The Synthesis and Crystal Structures of Novel Antimony Compounds: $A_4Sb_4O_8(X_4O_{12})$ (A: K, Rb, Cs, Tl; X = Si, Ge)

C. PAGNOUX, A. VERBAERE, Y. KANNO, Y. PIFFARD,*
AND M. TOURNOUX

Institut des Matériaux de Nantes (I.M.N.), Laboratoire de Chimie des Solides, 2, Rue de la Houssinière, 44072-Nantes Cedex 03, France

A series of $A_4Sb_4O_8(X_4O_{12})$ compounds (A = K, Rb, Cs, Tl; X = Si, Ge) have been prepared either by solid-state reaction or via a sol–gel route. Single crystals of the cesium compounds have been isolated and their structure determined by X-ray diffraction. $Cs_4Sb_4O_8(Si_4O_{12})$ crystallizes in the tetragonal system, space group $P4_2/mmc$ with a = 7.172(1) Å, c = 19.645(2) Å, Z = 2. The structure was determined from 557 reflections collected on a Nonius CAD4 diffractometer using the Mo$K\alpha$ radiation. The final R index and weighted R_w index are 0.026 and 0.024, respectively. The structure is built up from planes of cross-linked chains of corner-sharing SbO_6 octahedra, linked together via corner-sharing by four-membered Si_4O_{12} single rings. This three-dimensional arrangement delimits intercrossing tunnels wherein Cs cations are situated. $Cs_4Sb_4O_8(Ge_4O_{12})$ crystallizes in the tetragonal system, space group $I4_122$ with a = 10.241(1) Å, c = 40.073(6) Å, Z = 8. Its structure was determined from 1303 reflections and refined to R = 0.034 and R_w = 0.035. It appears as a slightly distorted form of the silicate analogue. © 1992 Academic Press, Inc.

Introduction

Within a research program devoted to layered or skeleton structures built up from MO_6 octahedra (M: high valent cation) and XO_4 tetrahedra (X = Si, P, Ge, As), and exhibiting fast alkali-ion mobility, we have recently extended our investigations to $A_2O–Sb_2O_5–XO_2$ systems (A: alkali; X = Si, Ge). Several phases have been identified, such as $ASbOSiO_4$ (A = Na, K) (1, 2), and $ASbOGeO_4$ (A = K, Rb) (2) which are isomorphous derivatives of $KTiOPO_4$ (3), and a monopolysilicate, $CsSbO(SiO_3)_2$ (4). In the course of our investigations for the synthesis of $KSbOSiO_4$ by sol–gel route (5) a new

$KSbSiO_5$ polymorph has been observed. Its structural characterization has been possible thanks to the preparation of single crystals of the cesium analogues (silicate and germanate) which allow complete structure determinations. $Cs_4Sb_4O_8(X_4O_{12})$ compounds (X = Si, Ge) appear as members of a series of isomorphous antimony cyclo-tetrasilicates and cyclotetragermanates. We report here on the preparation of some of these, and on the crystal structure of the cesium compounds.

Experimental Section

Synthesis

$K_4Sb_4O_8(Si_4O_{12})$. The starting materials for synthesizing this compound were

---

$KSb(OH)_6$ and $Si(OC_2H_5)_4$ (TEOS) (all p.a., Merck). $KSb(OH)_6$ (10 mmoles) was dissolved into water and the equimolar amount of TEOS, dissolved in ethanol, was added under magnetic stirring (the molar ratio of water to TEOS was about 1000). Ten mmoles of HNO_3 were introduced as polymerization catalyst. During the hydrolysis reaction the mixture was maintained at 273 K to prevent volatilization of TEOS. The gel-like product was then dried in an oven at 350 K and ground before calcining in a platinum crucible, under air. The crystallization of the cyclotetrasilicate occurs at 1213 K. Upon heating at 1373 K it undergoes a phase transformation leading to $KSbOSiO_4$.

$A_4Sb_4O_8(X_4O_{12})$, $(A = Rb, Cs$ with $X = Si$ and $A = Cs$ with $X = Ge$). One method of preparation includes a sol–gel route similar to that described above. Prior to the hydrolysis reaction the $KSb(OH)_6$ solution was passed over a strong cation exchange resin in the H^+-form (Dowex 50W-X2) and an equimolar amount of $RbNO_3$ (or $CsNO_3$) was added to the freshly prepared antimonic acid. When the germanium compound was prepared, $Ge(OC_2H_5)_4$ was used instead of TEOS. This method allowed to prepare very fine powders with high sinterability.

Single crystals of both Cs compounds were grown from mixtures of $CsNO_3$, $Sb_2O_5–xH_2O$, and SiO_2 (or GeO_2). The chemicals were weighed out in a molar ratio of $2:1:1$ and the mixture was heated in air in a platinum crucible first at 773 K for 3 hr and then at 1573 K for 3 hr.

$Tl_4Sb_4O_8(Si_4O_{12})$. $TlSbO_3$, which was prepared as has been described previously (6), was added to an equimolar amount of SiO_2 and the mixture was sealed in an evacuated silica tube. This sample was then heated for 24 hr at 1173 K.

X-ray Diffraction

Crystals of the Cs compounds are colorless thin square-shaped platelets. Their chemical analysis, conducted with an electron microprobe, leads to atomic Cs to Sb and Si (or Ge) ratios of $1:1:1$. Single-crystal X-ray studies indicate that the crystals are of tetragonal symmetry. For $Cs_4Sb_4O_8(Si_4O_{12})$ the symmetry of the diffraction pattern and the systematic absences $l = 2n + 1$ for hhl reflections are consistent with the space groups $P4_2/mmc$, $P\bar{4}2c$, and $P4_2mc$. The structure has been solved and refined in the centrosymmetric space group $P4_2/mmc$. For $Cs_4Sb_4O_8(Ge_4O_{12})$, a comparison of its X-ray powder diffraction pattern with that of the silicon analogue shows that their structures are isotypic. However, the single-crystal X-ray study reveals a superstructure leading to an I-centered unit-cell with a' and c' parameters related to the a and c parameters of $Cs_4Sb_4O_8(Si_4O_{12})$ as follows:

$$a' \simeq a\sqrt{2} \quad \text{and} \quad c' \simeq 2c.$$

The symmetry of the diffraction pattern and the systematic absences uniquely determine the space group of $Cs_4Sb_4O_8(Ge_4O_{12})$ as $I4_122$.

In order to know whether the title compounds exhibit superstructures or not, electron diffraction experiments have been performed with use of a JEOL 100 CX electron microscope. The unit-cell parameters (Table I) were refined by a least-squares procedure from powder diffraction data collected with an Inel curved multidetector (0.2 mm capillary, $\lambda(CuK\alpha_1) = 1.54059$ Å, silicon as standard). The powder patterns of $Cs_4Sb_4O_8(Si_4O_{12})$ and $Cs_4Sb_4O_8(Ge_4O_{12})$ (Tables IIa and IIb) include observed and

TABLE I

Unit-Cell Parameters of the $A_4Sb_4O_8(X_4O_{12})$ Compounds

Formula	a(Å)	c(Å)	V(Å^3)	Z	Space group
$K_4Sb_4O_8(Si_4O_{12})$	9.997(2)	38.364(8)	3834(1)	8	$P4_122$
$Rb_4Sb_4O_8(Si_4O_{12})$	10.046(1)	38.716(3)	3907.3(3)	8	$I4_122$
$Cs_4Sb_4O_8(Si_4O_{12})$	7.172(1)	19.645(2)	1010.5(2)	2	$P4_2/mmc$
$Tl_4Sb_4O_8(Si_4O_{12})$	10.075(1)	38.544(2)	3912.4(3)	8	$P4_122$
$Cs_4Sb_4O_8(Ge_4O_{12})$	10.241(1)	40.073(6)	4203(1)	8	$I4_122$

TABLE IIa

X-RAY POWDER PATTERN OF $Cs_4Sb_4O_8(Si_4O_{12})$

h	k	l	d_{obs}(Å)	d_{calc}(Å)	I/I_0	h	k	l	d_{obs}(Å)	d_{calc}(Å)	I/I_0
0	0	2	9.856	9.8224	100	2	2	6	2.005	2.0048	5
1	0	0	7.185	7.1721	28	3	2	1	1.9792	1.9791	7
1	0	1		6.7371	4	2	1	8 }	1.9498	1.9498	7
0	0	4	4.919	4.9112	4	3	2	2 }		1.9496	20
2	0	0	3.588	3.5861	36	3	0	6	1.9312	1.9308	16
1	1	4	3.529	3.5280	61	3	2	3	1.9036	1.9033	13
1	0	5	3.446	3.4458	25	1	0	10		1.8947	4
0	0	6	3.272	3.2741	4	2	0	9	1.8645	1.8645	4
2	1	0	3.208	3.2075	9	3	0	7	1.8199	1.8199	8
2	1	1	3.167	3.1655	63	4	0	0	1.7928	1.7930	32
2	0	3	3.145	3.1453	61	2	2	8 }	1.7640	1.7640	49
2	1	2	3.050	3.0490	93	4	0	2 }		1.7639	4
1	0	6	2.980	2.9785	60	1	0	11	1.7331	1.7330	10
2	1	3	2.882	2.8805	70	4	2	0	1.6032	1.6037	8
2	0	5	2.649	2.6487	37	2	0	11 }	1.5982	1.5986	4
1	0	7	2.615	2.6134	17	3	3	4 }		1.5984	9
2	2	2		2.4552	3	4	1	5	1.5902	1.5909	6
2	0	6		2.4179	3	4	0	6	1.5722	1.5726	4
3	1	4	2.059	2.0591	20	1	1	12 }	1.5576	1.5579	6
3	0	5	2.043	2.0423	10	4	2	3 }		1.5577	13
2	0	8	2.026	2.0261	8	2	2	10	1.5528	1.5530	6

Note. Reflections with $I/I_0 < 3$ have been omitted.

TABLE IIb

X-RAY POWDER PATTERN OF $Cs_4Sb_4O_8(Ge_4O_{12})$

h	k	l	d_{obs}(Å)	d_{calc}(Å)	I/I_0	h	k	l	d_{obs}(Å)	d_{calc}(Å)	I/I_0
0	0	4	10.024	10.0155	67	3	3	10	2.066	2.0673	4
1	1	0	7.246	7.2404	8	2	2	16	2.059	2.0593	7
1	1	2	6.815	6.8093	15	5	1	2	1.9985	1.9981	10
1	1	4	5.867	5.8677	5	3	1	16	1.9819	1.9807	3
0	0	8	5.000	5.0077	7	5	1	4	1.9689	1.9689	22
2	0	4 }	4.552	4.5587	3	3	3	12	1.9562	1.9559	16
2	1	1 }		4.5496	3	1	1	20		1.9280	4
2	2	0	3.620	3.6202	31	5	1	6	1.9214	1.9214	12
2	0	8	3.580	3.5799	56	3	3	14	1.8446	1.8449	13
1	1	10	3.504	3.5054	11	4	4	0	1.8100	1.8101	33
3	1	0	3.234	3.2380	3	4	0	16	1.7899	1.7899	47
3	1	2	3.197	3.1965	80	4	4	4	1.7817	1.7812	3
2	2	6	3.183	3.1825	61	1	1	22	1.7659	1.7660	10
3	1	4	3.081	3.0810	100	6	2	0	1.6188	1.6190	7
1	1	12	3.032	3.0317	75	6	0	8	1.6155	1.6154	8
3	1	6	2.914	2.9135	68	5	3	10	1.6081	1.6083	3
2	0	12	2.796	2.7965	3	2	0	24	1.5867	1.5870	3
2	2	10	2.687	2.6860	55	4	0	20	1.5775	1.5775	10
1	1	14	2.663	2.6613	27	6	2	6	1.5733	1.5734	9
4	2	8	2.082	2.0823	21	5	3	12	1.5541	1.5542	13

Note. Reflections with $I/I_0 < 3$ have been omitted.

TABLE III

CRYSTALLOGRAPHIC AND EXPERIMENTAL DATA

	Crystal data	
Formula	$Cs_4Sb_4O_8(Si_4O_{12})$	$Cs_4Sb_4O_8(Ge_4O_{12})$
Formula weight	1451.0	1629.0
Crystal dimensions (mm)	$0.10 \times 0.10 \times 0.006$	$0.10 \times 0.10 \times 0.03$
$a(\text{Å})$	7.172(1)	10.241(1)
$c(\text{Å})$	19.645(2)	40.073(6)
$V(\text{Å}^3)$	1010.5(2)	4203(1)
Space group	$P4_2/mmc$	$I4_122$
Z	2	8
D calc.(g cm^{-3})	4.768	5.166
$F(000)$	1280	5696
$\mu(MoK\alpha)$ (cm^{-1})	127.1	176.0
	Data collection	
Scan mode	ω	ω
Scan angle $\Delta\omega$ (°)	$1.0 + 0.35 \tan \theta$	$1.0 + 0.35 \tan \theta$
Recording angular range (°)	2.0–30.0	1.5–30.0
Measured reflections	1735	5065
Number of independent data observed with $\sigma(I)/I < 0.33$ (used in refinements)	557	1303
	Structure solution and refinement	
Transmission factors	0.29–0.84	0.09–0.48
Number of variables (isotropic temperature factors)	28	66
$R = \Sigma(\|F_o\| - \|F_c\|)/\Sigma \|F_o\|$	0.027	0.053
$R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w F_0^2]^{1/2}$	0.024	0.055
with $w =$	$1/(1 + [(F_{obs} - F_{ave})/F_{max}]^2)$	1
Number of variables (anisotropic temperature factors for all atoms except oxygen)	37	98
$R =$	0.026	0.034
$R_w =$	0.024	0.035
Extinction parameter refined $g =$	$1.79(4) \times 10^{-7}$	$9.4(1) \times 10^{-8}$

calculated interplanar distances of the reflection planes along with the intensities calculated from the LAZY-PULVERIX program (7). Intensity data were collected with a Nonius CAD4 diffractometer operating under the conditions given in Table III. For the data reduction, absorption corrections, structure solution, and refinement, the MOLEN program chain of Enraf–Nonius (8), was used.

Structure Determinations

The structure of $Cs_4Sb_4O_8(Si_4O_{12})$ was solved first. The starting positional parameters for the Cs and Sb atoms were inferred from the Patterson map, the remaining atoms being located from successive electron density difference syntheses. Refinements were carried out by the full-matrix least-squares method. Details are given in

TABLE IVa

$Cs_4Sb_4O_8(Si_4O_{12})$: Atomic Coordinates and Thermal Parameters

Atom	x	y	z	$B_{iso}^*/B_{eq}(\text{Å}^2)$
Cs(1)	0.0276(4)	0.0277(4)	0	0.85(4)*
Cs(2)	0	0.5	0.6357(6)	1.18(2)
Cs(3)	0.5	0.5	0.25	1.18(2)
Sb(1)	0	0.2483(1)	0.18425(3)	0.351(9)
Si(1)	0.2748(5)	0.5	0.0805(1)	0.46(5)
O(1)	0.1976(8)	0.198	0.25	0.7(1)*
O(2)	0.1943(9)	0.3122(9)	0.1144(2)	0.90(9)*
O(3)	0.230(2)	0.5	0	0.9(2)*
O(4)	0.5	0.5	0.0897(6)	1.1(2)*
O(5)	0	0.5	0.2180(5)	0.6(2)*
O(6)	0	0	0.1445(6)	0.8(2)*

Note. $B_{eq} = \frac{4}{3}\Sigma_i \Sigma_j \beta_{ij}\mathbf{a}_i \cdot \mathbf{a}_j$.

Table III. For the Cs(1) position it must be mentioned that the electron density is better accounted for when an $8q$ position, close to the origin, is statistically occupied. Consequently, anisotropic temperature factors were not assigned to Cs(1).

For $Cs_4Sb_4O_8(Ge_4O_{12})$ the starting positional parameters of cell atoms were taken by analogy with those of similar atoms in $Cs_4Sb_4O_8(Si_4O_{12})$ and in keeping with the possible unique positions of the $I4_122$ space group. The atomic positions have been labeled with the same numbers as their counterparts in the silicate structure, with use of prime, double prime, and triple prime superscripts when a given position in the silicate gives rise to several positions in the germanate.

A refinement of the enantiomorph was also undertaken but it led to a slightly higher R_w value.

Final atomic coordinates and thermal parameters for both structures are given in Tables IVa,b and Va,b, and important bond distances and angles in Tables VI and VII.

Structure Descriptions

The $Cs_4Sb_4O_8(Si_4O_{12})$ structure consists of a three-dimensional arrangement of SbO_6 octahedra and four-membered Si_4O_{12} single rings sharing corners (Fig. 1). Single chains of corner-sharing SbO_6 octahedra, running parallel to [010] at $z \simeq \pm 0.18$ are cross-linked to similar chains running parallel to [100] at $z \simeq \pm 0.32$. These networks of chains, parallel to (001), are linked together via corner-sharing by Si_4O_{12} rings. In that

TABLE IVb

Anisotropic Thermal Parameters (Å^2) for the Atoms of $Cs_4Sb_4O_8(Si_4O_{12})$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cs(2)	0.0146(5)	0.0164(5)	0.0138(4)	0	0	0
Cs(3)	0.0153(4)	0.0153(4)	0.0141(6)	0	0	0
Sb(1)	0.0047(2)	0.0045(3)	0.0042(2)	0	0	0.0001(3)
Si(1)	0.005(1)	0.008(1)	0.005(1)	0	−0.000(1)	0

PAGNOUX ET AL.

TABLE Va

$Cs_4Sb_4O_8(Ge_4O_{12})$: ATOMIC COORDINATES AND THERMAL PARAMETERS

Atom	x	y	z	$B_{iso}^*/B_{eq}(\text{Å}^2)$
Cs(1)	0.2691(1)	0.7309	0	2.28(1)
Cs(2)	0	0	0.42846(3)	1.20(2)
Cs(2')	0	0	0.06697(3)	1.49(2)
Cs(3)	0.2533(2)	0.25	0.125	1.24(2)
Sb(1)	0.38161(9)	0.86437(9)	0.09087(2)	0.43(1)
Sb(1')	0.36408(9)	0.88198(9)	0.59530(2)	0.50(1)
Ge(1)	0.3597(2)	0.1280(1)	0.03920(3)	0.50(2)
Ge(1')	0.3705(1)	0.1404(2)	0.54261(3)	0.49(2)
O(1)	0.249(1)	0.947(1)	0.1186(2)	0.7(2)*
O(1')	0.25	0.954(1)	0.375	0.3(2)*
O(1")	0.25	0.941(1)	0.875	0.6(2)*
O(2)	0.214(1)	0.469(1)	0.0673(3)	0.5(1)*
O(2')	0.520(1)	0.791(1)	0.0623(3)	0.9(2)*
O(2")	0.329(1)	0.967(1)	0.0498(3)	1.2(2)*
O(2''')	0.027(1)	0.675(1)	0.0557(3)	0.8(2)*
O(3)	0.414(1)	0.139(1)	0.9982(3)	1.5(2)*
O(4)	0.210(1)	0.206(1)	0.0443(2)	1.1(1)*
O(5)	0	0.5	0.1106(3)	0.8(2)*
O(5')	0.5	0	0.1051(3)	1.0(2)*
O(6)	0.268(1)	0.729(1)	0.0739(2)	0.7(1)*

Note. $B_{eq} = \frac{4}{3}\Sigma_i \Sigma_j \beta_{ij}\mathbf{a}_i \cdot \mathbf{a}_j$.

manner, each SbO_6 octahedron shares two oxygen atoms (O(5) and O(6)) with two octahedra in the same chain, two others (O(1) × 2) with two octahedra in the adjacent chain, and the last two (O(2) × 2) with two Si_4O_{12} rings. In these rings the four silicon atoms and the four bridging oxygen atoms (Si–O–Si) lie in the same plane; the symmetry of the Si_4O_{12} ring is *mmm*. The covalent framework delimits large intercrossing tunnels running parallel to [100] and [010], and wherein Cs cations are situated. It must be mentioned that some of the distances from Cs to oxygen atoms are unusually short (two

TABLE Vb

ANISOTROPIC THERMAL PARAMETERS (Å^2) FOR THE ATOMS OF $Cs_4Sb_4O_8(Ge_4O_{12})$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cs(1)	0.0359(5)	U_{11}	0.0146(4)	−0.0045(7)	−0.023(5)	U_{13}
Cs(2)	0.0106(5)	0.0127(5)	0.0221(5)	0.0001(4)	0	0
Cs(2')	0.0193(6)	0.0189(6)	0.0185(5)	−0.0055(5)	0	0
Cs(3)	0.0198(5)	0.0105(5)	0.0168(4)	0	0	0.0018(6)
Sb(1)	0.0041(3)	0.0028(3)	0.0093(3)	−0.0006(3)	−0.0006(3)	0.0012(3)
Sb(1')	0.0055(3)	0.0043(3)	0.0095(3)	−0.0011(3)	−0.0005(3)	0.0008(3)
Ge(1)	0.0046(5)	0.0045(6)	0.0099(5)	−0.0006(5)	−0.0002(5)	0.0006(5)
Ge(1')	0.0032(6)	0.0071(5)	0.0083(4)	0.0001(5)	−0.0003(5)	0.0007(5)

TABLE VI

$Cs_4Sb_4O_8(Si_4O_{12})$: SELECTED BOND DISTANCES (Å) AND BOND ANGLES (°) WITH e.s.d.'s

			Octahedra Sb(1)O$_6$			
Sb(1)	O(1)	O(1)	O(2)	O(2)	O(5)	O(6)
O(1)	1.952(9)	2.83(1)	2.79(1)	3.96(1)	2.67(1)	2.88(1)
O(1)	93.1(3)	1.952(9)	3.96(1)	2.79(1)	2.67(1)	2.88(1)
O(2)	89.5(4)	176.7(4)	2.01(1)	2.79(2)	2.81(2)	2.70(2)
O(2)	176.7(4)	89.5(4)	87.8(7)	2.01(1)	2.81(2)	2.70(2)
O(5)	86.9(4)	86.9(4)	91.2(6)	91.2(6)	1.924(7)	3.87(1)
O(6)	95.5(4)	95.5(4)	86.2(6)	86.2(6)	176.5(7)	1.944(9)

		Tetrahedra Si(1)O$_4$		
Si(1)	O(2)	O(2)	O(3)	O(4)
O(2)	1.61(1)	2.69(2)	2.63(1)	2.62(1)
O(2)	113.6(9)	1.61(1)	2.63(1)	2.62(1)
O(3)	109.5(6)	109.5(6)	1.614(8)	2.62(2)
O(4)	108.1(6)	108.1(6)	108.0(1)	1.625(7)

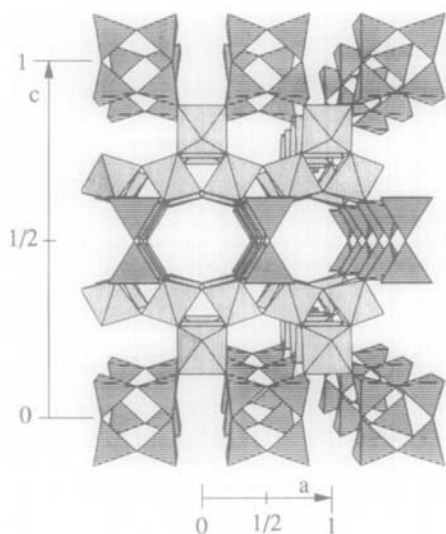|	Distances Cs–O		
	O(6) × 2	O(2) × 2	O(2) × 2
Cs(1)	2.85(2)	3.26(1)	3.42(1)
	O(5)	O(2) × 4	O(1) × 4
Cs(2)	2.87(2)	3.16(1)	3.428(5)
	O(1) × 4	O(4) × 2	
Cs(3)	3.067(8)	3.15(2)	

FIG. 1. Perspective [010] view of the [Sb$_4$O$_8$(Si$_4$O$_{12}$)]$^{4-}$ framework.

Cs(1)–O(6) distances of 2.85(2) Å and one Cs(2)–O(5) distance of 2.87(2) Å. However, this situation corresponds to Cs cations with a small coordination number, i.e., situated rather far from the next oxygen neighbors (Table VI).

In $Cs_4Sb_4O_8(Ge_4O_{12})$ the $[Sb_4O_8(X_4O_{12})]^{4-}$ framework exhibits a distortion with respect to that observed in $Cs_4Sb_4O_8(Si_4O_{12})$ as can be seen from Fig. 2. This distortion correlative with a lowering of the symmetry, minimizes the volume increase that one could expect from the replacement of SiO$_4$ tetrahedra by GeO$_4$ tetrahedra in the $Cs_4Sb_4O_8(Si_4O_{12})$ structure (4.5% instead of about 14%). Thereby it allows antimony to form rather regular SbO$_6$ octahedra and cesium to lie in sites of more adequate size.

PAGNOUX ET AL.

TABLE VII

$Cs_4Sb_4O_8(Ge_4O_{12})$: Selected Bond Distances (Å) and Bond Angles (°) with e.s.d.'s

Octahedra $Sb(1)O_6$

Sb(1)	O(1)	O(1')	O(2')	O(2'')	O(5')	O(6)
O(1)	1.948(5)	2.918(6)	3.914(8)	2.881(8)	2.683(5)	2.864(7)
O(1')	97.2(2)	1.943(3)	2.634(5)	3.952(6)	2.721(2)	2.799(6)
O(2')	176.7(3)	84.7(2)	1.968(5)	2.704(8)	2.748(6)	2.694(7)
O(2'')	92.9(2)	169.8(2)	85.3(2)	2.025(5)	2.844(7)	2.691(7)
O(5')	87.6(2)	89.3(2)	89.7(2)	92.0(2)	1.928(2)	3.858(6)
O(6)	95.2(2)	92.5(2)	87.4(2)	85.7(2)	176.4(2)	1.931(5)

Octahedra $Sb(1')O_6$

Sb(1')	O(1)	O(1'')	O(2)	O(2''')	O(5)	O(6)
O(1)	1.964(5)	2.811(6)	2.729(7)	3.988(7)	2.731(5)	2.929(7)
O(1'')	91.4(2)	1.965(3)	4.016(6)	2.894(5)	2.689(2)	2.969(7)
O(2)	85.5(2)	175.2(1)	2.055(5)	2.905(7)	2.809(6)	2.735(7)
O(2''')	175.7(2)	92.9(2)	90.2(2)	2.026(5)	2.851(7)	2.632(7)
O(5)	88.8(2)	87.0(2)	89.3(2)	91.8(2)	1.941(2)	3.896(6)
O(6)	96.5(2)	98.2(2)	85.8(2)	82.6(2)	172.5(2)	1.963(5)

Tetrahedra $Ge(1)O_4$

Ge(1)	O(2')	O(2'')	O(3)	O(4)
O(2')	1.748(5)	2.962(8)	2.747(7)	2.854(8)
O(2'')	116.8(3)	1.730(6)	2.844(7)	2.739(9)
O(3)	104.2(2)	110.4(2)	1.734(6)	2.865(8)
O(4)	109.9(2)	104.4(2)	111.3(2)	1.737(8)

Tetrahedra $Ge(1')O_4$

Ge(1')	O(2)	O(2''')	O(3)	O(4)
O(2)	1.722(5)	2.891(7)	2.789(7)	2.840(8)
O(2''')	115.2(2)	1.719(5)	2.888(7)	2.748(9)
O(3)	107.9(2)	113.9(2)	1.727(6)	2.818(8)
O(4)	108.6(2)	103.7(2)	107.2(2)	1.775(8)

Distances Cs–O

Cs(1)	O(6) × 2	O(2'') × 2	O(2''') × 2			
	2.955(3)	3.190(5)	3.383(5)			

Cs(2)	O(5')	O(2) × 2	O(2') × 2	O(6) × 2	O(1') × 2	
	2.934(6)	2.951(5)	3.008(6)	3.338(4)	3.368(1)	

Cs(2')	O(5)	O(4) × 2	O(1) × 2	O(2''') × 2	O(2'') × 2	
	2.896(6)	3.146(4)	3.322(5)	3.362(5)	3.450(6)	

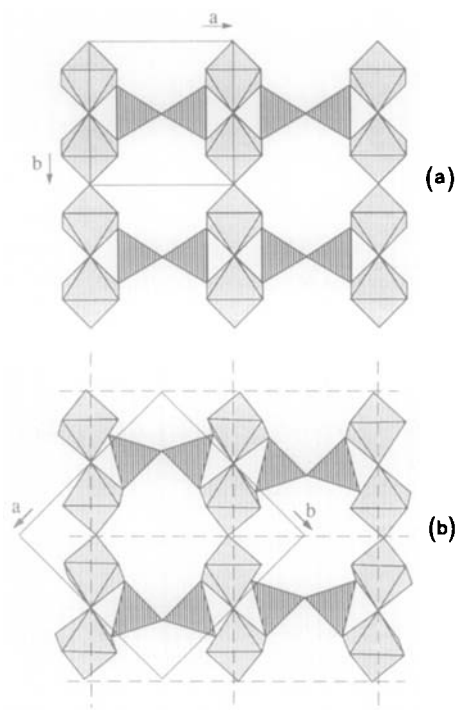| Cs(3)	O(1')	O(1) × 2	O(1'')	O(2) × 2	O(4) × 4	O(2') × 2
	2.999(7)	3.113(6)	3.192(8)	3.239(5)	3.290(4)	3.444(5)

FIG. 2. [001] view of a fragment of the $[Sb_4O_8(Si_4O_{12})]^{4-}$ framework (a) and of the corresponding fragment in the germanate counterpart (b) showing the distortion.

However, as in $Cs_4Sb_4O_8(Si_4O_{12})$, short Cs-O distances are observed, for Cs cations with a small number of close neighbors.

Conclusion

On account of the variety of $A_4Sb_4O_8$ (X_4O_{12}) compounds which have already

been prepared by solid-state reaction or via a sol–gel route, and of these structure descriptions, the $[Sb_4O_8(X_4O_{12})]^{4-}$ framework appears as rather open and flexible. By taking advantage of this property, ion-exchange reactions with some of the title compounds have been undertaken. They allow us to prepare $A_4Sb_4O_8(Si_4O_{12})$ compounds with A = Li, Na, H_3O^+, Ag, and $A_4Sb_4O_8(Ge_4O_{12})$ compounds with A = K, Rb. These ion-exchange reactions, along with a study of ionic conductivities in this series of compounds, will be presented in a forthcoming paper.

References

1. M.-P. CROSNIER, D. GUYOMARD, A. VERBAERE, AND Y. PIFFARD, *Eur. J. Solid State Inorg. Chem.* **27,** 845 (1990).
2. C. PAGNOUX, D. GUYOMARD, A. VERBAERE, Y. PIFFARD, AND M. TOURNOUX, *C.R. Acad. Sci. Paris, sér. II* **312,** 611 (1991).
3. I. TORDJMAN, R. MASSE, AND J.-C. GUITEL, *Z. Kristallogr.* **139,** 103 (1974).
4. C. PAGNOUX, A. VERBAERE, Y. PIFFARD AND M. TOURNOUX *Acta Crystallogr.* **C47,** 2297 (1991).
5. Y. KANNO, C. PAGNOUX, Y. PIFFARD, AND M. TOURNOUX, *J. Mater. Res.* **6**(12), 2499 (1991).
6. M. BOUCHAMA AND M. TOURNOUX, *C.R. Acad. Sci. Paris* **274,** 1576 (1972).
7. R. YVON, W. JEITSCHKO, AND E. PARTHE, *J. Appl. Crystallogr.* **10,** 73 (1977).
8. C. KAY FAIR, "MOLEN Structure Determination Package," Enraf–Nonius, Delft, The Netherlands (1990).