o and I_c being the observed and calculated intensities and $w = 1/(I^{1/2})$ being a weight related to the error. The number of observations, N_{obs}, is 9657 and the number of variables, N_{var}, is 41. $\chi^2 = 1.6$. Small discrepancies between the observed and calculated background points between d spacings of 0.5 and 1.0 Å^{-1} (Fig. 1) are responsible for slightly higher than expected R factors.

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Primary diffraction data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71156 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1048]

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The KInTe$_2$ Structure Revisited

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Abstract

The framework is built up from InTe$_4$ tetrahedra and KTe$_8$ square antiprisms. The InTe$_4$ tetrahedra share orthogonal edges to form infinite chains along the *c* axis. These parallel tetrahedral chains are interconnected *via* edge-sharing KTe$_8$ square antiprisms.

Comment

The tetragonal cell of KInTe$_2$ was first indexed by Franke & Schafer (1972) using the Weissenberg photographic method. Estimated atomic coordinates were given by the authors. The present study reports the single-crystal structure and detailed bond distances and angles for KInTe$_2$.

Crystals of KInTe$_2$ were isolated during studies of the Nd-In-Ti-Te system. The single crystals were grown at 1275 K from a reaction with the target composition Nd$_2$In$_3$Ti$_3$Te$_{12}$. Similar to a method previously reported (Carpenter & Hwu, 1992), the crystal-growth experiment was carried out using an eutectic halide flux (BaCl$_2$/KCl).

A projection onto the *ab* plane of the structure of KInTe$_2$ is shown in Fig. 1. The structure is built up of InTe$_4$ tetrahedra and KTe$_8$ square antiprisms. Each InTe$_4$ tetrahedron shares edges with two InTe$_4$ tetrahedra along the fourfold screw axis, 4_2, and the four KTe$_8$ square antiprisms. A chain of InTe$_4$ tetrahedra sharing orthogonal edges can be observed running along the *c* axis. The parallel face-sharing KTe$_8$ square antiprismatic chains edge-share with the InTe$_4$ tetrahedral chain to form a three-dimensional framework with the TlSe-type structure (Ketelaar, t'Hart, Moerel & Polder, 1939). It should be noted that the title compound is isostructural with TlInTe$_2$ (Müller, Eulenberger & Hahn, 1973). The bond distances and angles of the InTe$_4$ tetrahedra and the KTe$_8$ square antiprisms are listed in Table 2.

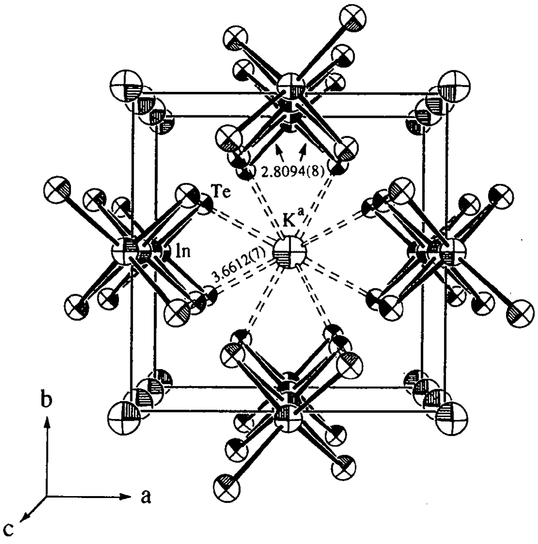

Fig. 1. *ORTEP* (Johnson, 1976) drawing of the KInTe$_2$ structure viewed approximately along the *c* axis. The anisotropic atoms are presented in 90% probability. The bond lengths are given in Å. K^a is at $\frac{1}{2}$, $\frac{1}{2}$, $\frac{5}{4}$.

Experimental

Crystal data

KInTe$_2$
M_r = 409.12
Tetragonal
$I4/mcm$
a = 8.598 (2) Å
c = 7.312 (3) Å
V = 540.6 (3) Å^3
Z = 4
D_x = 5.027 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 3.35–12.05°
μ = 15.52 mm^{-1}
T = 296 K
Needle
0.7 × 0.05 × 0.05 mm
Dark red

Data collection

Rigaku AFC-5*S* four-circle diffractometer
ω scans
Absorption correction: three azimuthal scans (2θ = 11.16, 22.43, 35.30°)
$T_{\min}$ = 0.67, $T_{\max}$ = 1.00
208 measured reflections
176 independent reflections

176 observed reflections [$I > 3\sigma(I)$]
$\theta_{\max}$ = 27.5°
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 9$
3 standard reflections monitored at the end of each shell intensity variation: none detectable

Refinement

Refinement on F
Final R = 0.021
wR = 0.032
S = 1.61
176 reflections
10 parameters
$w = [\sigma^2(F_o)]^{-1}$
$(\Delta/\sigma)_{\max}$ = 0.003

$\Delta\rho_{\max}$ = 1.78 e Å^{-3}
$\Delta\rho_{\min}$ = −3.43 e Å^{-3}
Extinction correction: Zachariasen (1968)
Extinction coefficient: 1.9 (1) × 10^{-6}
Atomic scattering factors from Cromer & Waber (1974)

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