JOURNAL OF SOLID STATE CHEMISTRY **121,** 350–355 (1996)
ARTICLE NO. 0047

Synthesis and Structural Study of Copper(II) Diarsenates

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Received June 20, 1995; in revised form October 3, 1995; accepted October 5, 1995

Three new copper(II) diarsenates, $A\mathrm{CuAs_2O_7}$ (A = Ca, Sr, Ba), have been synthesized hydrothermally and characterized by single-crystal X-ray diffraction. All three compounds crystallize in monoclinic system with $Z = 4$. Crystal data: $\mathrm{CaCuAs_2O_7}$, $a = 7.248(2)$ Å, $b = 8.952(2)$ Å, $c = 9.258(2)$ Å, $\beta = 109.66(2)°$, $V = 565.7(3)$ Å^3, space group $P2_1/c$, $R = 0.0327$; $\mathrm{SrCuAs_2O_7}$, $a = 5.550(1)$ Å, $b = 8.299(2)$ Å, $c = 12.858(3)$ Å, $\beta = 91.75(3)°$, $V = 592.0(3)$ Å^3, space group $P2_1/n$, $R = 0.0207$; $\mathrm{BaCuAs_2O_7}$, $a = 5.736(1)$, $b = 8.458(2)$, $c = 13.044(3)$ Å, $\beta = 91.16(3)°$, $V = 632.7(3)$ Å^3, space group $P2_1/n$, $R = 0.0373$. The structures of these compounds consist of corner-sharing $\mathrm{CuO_5}$ square pyramids and $\mathrm{As_2O_7}$ disarsenate units. The calcium compound adopts a new structural type. The strontium compound is isotypic with the phosphate analog $\mathrm{SrCuP_2O_7}$ (Moqine *et al., J. Solid State Chem.* 107, 368, 1993). The barium compound adopts the same structure as $\mathrm{SrCuAs_2O_7}$ instead of the triclinic $\mathrm{BaCuP_2O_7}$ (Moqine *et al. Acta Crystallogr.* C47, 2294, 1991). The relationship between (R_A–R_B) and space group symmetry as observed in the $A^{\mathrm{II}}B^{\mathrm{II}}\mathrm{P_2O_7}$ system (Elmarzouki *et al.,* ACA abstract L07, 1994) does not exist in this diarsenate system. The structures of these diarsenates are discussed along with their phosphate analogues. © 1996 Academic Press, Inc.

INTRODUCTION

In comparison with the rich structural chemistry of transition metal phosphates, reports on the arsenates are rare. Recently we have investigated the structural chemistry of transition metal arsenates and have synthesized a number of new compounds in the A–M–As$^{\mathrm{V}}$–O system (A = alkali or alkaline-earth metals and M = V, Fe, Co, Ni, and Mo) (1–8) by using hydrothermal methods. Most of these arsenates adopt new structural types and have stoichiometries not found in the phosphates. Although a few arsenates have stoichiometries similar to those of the phosphate analogues, their structures are considerably different. For example, $\mathrm{Sr(VOAsO_4)_2}$ (5, 9), Ba $\mathrm{(VOAsO_4)_2}$ (5), and $\mathrm{LiFeAs_2O_7}$ (6) adopt rather different structures from their phosphate analogues; $\mathrm{K_2(VO)_2(H_2O)(AsO_4)}$ $\mathrm{(HAsO_4)}$ $\mathrm{(H_2AsO_4) \cdot 0.5\ H_2O}$ (7) and the corresponding phosphate (10) differ in H-bonding schemes and content of lattice water.

Phosphates with the stoichiometry $A^{\mathrm{II}}B^{\mathrm{II}}\mathrm{As_2O_7}$ have been extensively studied (11). They crystallize in several different structural types and their structures can be related to the sizes of A^{II} and B^{II} cations. It is of great interest whether the relationship remains unchanged in the corresponding arsenates. Consequently, we began an investigation on the structural chemistry of divalent mixed-metal diarsenates. Three copper(II) diarsenates, $\mathrm{CaCuAs_2O_7}$, $\mathrm{SrCuAs_2O_7}$, and $\mathrm{BaCuAs_2O_7}$, have been prepared hydrothermally and structurally characterized. The Ca and Ba compounds adopt different structures from their phosphate analogues. The relationship between ionic radii and structures as observed in the phosphates does not hold in these arsenates. Herein the synthesis and crystal structures of these three copper arsenates are presented. They are discussed along with the phosphate analogues.

EXPERIMENTAL

Synthesis

Reagent-grade $\mathrm{Ca(OH)_2}$, $\mathrm{Sr(OH)_2 \cdot 8H_2O}$, $\mathrm{Ba(OH)_2 \cdot 8H_2O}$, Cu (−325 mesh), CuO, KCl, pyridine, and 80% $\mathrm{H_3AsO_4}$, obtained from Merck, were used as received. A green crystalline product was obtained by heating a mixture of $\mathrm{Ca(OH)_2}$ (0.21 g), Cu (0.4 g), KCl (0.1 g), $\mathrm{H_3AsO_4}$ (2 mL, 80%) (molar ratio Ca : Cu : As = 1 : 2 : 7.5) and water (10 mL) in a Teflon-lined autoclave (23 mL) at 230°C for 4 d followed by slow cooling to room temperature at 5°C/h. The product was filtered off, washed with water, rinsed with ethanol, and dried in a desiccator at ambient temperature. The product contained pale-green columnar crystals of $\mathrm{CaCuAs_2O_7}$. Energy dispersive X-ray fluorescence analysis on the crystal confirmed that there was no potassium atoms present and gave a Ca : Cu : As mole ratio of 1.0 : 0.94 : 1.87. Synthesis of a pure phase can be achieved by heating a mixture of $\mathrm{Ca(OH)_2}$ (0.232 g), CuO (0.25 g), KCl (0.1 g), $\mathrm{H_3AsO_4}$ (2 mL, 80%), pyridine (2 mL), and water (8 mL) under the same conditions as described above. Its bulk X-ray powder pattern compared very well with that calculated from the single-crystal data. Although

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0022-4596/96 $18.00

TABLE 1
Summary of Crystal Data, Intensity Measurements, and Structure Refinement Parameters

Compound	$CaCuAs_2O_7$	$SrCuAs_2O_7$	$BaCuAs_2O_7$
Crystal color	Green	Blue	Blue
Crystal size (mm)	0.12 × 0.20 × 0.40	0.09 × 0.31 × 0.40	0.09 × 0.12 × 0.15
Mr	365.5	413.0	462.7
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
a(Å)	7.248(2)	5.550(1)	5.736(1)
b(Å)	8.952(2)	8.299(2)	8.458(2)
c(Å)	9.258(2)	12.858(3)	13.044(3)
β(°)	109.66(2)	91.75(3)	91.16(3)
V(Å^3)/Z	565.7(3)/4	592.0(3)/4	632.7(3)/4
D_x (g cm^{-3})	4.291	4.634	4.858
μ (mm^{-1})	16.36	23.68	19.91
2θ range for lattice parameters	9–38	6–27	12–27
Diffractometer	Nicolet R3m/V	Nicolet R3m/V	Nicolet R3m/V
Scan mode, max 2θ (°)	$\theta/2\theta$, 50	$\theta/2\theta$, 50	$\theta/2\theta$, 50
Scan range	1° plus separation between $K\alpha_1$ and $K\alpha_2$		
Standard reflections	3 measured every 50		
Reflections measured	1618	833	886
Independent reflections with $I > 3\sigma$	1093	720	779
Parameters refined	101	96	96
Agreement factor $R^a(R_w^b)$	0.033 (0.047)	0.021 (0.041)	0.037 (0.042)
Weighting scheme χ^b	0.0035	0.0010	0.0002
Largest difference peak/hole (eÅ^{-1})	1.3/−0.86	0.68/−0.75	1.49/−1.39

[a] $R = \Sigma \| F_0 | - | F_c \| / \Sigma | F_0 |$.

[b] $R_W = [\Sigma w(|F_0| - |F_c|)^2 / \Sigma w F_0^2]$, $w = 1/[\sigma^2(F_0) + \chi F_0^2]$ with $\sigma(F_0^2)$ from counting statistics.

the role of KCl is not well understood, it appears crucial to obtain $CaCuAs_2O_7$ as a major product under these conditions.

The crystal growth of the Sr and Ba compounds were achieved under the following conditions. For $SrCuAs_2O_7$, a mixture of 0.420 g of $Sr(OH)_2 \cdot 8H_2O$, 0.4 g of Cu, 2 mL of 80% H_3AsO_4 (molar ratio Sr : Cu : As = 1 : 4 : 15), 0.1 g of KCl and water (10 mL) was heated in a 23-mL Teflon-lined autoclave at 230°C for 4 d followed by slow cooling to room temperature at 5°C/h. The product was a mixture of light-blue rod-like crystals of the Sr compound and unidentified materials. For $BaCuAs_2O_7$, a mixture of 0.5 g of $Ba(OH)_2 \cdot 8H_2O$, 0.2 g of Cu, 1 mL of 80% H_3AsO_4 (molar ratio Ba : Cu : As = 1 : 2 : 7.5) and water (11 mL) was heated under the same conditions as those for the Ca and Sr compounds. The product contained blue rod-like crystals of the Ba compound. Powder X-ray diffraction of the bulk product indicated a small amount of unknown impurities.

Single-Crystal X-Ray Diffraction

Three crystals have the dimensions of 0.12 × 0.20 × 0.40 mm for $CaCuAs_2O_7$, 0.09 × 0.31 × 0.40 mm for $SrCuAs_2O_7$, and 0.09 × 0.13 × 0.16 mm for $BaCuAs_2O_7$, selected for indexing and intensity data collection on a Siemens R3m/V four-circle diffractometer using monochromated Mo$K\alpha$ radiation. Axial oscillation photographs along the three axes were taken to check the symmetry properties and unit cell parameters. The intensity data for all three crystals were corrected for Lp and absorption effects. Corrections for absorption effects were based on φ scans of a few suitable reflections with χ values close to 90° using the program XEMP from the SHELXTL Plus program package (12). On the basis of the systematic absences, the space groups were determined to be $P2_1/c$ for the Ca compound and $P2_1/n$ for both the Sr and Ba compounds. Direct methods (SHELXTL Plus) were used to locate the metal and several O atoms with the remaining oxygen atoms found on difference Fourier maps. All three structures were refined by full-matrix least-squares re-

TABLE 2
Atomic Coordinates and Temperature Factors (100 × Å^2)

	x	y	z	$U_{eq}{}^a$
$CaCuAs_2O_7$				
Ca	0.74960(19)	0.43428(14)	0.05958(15)	0.88(4)
Cu	0.21398(11)	0.55188(8)	0.31840(9)	0.70(3)
As(1)	0.02113(9)	0.20013(7)	0.95481(7)	0.50(2)
As(2)	0.41919(9)	0.23810(7)	0.23444(7)	0.52(2)
O(1)	0.8504(7)	0.1790(5)	0.0367(5)	1.11(15)
O(2)	0.0028(7)	0.0883(5)	0.80632(5)	1.11(15)
O(3)	0.0110(7)	0.3809(5)	0.9136(5)	1.12(15)
O(4)	0.2485(7)	0.1436(5)	0.0821(5)	1.21(14)
O(5)	0.4261(7)	0.1413(5)	0.3892(5)	0.92(14)
O(6)	0.3493(7)	0.4159(5)	0.2194(6)	1.29(15)
O(7)	0.6316(7)	0.2277(5)	0.1985(5)	0.94(14)
$SrCuAs_2O_7$				
Sr	0.21136(12)	0.16273(8)	0.71628(5)	0.99(3)
Cu	0.19920(15)	0.13946(10)	0.38228(6)	0.91(3)
As(1)	0.24855(12)	0.52876(8)	0.34260(5)	0.65(3)
As(2)	0.32517(12)	0.81174(8)	0.49240(5)	0.63(3)
O(1)	0.4389(7)	0.6256(5)	0.2654(3)	0.82(14)
O(2)	0.0374(7)	0.4505(5)	0.6966(3)	1.26(15)
O(3)	0.3499(8)	0.3407(5)	0.3483(4)	1.14(16)
O(4)	0.2828(8)	0.6063(6)	0.4677(3)	1.01(15)
O(5)	0.2056(8)	0.8369(5)	0.6070(4)	1.04(15)
O(6)^b	0.6233(1)	0.8476(5)	0.4812(4)	0.76(11)
O(7)	0.1716(7)	0.9036(6)	0.3933(3)	0.95(14)
$BaCuAs_2O_7$				
Ba	0.21598(14)	0.15180(10)	0.71374(6)	1.08(4)
Cu	0.20968(31)	0.14114(20)	0.38030(14)	1.07(6)
As(1)	0.24650(24)	0.53402(16)	0.34476(11)	0.84(5)
As(2)	0.32829(24)	0.81689(17)	0.49216(10)	0.82(5)
O(1)	0.4249(17)	0.6230(12)	0.2624(8)	1.4(3)
O(2)	0.0314(18)	0.4383(13)	0.6887(9)	2.1(3)
O(3)	0.3362(19)	0.3487(11)	0.3610(8)	1.6(3)
O(4)	0.2996(17)	0.6158(13)	0.4670(8)	1.4(3)
O(5)^b	0.1978(17)	0.8400(11)	0.6046(7)	1.1(2)
O(6)	0.6188(17)	0.8498(11)	0.4876(8)	1.2(3)
O(7)	0.1982(17)	0.9068(12)	0.3916(8)	1.4(3)

[a] U_{eq} is defined as one-third of the trace of the orthorgonalized U_{ij} tensor.

[b] Isotropically refined only.

TABLE 3
Selected Bond Lengths (Å) and Bond-Valence Sums (Σs)

$CaCuAs_2O_7$		$SrCuAs_2O_7$		$BaCuAs_2O_7$	
Cu–O(1)	1.932(5)	Cu–O(1)	2.029(4)	Cu–O(1)	2.01(1)
Cu–O(2)	1.953(5)	Cu–O(3)	1.924(4)	Cu–O(3)	1.94(1)
Cu–O(3)	2.298(4)	Cu–O(5)	2.264(5)	Cu–O(5)	2.36(1)
Cu–O(6)	1.972(6)	Cu–O(6)	1.990(5)	Cu–O(6)	1.97(1)
Cu–O(7)	1.968(5)	Cu–O(7)	1.969(5)	Cu–O(7)	1.99(1)
Σs(Cu–O) = 2.08		Σs(Cu–O) = 1.99		Σs(Cu–O) = 1.96	
As(1)–O(1)	1.665(6)	As(1)–O(1)	1.676(4)	As(1)–O(1)	1.68(1)
As(1)–O(2)	1.669(5)	As(1)–O(2)	1.659(4)	As(1)–O(2)	1.66(1)
As(1)–O(3)	1.658(5)	As(1)–O(3)	1.660(4)	As(1)–O(3)	1.65(1)
As(1)–O(4)	1.748(4)	As(1)–O(4)	1.738(4)	As(1)–O(4)	1.76(1)
Σs(As(1)–O) = 5.02		Σs(As(1)–O) = 5.04		Σs(As(1)–O) = 5.00	
As(2)–O(4)	1.749(4)	As(2)–O(4)	1.749(5)	As(2)–O(4)	1.74(1)
As(2)–O(5)	1.662(5)	As(2)–O(5)	1.648(5)	As(2)–O(5)	1.67(1)
As(2)–O(6)	1.662(5)	As(2)–O(6)	1.692(4)	As(2)–O(6)	1.69(1)
As(2)–O(7)	1.684(6)	As(2)–O(7)	1.693(4)	As(2)–O(7)	1.68(1)
Σs(As(1)–O) = 4.96		Σs(As(1)–O) = 4.88		Σs(As(1)–O) = 4.87	
Ca–O(1)	2.430(5)	Sr–O(1)	2.623(4)	Ba–O(1)	2.82(1)
Ca–O(2)	2.410(4)	Sr–O(1)	2.910(4)	Ba–O(1)	2.94(1)
Ca–O(3)	2.350(5)	Sr–O(2)	2.491(4)	Ba–O(2)	2.63(1)
Ca–O(3)	2.714(5)	Sr–O(2)	2.586(4)	Ba–O(2)	2.66(1)
Ca–O(5)	2.440(4)	Sr–O(3)	2.668(5)	Ba–O(3)	2.85(1)
Ca–O(5)	2.383(5)	Sr–O(5)	2.720(5)	Ba–O(5)	2.89(1)
Ca–O(6)	2.782(5)	Sr–O(5)	3.047(4)	Ba–O(5)	2.99(1)
Ca–O(7)	2.559(5)	Sr–O(6)	2.727(5)	Ba–O(6)	2.81(1)
		Sr–O(7)	2.573(4)	Ba–O(7)	2.77(1)
Σs(Ca–O) = 2.06		Σs(Sr–O) = 2.01		Σs(Ba–O) = 2.24	

TABLE 4
Comparison of the $A^{II}CuX_2O_7$

Compound:	$CaCuP_2O_7$	$SrCuP_2O_7$	$BaCuP_2O_7$	$CaCuAs_2O_7$	$SrCuAs_2O_7$	$BaCuAs_2O_7$
Structure type[a]	II	II	III	I	II	II
Space group	$P2_1/n$	$P2_1/n$	$P1$-bar	$P2_1/c$	$P2_1/n$	$P2_1/n$
R_A (Å)	1.26	1.45	1.61	1.26	1.45	1.61
R_A-R_B (Å)[b]	0.47	0.66	0.82	0.47	0.66	0.82
X–O–X (°)	127.0	128.1	122.1	130.9	122.7	124.7
Torsion (°)[c]	36.9	39.0	6.5	18.8	39.3	43.5

[a] See text for description.

[b] R_B is 0.79 Å for Cu.

[c] The torsional angle between the two XO_4 tetrahedra in X_2O_7 groups.

finement based on F values. All atoms, except O(6) in $SrCuAs_2O_7$ and O(7) in $BaCuAs_2O_7$, were refined with anisotropic displacement factors. Corrections for anomalous dispersion and secondary extinction were applied. Neutral-atom scattering factors for all atoms were taken from the International Tables for X-ray Crystallography. Calculations were performed on a DEC VAX 4000/90 computers using SHELXTL-Plus programs.

RESULTS AND DISCUSSION

The crystallographic data for the three compounds are listed in Table 1. The atomic coordinates, thermal parameters, selected bond distances, and bond valence sums (13) are listed in Tables 2 and 3. The coordination numbers of Ca^{2+}, Sr^{2+}, and Ba^{2+} are determined on the basis of the maximum gap in the cation–oxygen distances ranked in increasing order. The Ca^{2+} cation is coordinated by eight

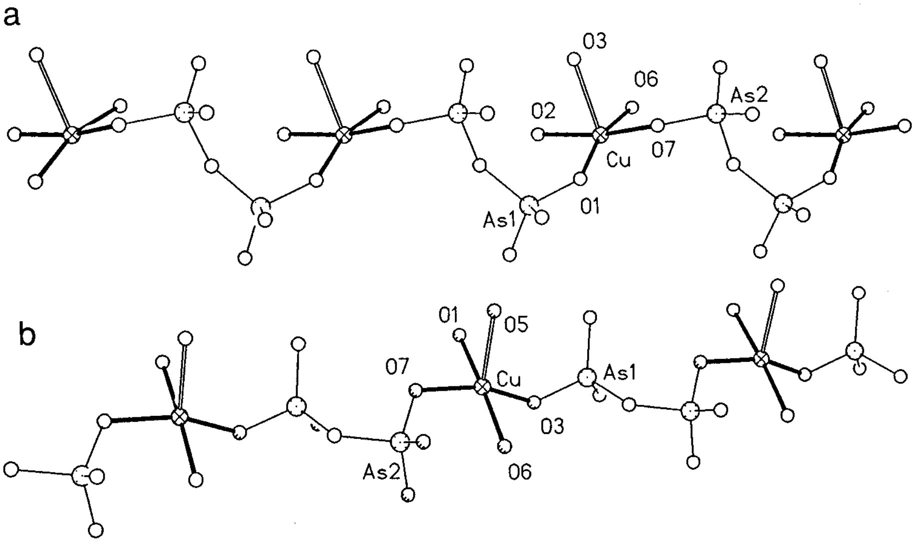

FIG. 1. Infinite chains in structures I and II, respectively. (a) A section of the chain running along the a-axis in $CaCuAs_2O_7$. Bond angles are 82.0° for O1-Cu-O7, 92.9° for O1-Cu-O2, 94.6° for O2-Cu-O6, and 94.1° for O6-Cu-O7. (b) A section of the chain running along the b-axis in $SrCuAs_2O_7$. Bond angles are 172.5° for O1-Cu-O6 and 156.1° for O3-Cu-O7. This kind of chain also appears in other compounds having structure II.

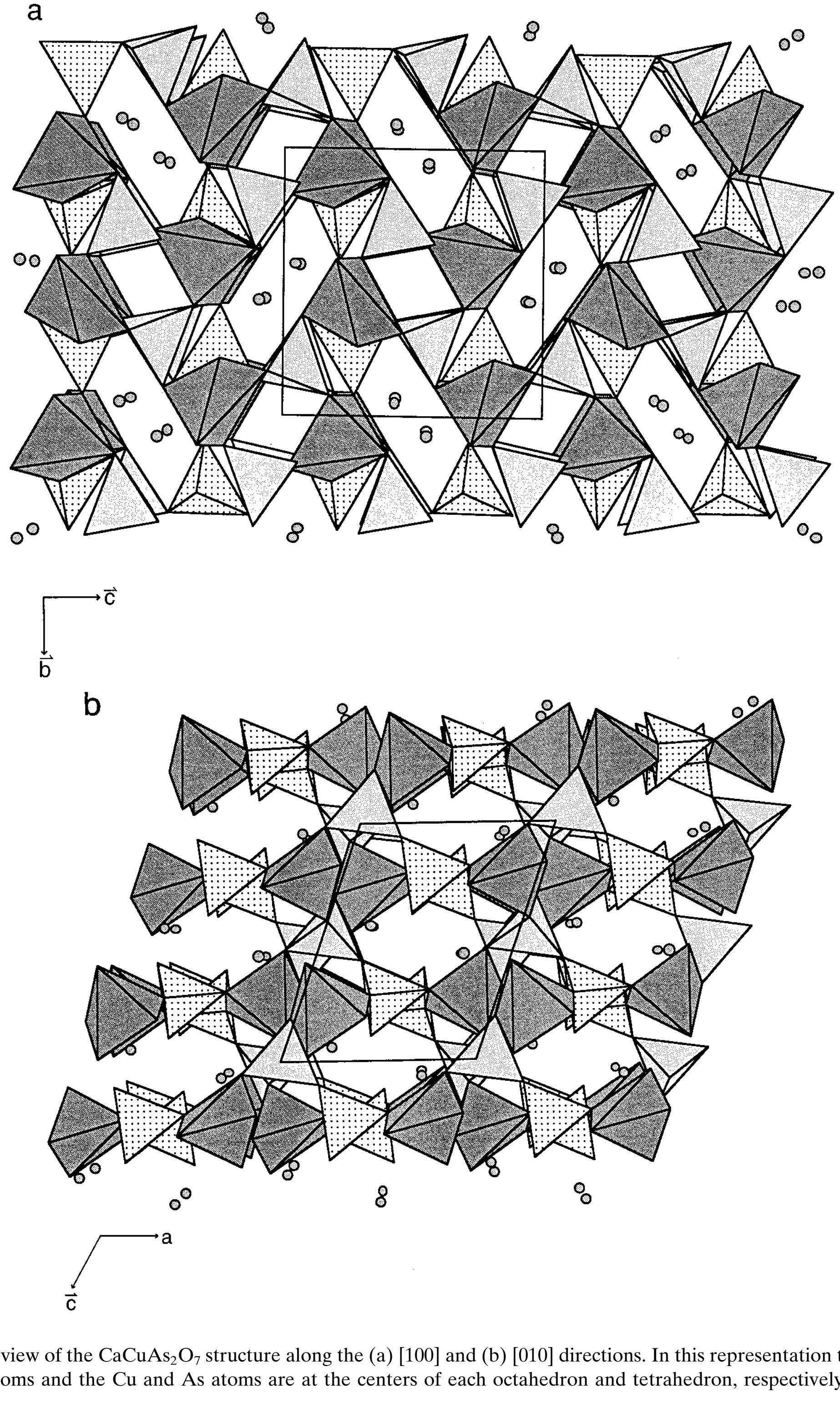

FIG. 2. Perspective view of the $CaCuAs_2O_7$ structure along the (a) [100] and (b) [010] directions. In this representation the corners of octahedra and tetrahedra are O atoms and the Cu and As atoms are at the centers of each octahedron and tetrahedron, respectively.

oxygen atoms, the ninth Ca–O bond length is 3.48 Å. Both the Sr^{2+} and Ba^{2+} cations are coordinated by nine oxygen atoms. The tenth Sr–O and Ba–O bond lengths are 3.78 and 3.69 Å, respectively. Bond valence sums for the Ca, Sr, Ba, and Cu atoms are in good accordance with their formal oxidation states.

The frame work of $CaCuAs_2O_7$ (structure I) consists of infinite chains of alternate corner-sharing CuO_5 square

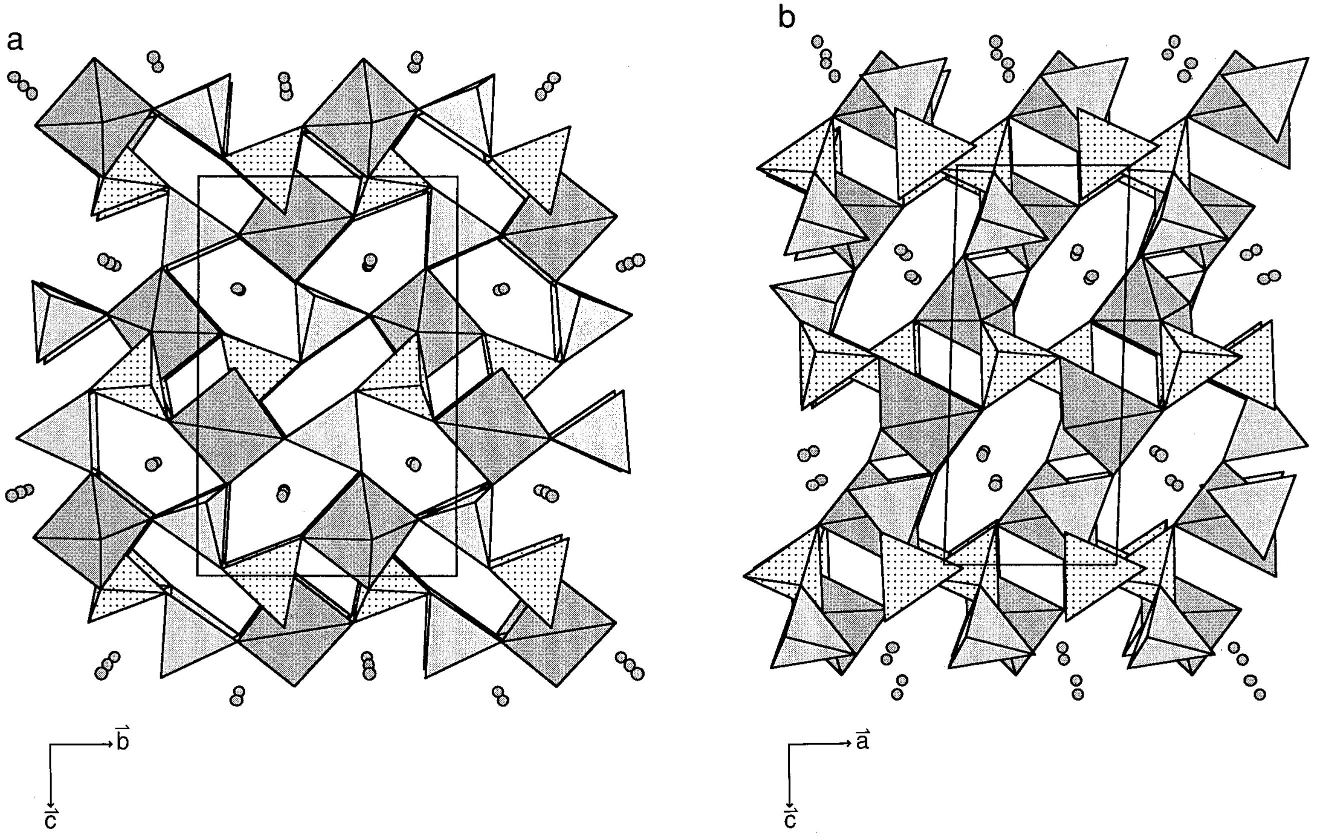

FIG. 3. Perspective view of the $SrCuAs_2O_7$ structure along the (a) [100] and (b) [010] directions. The open circles are Sr atoms.

pyramids and As_2O_7 groups running parallel to the *a*-axis (Fig. 1). Two chains which are related by an inversion center link through O atoms to form a tetragonal tunnel along the [100] direction. As shown in Fig. 2a, the edges of four such tunnels in turn form larger tunnels in which two arrays of calcium atoms are located. These tunnels show lateral windows which also form straight tunnels parallel to the [010], [101], and ⟨011⟩ directions (Fig. 2b). Therefore, the structure consists of intersecting tunnels and the calcium ions are located at the intersections of these tunnels.

In $CaCuAs_2O_7$, the average length of the four equatorial Cu–O bonds for each CuO_5 pyramid is 1.96 Å and the axial is 2.296(4) Å (Table 3). The Cu atom falls perfectly on the square basal plane with the shortest edge participating in an infinite chain. The rest of the apices (two equatorial and one axial) link to three other chains. The sixth nearest O atom (the bridging oxygen in the As_2O_7 group) is at 2.945(5) Å. The Cu environment of the O atoms can be a severely distorted octahedron if the sixth coordination is taken into account. Each of the As_2O_7 group shares five corners with five different CuO_5 pyramids which belong to four different chains and leaves one free corner participating in the coordination of Ca. In each diarsenate group the two AsO_4 tetrahedra point in opposite directions to form a staggered conformation and the As atoms are displaced away from the bridging oxygen, O(4), so that one longer and three shorter As–O bonds result. Both the AsO_4 tetrahedra are distorted as shown by the O $\cdots$ O distance (2.61–2.87 Å) and O–As–O angles (100.2–119.5°). The As–O–As bond angle involving the bridging oxygen is 130.9°.

$CaCuAs_2O_7$ adopts a different structure from that of the corresponding phosphate, $CaCuP_2O_7$ (structure II) (14). Although the latter also contains intersecting tunnels formed of infinite chains, the conformation of these chains are different in that each of the CuO_5 pyramid participates an infinite chain via a *trans* edge (Fig. 1b) instead of the *cis* edge in structure I.

Both $SrCuAs_2O_7$ and $BaCuAs_2O_7$ adopt structure II. The infinite chains in these structures run parallel to the *b*-axis and two adjacent chains which are related by a 2_1 symmetry form a pentagonal tunnel perpendicular to the chain direction (Fig. 3). One array of the Sr or Ba cations resides in these tunnels. Larger tunnels in which two arrays of cations reside also form along the chain direction. The average length of the four equatorial Cu–O bonds for the CuO_5 pyramids is about 1.98 Å for both $SrCuAs_2O_7$ and

$BaCuAs_2O_7$, and the axial is 2.264(5) Å for the Sr compound and 2.355(10) Å for the Ba compound. In both structures, the Cu atom deviates from the least-squares basal plane (~0.25 Å) toward the axial O atom with a *trans* edge participating in an infinite chain. The remaining three apices link to three other chains. The sixth nearest O atom (~3.2 Å from Cu) is the free apex of the diarsenate group. As in structure I, each of the As_2O_7 group shares its five corners with five different CuO_5 pyramids which belong to four different chains and leaves one free corner participating in the coordination of Sr or Ba. The two tetrahedra in the As_2O_7 groups are also staggered and the As–O–As bond angles involving the bridging oxygen are 122.7° and 124.7° for $SrCuAs_2O_7$ and $BaCuAs_2O_7$, respectively.

It is interesting to note that in the alkaline–earth series, only the Sr compound is isotypic with the phosphate analog $SrCuP_2O_7$ (15). $BaCuAs_2O_7$ adopts the same structure as the Sr compound instead of the triclinic $BaCuP_2O_7$ (structure III) (16), which is a sheet structure characterized by edge-sharing dimers of CuO_5 pyramids and bidentate P_2O_7 groups. In each disphosphate group, the two PO_4 tetrahedra are nearly eclipsed rather than staggered. A comparison of the compounds in the $A^{II}CuX_2O_7$ (X = P, As) family adopting structures from I and III are given in Table 4.

The structures with the stoichiometry $A^{II}B^{II}P_2O_7$ can be related to the sizes of A^{II} and B^{II} cations. As reported by Elmarzouki *et al.* (11), straight lines could be obtained when plotting R_A (or R_B) versus $R_A - R_B$, where R is Shannon's ionic radii appropriate for the multiplicity and geometry of oxygen environment and "isotypical" $A^{II}B^{II}P_2O_7$ compounds could be found in the neighborhoods along lines. This relationship, however, does not hold in the $A^{II}B^{II}As_2O_7$ system. This study shows that the As_2O_7 group is very adaptive to the bonding requirements of other groups in the structure by adjusting the As–O–As bond angle and the torsional angle between the two AsO_4 tetrahedra. The size of the alkali–earth metal cation seems not to play as an important role in deciding on the structural types of the arsenates as it does on the corresponding phosphates. Further investigation on the $A^{II}B^{II}As_2O_7$ system with different B^{II} ions are underway to exploit more structures in the diarsenate phase space.

ACKNOWLEDGMENTS

Support of this work by the National Science Council of Taiwan, Republic of China, is gratefully acknowledged.

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