Journal of Solid State Chemistry **147,** 132–139 (1999)
Article ID jssc.1999.8187, available online at http://www.idealibrary.com on

$RbCu_{1.2}Ag_{3.8}Se_3$ and $Cs_2Cu_2Sb_2Se_5$: Novel Quaternary Intermetallics Synthesized from Superheated Organic Media[1]

Zhen Chen, Ru-Ji Wang, Kieran J. Dilks, and Jing Li[2]

Department of Chemistry, Rutgers University, Camden, New Jersey 08102

Received November 9, 1998; in revised form January 28, 1999; accepted January 29, 1999

Reactions in superheated ethylenediamine (en) solutions at 160°C resulted in two novel quaternary intermetallic copper selenides, $RbCu_{1.2}Ag_{3.8}Se_3$(I) and $Cs_2Cu_2Sb_2Se_5$(II). Both I and II are metal rich and represent new layered structure types. Compound I crystallizes in the tetragonal crystal system, space group *P4/nbm* (No. 125) with $a = 5.991(1)$ Å, $c = 10.918(2)$ Å, $Z = 2$, $V = 391.9(1)$ Å^3, $R1/wR2 = 0.0373/0.0458$ for all reflections. Compound II belongs to the triclinic crystal system, space group $P\bar{1}$ (No. 2), $a = 7.645(1)$ Å, $b = 8.768(2)$ Å, $c = 10.264(1)$ Å, $\alpha = 91.97(2)°$, $\beta = 92.07(2)°$, $\gamma = 103.05(1)°$, $Z = 2$, $V = 669.2(3)$ Å^3, $R1/wR2 = 0.0685/0.0740$ for all reflections. I consists of $^2_\infty[(Cu_{1.2}Ag_{3.8}Se_3)^-]$ layers and Rb^+ counterions located between these layers. There are two types of metal-to-selenium coordination, a square planar (Ag) and a trigonal pyramidal (Cu/Ag). The Se(1) atom displays an unusual eight coordination with Ag and Cu. II contains alternating $^2_\infty[(Cu_2Sb_2Se_5)^{2-}]$ anionic and Cs^+ cationic layers. Each copper atom has a distorted tetrahedral coordination to four Se atoms, and each antimony atom bonds to three Se atoms to result in a trigonal pyramidal geometry. Both I and II are semiconductors with estimated band gaps of 0.7–0.8 and 1.2–1.3 eV, respectively. © 1999 Academic Press

INTRODUCTION

Much of the effort and progress in the development of soft hydro(solvo)thermal synthesis has been made by solid-state synthetic chemists during the past decade. In the area of metal chalcogenides, several solvent systems have been extensively investigated and have shown great promise in crystal growth of these materials. Use of water (an inorganic solvent) in the temperature range 110–220°C has produced many Group 14–16 metal sulfides and selenides (1–4), as well as transition-metal-containing chalcogenides such as Mo (5), Pd (6), and Cu (7). Reactions in methanol in the same temperature range have also resulted in a variety of new compounds, including binary alkali-metal polychalcogenides (8) and ternary Group 14–15 phases (9–10). In the case of ammonia, a number of sulfides and polysulfides have been synthesized from reactions at 160–170°C (11).

J. W. Kolis and coworkers have reported the synthesis of several Group-11 metal sulfides and selenides in supercritical ethylenediamine or en (12). While these reactions were conducted under relatively vigorous conditions (300–350°C), we have focused primarily on a softer synthetic route in which reactions are carried out in en medium below 180°C. Our synthesis has thus far led to the formation of a variety of new compounds with diverse and rich structural properties. The organic solvent may function differently in these compounds. In some cases, it incorporates into the products by chelating to a metal center to form a complex cation, such as in $[M(en)_3]_2(Hg_2Te_9)$, M = Fe, Mn and $\{Mn(en)_3]_2Cl_2\}Hg_2Te_4$ (13), $[M(en)_3]_2SnQ_6$, M = Mn, Zn, Q = Se (14), Te (15), $[M(en)_3]In_2Te_6$ (M = Fe, Zn), $[Mo_3(en)_3(Te_2)_3(O)(Te)]In_2Te_6$ (16), $[La(en)_4Cl]In_2Te_4$ (17), $[Fe(en)_3[enH]SbSe_4$ (18), $[Ga(en)_3]In_3Te_7$ (19), and $[Mn(en)_3]CdSnTe_4$ (20). It can also enter the structures as free molecules, as in $Cu_2SbSe_3 \cdot 0.5en$ and $Cu_2SbSe_3 \cdot en$ (21), where en molecules fill the spaces between the covalent layers. In other cases, en acts as a solvent solely, in which synthesis produces intermetallic phases such as $Rb_2Hg_3Te_4$ (22), $KCuSe_4$ (23), $RbHgSbTe_3$ (24), AHgSbSe$_3$ (25), (A = Rb, Cs), Cs_2PdSe_8 (26), $Rb_2Hg_6Se_7$, and $K_4Cu_8Te_{11}$ (27). Here we report the solvothermal synthesis, crystal structures, and optical properties of two new types of intermetallic selenides, $RbCu_{1.2}Ag_{3.8}Se_3$ (**I**) and $Cs_2Cu_2Sb_2Se_5$ (**II**), both are Cu-based quaternary compounds and belong to the third group described above.

EXPERIMENTAL

Materials

CuCl (99.9%, Strem Co.), AgCl (99.8%, Strem Co.), $SbCl_3$ (99 + %, Strem Co.), and Se (99.5%, Strem Co.) were used as purchased without further treatment. Rb_2Se and Cs_2Se were prepared by reactions of alkali metal and elemental selenium in a 2 : 1 ratio in liquid ammonia. Ethylenediamine (99%, anhydrous, Fisher Scientific) was used as a solvent in all reactions.

---

[1] In memory of Professor Jean Rouxel.

[2] To whom correspondence should be addressed.

0022-4596/99 $30.00

TABLE 1
Crystallographic Data for $RbCu_{1.2}Ag_{3.8}Se_3$ (I) and $Cs_2Cu_2Sb_2Se_5$(II)

Compound	**I**	**II**
Formula	$RbCu_{1.2}Ag_{3.8}Se_3$	$Cs_2Cu_2Sb_2Se_5$
Formula weight	808.50	1031.20
Crystal system	Tetragonal	triclinic
Space group	$P4/nbm$ (No. 125)	$P\bar{1}$ (No. 2)
a (Å)	5.991(1)	7.645(1)
b (Å)	5.991(1)	8.768(2)
c (Å)	10.918(2)	10.264(1)
α (°)	90.00	91.97(2)
β (°)	90.00	92.07(2)
γ (°)	90.00	103.05(1)
V (Å^3)	391.9(1)	669.2(3)
Z	2	2
Density (calculated, g cm^{-3})	6.852	5.118
Temperature (K)	294	294
Diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
Radiation	Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å)	
Monochromator	Oriented graphite	
Crystal color	dark brown	black
Morphology	plate	block
Crystal size (mm^3)	$0.03 \times 0.2 \times 0.4$	$0.1 \times 0.1 \times 0.2$
Linear absorption coefficient (mm^{-1})	32.528	26.035
Scan mode	ω-scan	ω-scan
Recording range 2θ (°)	4-50	4-50
hkl range	$-7/7$ $0/7$ $-12/12$	$-9/9$ $-10/10$ $0/12$
Number of measure reflections	1261	2495
Number of independent reflections	202	2350
Number of observed reflections $[I > 2\sigma(I)]$	171	1807
R_{int}	0.0651	0.0282
Absorption correction	ψ-scan	ψ-scan
Transmission (min–max)	0.7784–0.9931	0.7671–0.9999
Refinement	F^2	F^2
Calculated weights	$w = 1/\sigma^2(F_o^2)$	$w = 1/\sigma^2(F_o^2)$
R $[I > 2\sigma(I)]$	$R1$ 0.0273, $wR2$ 0.0445	$R1$ 0.0437, $wR2$ 0.0701
R (all data)	$R1$ 0.0373, $wR2$ 0.0458	$R1$ 0.0685, $wR2$ 0.0740
S (all data on F^2)	1.673	1.317
Number of refined parameters	22	101

Synthesis

Single crystals of **I** were obtained from a solvothermal reaction in en. A sample containing 0.25 mmol of Rb_2Se

TABLE 2
Atmoic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for $RuCu_{1.2}Ag_{3.8}Se_3$ (I)

Atoms	x	y	z	U_{eq}[a]
Ag(1)	0.2500	0.2500	0.0000	0.0280(5)
$M(1)$[b]	0.0500(1)	0.5500(1)	0.18848(8)	0.047(4)
Rb(1)	0.2500	0.7500	0.5000	0.0247(5)
Se(1)	0.2500	−0.2500	0.0000	0.0334(6)
Se(2)	0.2500	0.2500	0.3162(1)	0.0282(5)

[a] U_{eq} defined as one-third of the trace of the orthogonalized U tensor.

[b] $M(1) = 0.7$ Ag $+ 0.3$ Cu, and the U_{eq} is the average of those for Ag and Cu.

TABLE 3
Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for $Cs_2Cu_2Sb_2Se_5$ (II)

Atoms	x	y	z	U_{eq}[a]
Cs(1)	0.2632(1)	0.1953(1)	0.0936(1)	0.0327(3)
Cs(2)	−0.2641(1)	0.9433(1)	0.3871(1)	0.0347(3)
Sb(1)	0.2002(1)	0.6408(1)	0.1162(1)	0.0208(3)
Sb(2)	0.1857(1)	0.5804(1)	−0.2614(1)	0.0193(3)
Cu(1)	0.4031(3)	0.5070(2)	0.3859(2)	0.0310(5)
Cu(2)	0.1278(3)	0.6405(2)	0.4324(2)	0.0336(5)
Se(1)	0.0805(2)	0.3408(2)	0.3853(1)	0.0198(3)
Se(2)	0.1440(2)	0.8434(2)	0.2778(2)	0.0341(4)
Se(3)	0.5128(2)	0.6180(2)	0.1831(2)	0.0245(4)
Se(4)	0.2555(2)	0.8160(2)	−0.0882(1)	0.0257(4)
Se(5)	0.4270(2)	0.7008(2)	−0.4202(1)	0.0192(3)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized **U** tensor.

TABLE 4
Selected Bond Lengths (Å) and Angles (°) for $RuCu_{1.2}Ag_{3.8}Se_3$ (I)

Ag(1)–*M*(1) × 8	2.9834(7)	*M*(1)–Se(1)	2.666(1)
Ag(1)–Se(1) × 4	2.9955(5)	*M*(1)–Se(2) × 2	2.571(1)
M(1)–*M*(1) × 4	3.0548(6)	Rb(1)–Se(2) × 4	3.606(1)
Se(1)–Ag(1)–Se(1) × 2	180.0	Ag(1)–Se(1)–*M*(1) × 8	63.29(1)
Se(1)–Ag(1)–Se(1) × 4	90.0	Ag(1)–Se(1)–*M*(1) × 8	116.71(1)
Se(2)–*M*(1)–Se(1) × 2	121.56(3)	*M*(1)–Se(1)–*M*(1) × 4	126.58(3)
Se(2)–*M*(1)–Se(2)	110.95(6)	*M*(1)–Se(1)–*M*(1) × 2	78.94(5)
Ag(1)–Se(1)–Ag(1) × 4	90.0	*M*(1)–Se(2)–*M*(1) × 4	72.90(3)
Ag(1)–Se(1)–Ag(1) × 2	180.0	*M*(1)–Se(2)–*M*(1) × 2	114.32(6)

(0.060 g), CuCl (0.025 g), and AgCl (0.036 g), respectively, and 0.75 mmol of Se (0.059 g) was weighed and mixed in a glove box under argon atmosphere. The sample was then transferred to thick-walled Pyrex tubes and approximately 0.4 ml of solvent was added to the tube. After the liquid was condensed by liquid nitrogen, the tube was sealed with a torch under vacuum ($\sim 10^{-3}$ Torr). The samples were then heated at 160°C for 5 days. After being cooled to room temperature, the sample was washed with water and ethanol and dried with anhydrous diethyl ether. Single crystals of **II** were grown from a reaction using 0.25 mmol of Cs_2Se (0.088 g), 0.25 mmol of $SbCl_3$ (0.057 g) and CuCl (0.025 g), and 0.75 mmol of Se (0.059 g). The approximate compositions of **I** (Rb : Cu : Ag : Se $\approx$ 1 : 1 : 4 : 3) and **II** (Cs : Cu : Sb : Se $\approx$ 2 : 2 : 2 : 6) were established from microprobe analysis on a JEOL JXA-8600 Superprobe.

TABLE 5
Selected Bond Lengths (Å) and Angles (°) for $Cs_2Cu_2Sb_2Se_5$ (II)

Sb(1)–Se(2)	2.507(2)	Cu(1)–Se(3)	2.425(3)
Sb(1)–Se(3)	2.515(2)	Cu(1)–Se(5*b*)	2.493(2)
Sb(1)–Se(4)	2.633(2)	Cu(1)–Se(5*c*)	2.546(3)
Sb(2)–Se(1*a*)	2.597(2)	Cu(2)–Se(1)	2.596(2)
Sb(2)–Se(4)	2.625(2)	Cu(2)–Se(1*d*)	2.525(3)
Sb(2)–Se(5)	2.575(2)	Cu(2)–Se(2)	2.410(3)
Cu(1)–Se(1)	2.565(3)	Cu(2)–Se(5*c*)	2.637(3)
Se(2)–Sb(1)–Se(3)	102.68(7)	Se(2)–Cu(2)–Se(5*c*)	108.8(1)
Se(2)–Sb(1)–Se(4)	98.47(6)	Cu(1)–Se(1)–Cu(2)	62.52(7)
Se(3)–Sb(1)–Se(4)	102.44(7)	Cu(1)–Se(1)–Sb(2*a*)	122.27(8)
Se(1*a*)–Sb(2)–Se(5)	96.05(6)	Cu(1)–Se(1)–Cu(2*d*)	122.76(9)
Se(1*a*)–Sb(2)–Se(4)	97.19(6)	Cu(2)–Se(1)–Sb(2*a*)	74.77(7)
Se(4)–Sb(2)–Se(5)	96.40(6)	Cu(2)–Se(1)–Cu(2*d*)	76.58(9)
Se(1)–Cu(1)–Se(3)	118.3(1)	Sb(2*a*)–Se(1)–Cu(2*d*)	78.36(7)
Se(1)–Cu(1)–Se(5*b*)	99.79(9)	Sb(1)–Se(2)–Cu(2)	84.68(7)
Se(1)–Cu(1)–Se(5*c*)	104.67(9)	Sb(1)–Se(3)–Cu(1)	89.86(8)
Se(3)–Cu(1)–Se(5*b*)	103.51(9)	Sb(1)–Se(4)–Sb(2)	95.35(6)
Se(3)–Cu(1)–Se(5*c*)	115.84(9)	Cu(1*b*)–Se(5)–Cu(1*e*)	66.08(9)
Se(5*b*)–Cu(1)–Se(5*c*)	113.92(9)	Cu(1*b*)–Se(5)–Sb(2)	92.56(7)
Se(1)–Cu(2)–Se(1*d*)	103.42(9)	Cu(1*b*)–Se(5)–Cu(2*e*)	120.29(9)
Se(1)–Cu(2)–Se(2)	128.2(1)	Cu(1*e*)–Se(5)–Sb(2)	107.43(7)
Se(1)–Cu(2)–Se(5*c*)	101.30(9)	Cu(1*e*)–Se(5)–Cu(2*e*)	62.20(7)
Se(1*d*)–Cu(2)–Se(2)	113.71(9)	Sb(2)–Se(5)–Cu(2*e*)	76.75(7)
Se(1*d*)–Cu(2)–Se(5*c*)	96.29(8)		

Note. Symmetry transformation: *a* $(-x, 1-y, -z)$; *b* $(1-x, 1-y, -z)$; *c* $(x, y, 1+z)$; *d* $(-x, 1-y, 1-z)$; *e* $(x, y, -1+z)$; *f* $(1-x, 1-y, 1-z)$.

Crystal Structure Determination

A dark-brown plate crystal of **I** (0.03 × 0.2 × 0.4 mm) and a black block crystal of **II** (0.1 × 0.1 × 0.2 mm) were mounted on glass fibers in air on an Enraf-Nonius CAD4 automated diffractometer equipped with graphite monochromatized Mo$K\alpha$ radiation. Room temperature (294 ± 1°K) single-crystal X-ray experiments were performed on both crystals. Unit cells were obtained and refined by 25 well-centered reflections with $5.5° < \theta < 11.6°$ (**I**) and $6.2° < \theta < 13.5°$ (**II**). Data collections were monitored by three standards

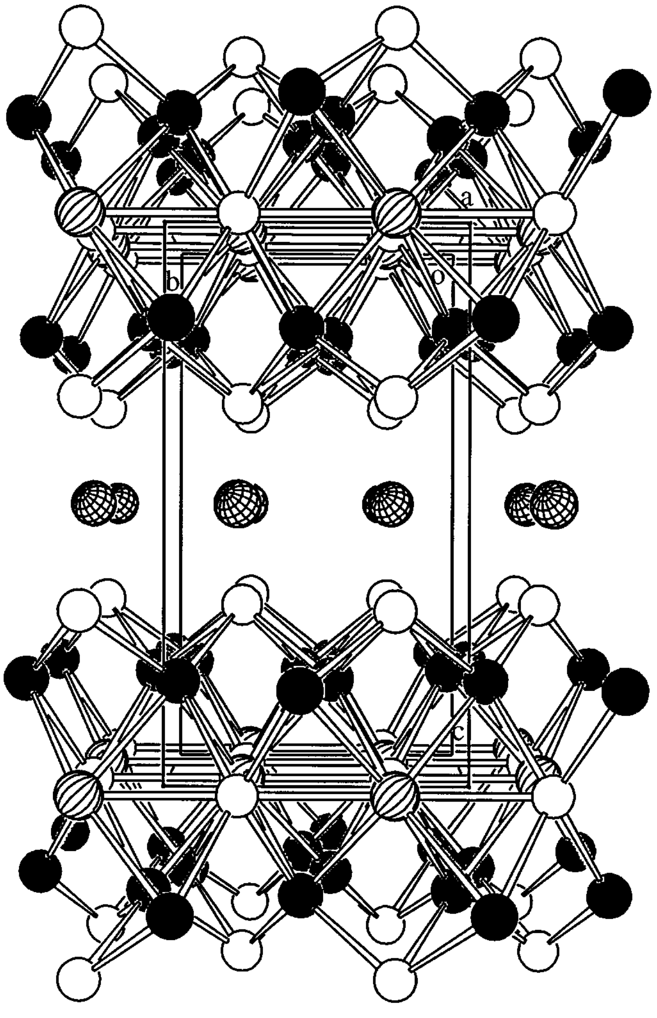

FIG. 1. Perspective views of $RbCu_{1.2}Ag_{3.8}Se_3$ (**I**) along the ***a*** direction. Open circles are Se atoms, shaded circles are Cu, black circles are Cu/Ag, and cross shaded circles are Rb.

every two hours. No decay was observed in either case except the statistic fluctuations in the range of ± 2.1% (**I**) and ± 1.2% (**II**). Raw intensities were corrected for Lorentz and polarization effects, and for absorption by empirical method based on ψ-scan data. Direct phase determination yielded the positions of all atoms. There are two independent metal positions in **I**, one (Wyckoff position $2a$) is entirely occupied by Ag, while the other (Wyckoff position $8m$) is shared randomly by Cu and Ag. The s.o.f. of the two atoms were assigned 0.3 and 0.7 for copper and silver, respectively, in the final refinement, which agrees with the results from the refinement for their s.o.f. and from the microprobe analysis. All atoms were subjected to anisotropic refinement. For compound **I**, the final full-matrix least-square refinement on F^2 converged with $R1 = 0.0273$ and $wR2 = 0.0445$ for observed reflections, and with $R1/wR2 = 0.0373/0.0458$ for all reflections. $R1$ and $wR2$ for compound **II** were refined to be 0.0437 and 0.0701 for observed reflections, and 0.0685 and 0.0740 for all reflections. The final difference electron density map showed no features in both cases. Details of crystal parameters, data collection and structure refinement are given in Table 1. Anisotropic thermal displacements were assigned to all atoms. All calculations were performed using SHELX-97 (28). Crystal structure drawings were produced with SCHAKAL 92 (29). Final atomic coordinates and average temperature factors are listed in Tables 2 and 3 for **I** and **II**, respectively. Bond lengths and angles are reported in Tables 4 (**I**) and 5 (**II**), respectively.

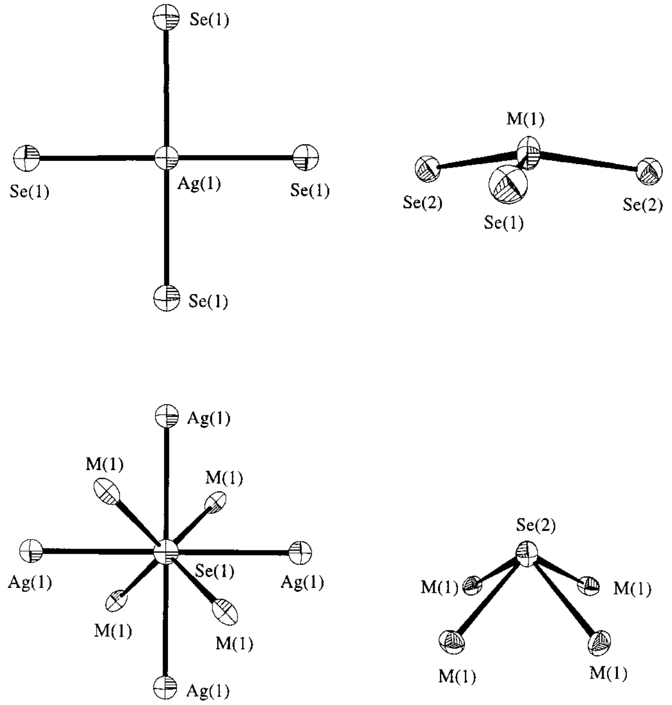

FIG. 3. ORTEP drawings with displacement ellipsoids at 50% probability level showing coordination of each atom in $RbCu_{1.2}Ag_{3.8}Se_3$ (**I**).

Diffuse Reflectance Measurements

Optical diffuse reflectance measurements of powder samples of **I** and **II** were performed on a Shimadzu UV-3101PC double-beam, double-monochromator spectrophotometer

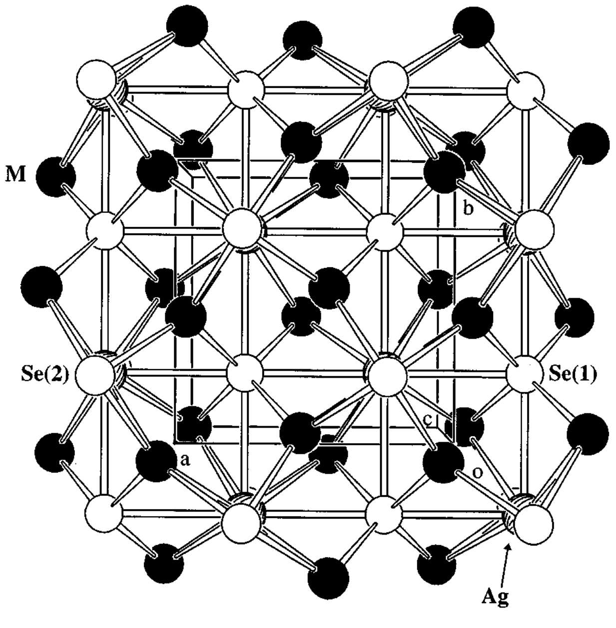

FIG. 2. View of a single layer in $RbCu_{1.2}Ag_{3.8}Se_3$ (**I**) along the c axis. The labeling scheme is the same as in Fig. 1. The $8m$ positions are labeled as M (=Cu/Ag).

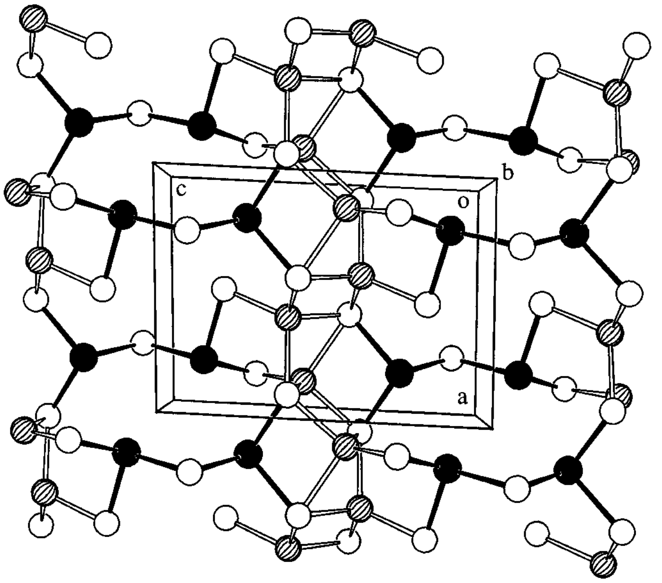

FIG. 4. View of the anionic layer along the $\boldsymbol{b}$ axis in $Cs_2Cu_2Sb_2Se_5$ (**II**). Open circles are Se atoms, shaded circles are Cu, and black circles are Sb. The alternating M–Se 12-membered rings are shown clearly in the figure.

at room temperature. Data were collected in the wavelength range 250–1800 nm. $BaSO_4$ powder was used as a standard (100% reflectance). A similar procedure as previously described (24) was used to collect and convert the data using the Kubelka–Munk function. The scattering coefficient (*S*) was treated as a constant since the average particle size of the samples used in the measurements was significantly larger than 5 μm (>20 μm).

RESULTS AND DISCUSSION

Structure of $RbCu_{1.2}Ag_{3.8}Se_3$

Compound **I** is a quaternary compound rich in metal content (metal : chalcogen ratio, 6 : 3). As shown in Fig. 1, it has a layered structure composed of infinite two-dimensional anionic $^2_\infty[(Cu_{1.2}Ag_{3.8}Se_3)^-]$ slabs separated by Rb^+ counterions. While the composition of **I** is the same as $CsAg_5Te_3$ (30), its crystal structure has no relation to the latter, which is a three-dimensional network containing large channels. Some relations may be drawn between compound **I** and the $ThCr_2Si_2$ type structure (31), such as $CsFe_{0.72}Ag_{1.28}Te_2$ (32) and KCuZnTe$_2$ (33), although the differences in the anionic layers are significant. There are two independent metal positions within a single layer of **I** (Fig. 2). Position 2*a* is occupied by Ag only, while position 8*m* is occupied randomly by both Ag and Cu, indicated as M in the figure. The coordination of each atom is shown in Fig. 3. The Ag(1) to Se(1) coordination is a square-planar with a single Ag(1)–Se(1) bond distance of 2.996(1) Å. This is significantly longer than those found in $Rb_2NbAgSe_4$ (34), in which Ag has a tetrahedral coordination to Se with a Ag–Se bond length of 2.640 Å, in $K_5Ag_2As_3Se_9$ (av. 2.676 Å) (35) and in KAg_3Se_2 (av. 2.794 Å) (36), where Ag has a trigonal coordination with Se. The square-planar geometry of Ag is scarce, and there are no known examples of such a geometry previously reported for the *A*–Ag–Se systems. The *M* (Ag/Cu) atoms bond to three Se to give a trigonal pyramidal coordination [M–Se(1) = 2.666(1) Å

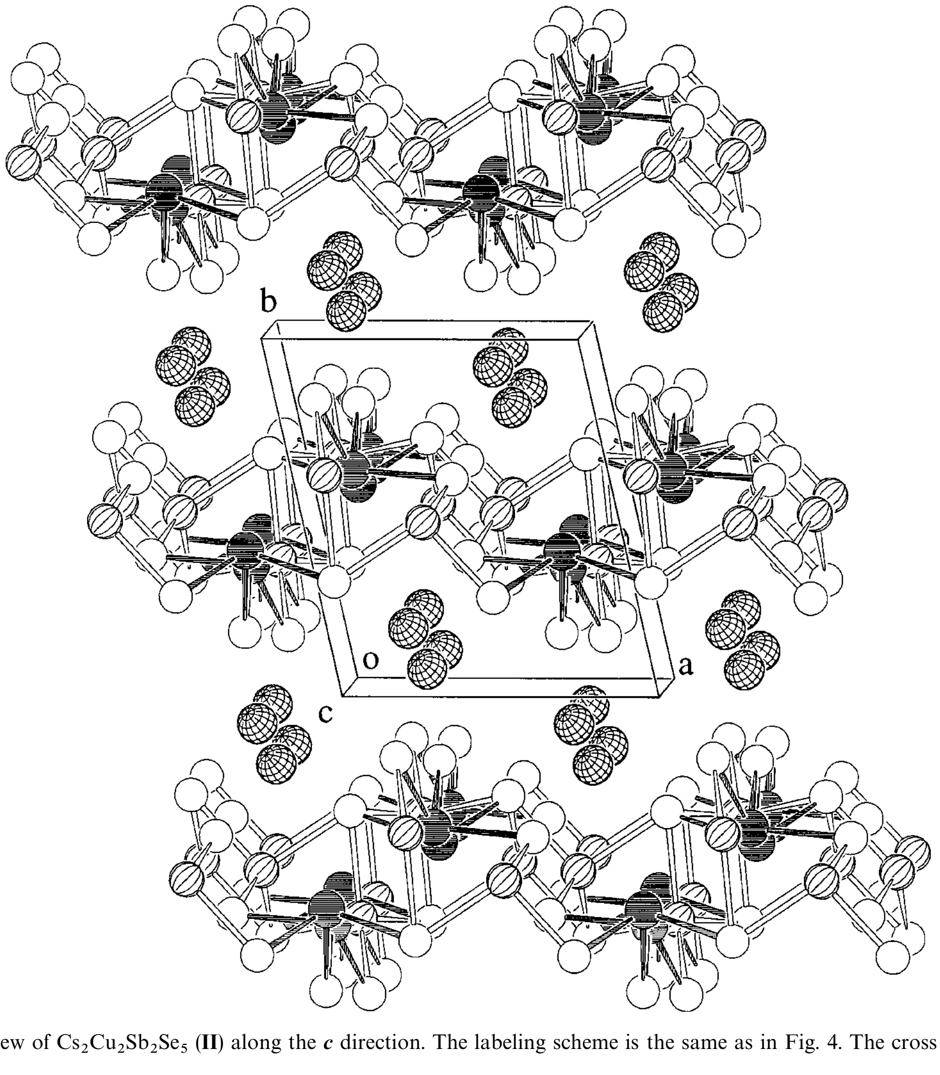

FIG. 5. Perspective view of $Cs_2Cu_2Sb_2Se_5$ (**II**) along the *c* direction. The labeling scheme is the same as in Fig. 4. The cross shaded circles are Rb.

and M–Se(2) = 2.571(1) Å × 2]. The M–Se distances are slightly longer than those found in $RbCuSe_4$ (2.400, 2.425, 2.433, and 2.572 Å) (37) and are comparable with those in the aforementioned silver compounds. The Se(1) atoms in the title compound display a very unusual coordination with the metals. Instead of taking the usual capping positions, they reside in the interior of the layers and are eightfold coordinated to four Ag(1) (in the center of the Ag_4 square) and four M (in the center of the M_4 tetrahedron). While a high coordination number is quite common for chalcogen elements, encapsulation of these atoms by metals is very unusual. To the best of our knowledge, **I** represents the first example in which the chalcogens are encapsulated by the metal elements.

Structure of $Cs_2Cu_2Sb_2Se_5$

Compound II is also a quaternary intermetallic phase having a new type of layered structure. Figure 4 gives a perspective view of its crystal structure along the ***b*** axis. The $^2_\infty[(Cu_2Sb_2Se_5)^{2-}]$ layers stack on top of each other along the ***b*** axis with Cs^+ cations located between them. The cations themselves form double layers that extend in the ***ac*** plane in a zigzag fashion (see Fig. 5). Each antimony atom is surrounded by three selenium atoms to give a trigonal pyramidal geometry and each copper atom by four selenium atoms to form a tetrahedral coordination. Of the five independent sleneium atoms, Se(1) and Se(5) and μ_4-bridging ligands, each bonds to three copper and an antimony atom, while Se(2), Se(3), and Se(4) are μ_2-bridging ligands bonded to two metal (M = Cu, Sb) atoms, as shown in Fig. 6. The anionic layer may be constructed by connecting the edge-sharing $CuSe_4$ tetrahedral chains with bridging Sb_2Se_3 units, or it may be described as composed of fused 12-membered, alternating M–Se rings linked by interring Cu–Se and/or Sb–Se bonds. The approximate dimension of these rings is 4.6 × 7.0 Å. The Cu–Se bond distances range from 2.410 to 2.596 Å, slightly shorter than those of **I** (2.571, 2666 Å) and compare well with those of $RbCuSe_4$ (37) and $RbCuSb_2Se_4 \cdot H_2O$ (38). The Sb–Se distances are between 2.515 and 2.625 Å, comparable with those observed in AHgSbSe$_3$, 2.520, 2.594 Å (A = Rb), 2.780, 2.851 Å (A = Cs) (25), and in $RbCuSb_2Se_4 \cdot H_2O$, 2.556–2.726 Å (38). There are also short–metal contacts between the copper atoms, giving 2.748 Å for Cu(1)–Cu(1) and 2.678 Å for Cu(1)–Cu(2). These are similar to 2.674 Å in $Cu_2SbSe_3 \cdot 1/2$en (21), 2.649 Å in $Cu_2SbSe_3 \cdot$ en (21), 2.665 Å in Cu_3SbSe_3 (39), and 2.830 Å in Cu_3SbSe_4 (40).

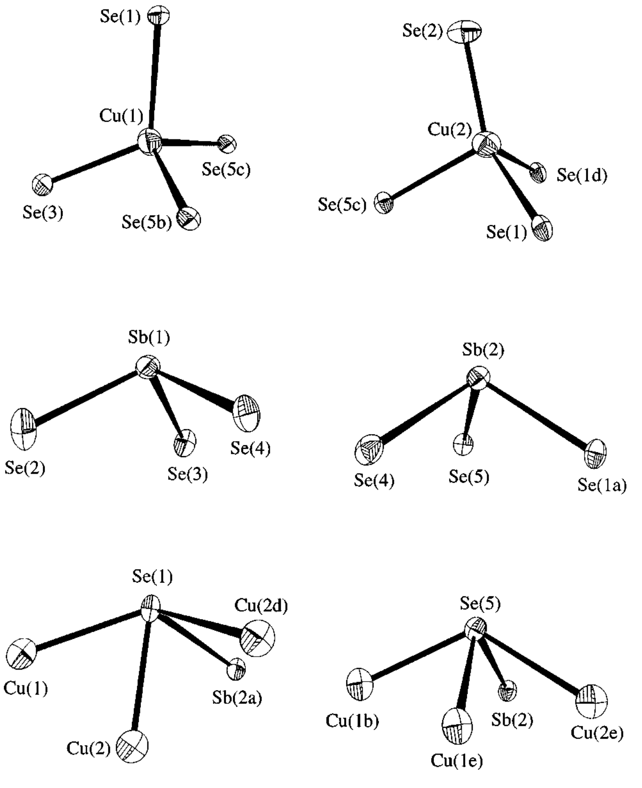

FIG. 6. ORTEP drawing with displacement ellipsoids at 50% probability level showing the coordination of Cu(1), Cu(2), Sb(1), Sb(2), Se(1), and Se(5) in $Cs_2Cu_2Sb_2Se_5$ (**II**).

Optical Properties

The optical properties of **I** and **II** were examined by analyzing the diffuse reflectance data. The Kubelka–Munk (or remission, F) functions (41) for both **I** and **II** were converted from the diffuse reflectance data ($F = (1 - R_\infty)^2/2R_\infty$, where R_∞ is the relative diffuse reflectance of an infinitely thick layer. For practical purposes, this can be achieved at a layer depth of a few millimeters). The remission functions are plotted in Fig. 7 versus the wavelength

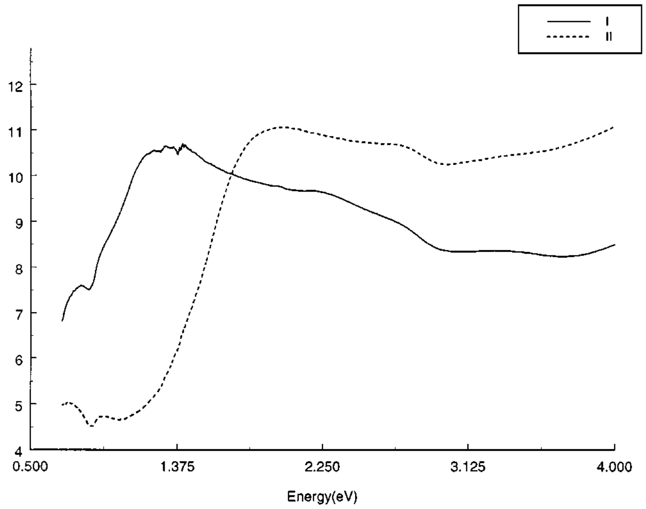

FIG. 7. Optical absorption spectra (Kubelka–Munk Function) for $RbCu_{1.2}Ag_{3.8}Se_3$ (**I**) (solid line) and $Cs_2Cu_2Sb_2Se_5$ (**II**) (dotted line) plotted over the energy range of 0.5–4.0 eV.

(in the unit of electron volts). The absorption coefficient (α) can be computed from the remission function ($F = \alpha/S$) where S is the scattering factor (24, 41). The band gaps can be estimated from the sharp absorption edges. The values obtained for **I** and **II** are 0.7–0.8 and 1.2–1.3 eV, respectively, suggesting that both compounds are semiconductors with relatively small band gaps. The results from tight-binding band structure calculations performed on compound **I** are consistent with those of optical experiments (42).

ACKNOWLEDGMENTS

Financial support from the National Science Foundation (Grant DMR-9553066 and supplementary funds) is greatly appreciated. J.L. is grateful to the Camille and Henry Dreyfus Foundation for a Henry Dreyfus Teacher–Scholar Award.

REFERENCES

1. K. Volk and H. Schäfer, *Z. Naturforsch. B* **34,** 172 (1979); G. Dittmar and H. Schäfer, *Z. Anorg. Allg. Chem.* **441,** 98 (1978); K. Volk and H. Schäfer, *Z. Naturforsch. B* **34,** 1637 (1979); K. Volk and H. Schäfer, *Z. Naturforsch. B* **33,** 827 (1978); H. A. Graf and H. A. Schäfer, *Z. Anorg. Allg. Chem.* **414,** 211 (1975); *Z. Naturforsch. B* **27,** 735 (1972); B. Eisenmann and H. Schäfer, *Z. Naturforsch. B* **34,** 383 (1979); G. Dittmar and H. Schäfer, *Z. Anorg. Allg. Chem.* **441,** 93 (1978); G. Cordier, H. Schäfer, and C. Schwidetzky, *Rev. Chim. Miner.* **22,** 722 (1981); *Z. Naturforsch. B* **39,** 131 (1984).
2. W. S. Sheldrick and J. Kaub, *Z. Naturforsch. B* **40,** 571 (1985); *Z. Anorg. Allg. Chem.* **535,** 179 (1986); W. S. Sheldrick, *Z. Anorg. Allg. Chem.* **562,** 23 (1988).
3. J.-H. Chou and M. G. Kanatzidis, *Inorg. Chem.* **33,** 1001 (1994); *Chem. Mater.* **7,** 5 (1995); *J. Solid State Chem.* **123,** 115 (1996); *Inorg. Chem.* **33,** 1001 (1994). H.-O. Stephan and M. G. Kanatzidis, *Inorg. Chem.* **36,** 6050 (1997).
4. Y. Ko, K. Tan, D. M. Nellis, S. Koch, and J. B. Parise, *J. Solid State Chem.* **114,** 506 (1995); J. B. Parise, Y. Ko, J. Rijssenbeek, D. M. Nellis, K. Tan, K. and S. Koch, *J. Chem. Soc., Chem. Commun.* 527 (1994); K. Tan, Y. Ko, and J. B. Parise, *Acta Crystallogr. Sect. C* **51,** 398 (1995); J. B. Parise, Y. Ko, K. Tan, D. M. Nellis, and S. Koch, *J. Solid State Chem.* **117,** 219 (1995); J. B. Parise, *J. Chem. Soc., Chem. Commun.* 1553 (1990).
5. J.-H. Liao, L. Hill, and M. G. Kanatzidis, *Inorg. Chem.* **32,** 4650 (1993); J.-H. Liao and M. G. Kanatzidis, *J. Am. Chem. Soc.* **112,** 7400 (1990); *Inorg. Chem.* **31,** 431 (1992); J.-H. Liao, J. Li, and M. G. Kanatzidis, *Inorg. Chem.* **34,** 2658 (1995); R. A. Stevens, C. C. Raymond, and P. K. Dorhout, *Agnew. Chem. Int. Ed. Engl.* **34,** 2509 (1995); A. Müller, V. Wittenben, and E. Krickemeyer, H. Bögge, and M. Lemke, *Z. Anorg. Allg. Chem.* **605,** 175 (1991); C. C. Raymond, P. K. Dorhout, and S. M. Miller, *Inorg. Chem.* **33,** 2703 (1994); **210,** 775 (1995).
6. K.-W. Kim and M. G. Kanatzidis, *J. Am. Chem. Soc.* **114,** 4878 (1992); *Inorg. Chem.* **32,** 4161 (1993).
7. N. S. Hartig, P. K. Dorhout, and S. M. Miller, *J. Solid State Chem.* **113,** 88 (1994); *Z. Kristallogr.* **210,** 776 (1995).
8. W. S. Sheldrick and B. Schaaf, *Z. Naturforsch. B* **49,** 993 (1994); W. S. Sheldrick and M. Wachhold, *Angew. Chem. Int. Ed. Engl.* **34,** 450 (1995); *Chem. Commun.* 607 (1996); W. S. Sheldrick and H. G. Braunbeck, *Z. Naturforsch. B* **44,** 1397 (1989); W. S. Sheldrick and B. Schaaf, *Z. Anorg. Allg. Chem.* **620,** 1041 (1994); M. Wachhold and W. S. Sheldrick, unpublished results.
9. W. S. Sheldrick and H.-J. Haüsler, *Z. Anorg. Allg. Chem.* **561,** 139 (1988); **561,** 149 (1988); W. S. Sheldrick and H. G. Braunbeck, *Z. Naturforsch. B* **44,** 851 (1989); W. S. Sheldrick and B. Schaaf, *Z. Naturforsch. B* **49,** 655 (1995); W. S. Sheldrick, *Z. Naturforsch.* **43,** 249 (1988); W. S. Sheldrick and H. Schaaf, *Z. Naturforsch.* **49,** (1994); G. Dittmar, and H. Schäfer, *Z. Naturforsch. B* **32,** 1346 (1977); W. S. Sheldrick, and G. Z. Braunbeck, *Anorg. Allg. Chem.* **619,** 1300 (1993); W. S. Sheldrick, and H. G. Braunbeck, *Z. Naturforsch. B.* **47,** 151 (1992); W. S. Sheldrick and H.-J. Häusler, *Z. Anorg. Allg. Chem.* **557,** 105 (1988); M. Wachhold, B. Schaaf, and W. S. Sheldrick, unpublished results. W. S. Sheldrick and H. G. Braunbeck, *Z. Naturforsch. B* **45,** 1643 (1990).
10. A. S. Kanichtschewa, J. N. Mikhajlov, V. B. Lazarev, and N. A. Moschchalkova, *Dokl. Akad. Nauk.* **252,** 872 (1980); B. Eisenmann, H. Schwerer, and H. Schäfer, *Mater. Res. Bull.* **18,** 383 (1983); C. Brinkmann, B. Eisenmann, and H. Schäfer, *Mater. Res. Bull.* **20,** 299 (1985); T. Jiang, A. J. Lough, G. A. Ozin, D. Young, and R. L. Bedard, *Chem. Mater.* **7,** 245 (1995); H. Ahari, C. L. Bowes, T. Jiang, A. Lough, G. A. Orzin, R. L. Bedard, S. Petrov, and D. Young, *Adv. Mater.* **7,** 375 (1995); H. Ahari, G. A. Ozin, R. L. Bedard, S. Petrov, and D. Young, *Adv. Mater.* **7,** 370 (1995).
11. G. L. Schimek, W. T. Pennington, and J. W. Kolis, *J. Solid State Chem.* **123,** 277 (1996); P. T. Wood, G. L. Schimek, and J. W. Kolis, *Chem. Mater.* **8,** 721 (1996); D. M. Young, G. L. Schimek, and J. W. Kolis, *Inorg. Chem.* **35,** 7620 (1996); G. L. Schimek, and J. W. Kolis, *Chem. Mater.* **9,** 2771 (1997); G. L. Schimek, and J. W. Kolis, *Inorg. Chem.* **36,** 1689 (1997).
12. P. T. Wood, W. T. Pennington, and J. W. Kolis, J. W. *J. Am. Chem. Soc.* **114,** 9233 (1992); P. T. Wood, W. T. Pennington, and J. W. Kolis, *J. Chem. Soc., Chem. Commun.* 235 (1993); P. T. Wood, W. T. Pennington, and J. W. Kolis, *Inorg. Chem.* **33,** 1556 (1994); J. E. Jerome, P. T. Wood, W. T. Pennington, and J. W. Kolis, *Inorg. Chem.* **33,** 1733 (1994).
13. J. Li, B. G. Rafferty, S. Mulley, and D. M. Proserpio, *Inorg. Chem.* **34,** 6417 (1995); J. Li, Z. Chen, J. L. Kelley, and D. M. Proserpio, *in* "Solid State Chemistry of Inorganic Materials," Vol. 453, pp. 29–34, 1997.
14. T. K. Whittingham, Z. Chen, J. Li, and D. M. Proserpio, *Bull. N. J. Acad. Sci.* **42,** 11 (1998); Z. Chen, T. K. Whittingham, R.-J. Wang, and J. Li, *J. Alloys Compounds*, submitted.
15. Z. Chen, J. Li, T. J. Emge, T. Yuen, and D. M. Proserpio, *Inorg. Chim. Acta* **273,** 310 (1998).
16. J. Li, Z. Chen, T. J. Emge, and D. M. Proserpio, *Inorg. Chem.* **36,** 1437 (1997).
17. J. Li, Z. F. Chen, and D. M. Proserpio, *Inorg. Chim. Acta* **273,** 255 (1998).
18. M. R. Girard, J. Li, and D. M. Proserpio, *Main Group Metal Chem.* **21,** 231 (1998).
19. Z. Chen, J. Li, and D. M. Proserpio, submitted for publication.
20. Z. Chen, R.-J. Wang, and J. Li, J. submitted for publication.
21. Z. Chen, R. E. Dilks, R.-J. Wang, J. Y. Lu, and J. Li, *Chem. Mater.* **10,** 3184 (1998).
22. J. Li, Z. Chen, K.-C. Lam, S. Mulley, and D. M. Proserpio, *Inorg. Chem.* **36,** 684 (1997).
23. M. R. Girard and J. Li, unpublished results.
24. J. Li, Z. Chen, X.-X. Wang, and D. M. J. Proserpio, *Alloys Compounds* **262–263,** 28 (1997).
25. Z. Chen, R.-J. Wang, and J. Li, "Solid State Chemistry of Inorganic Materials II," in press.
26. J. Li, Z. Chen, R.-J. Wang, and J. Lu, *J. Solid State Chem.* **140,** 149 (1998).
27. Lam, K.-C.; Chen, Z. and Li, J. unpublished results.
28. G. M. Sheldrick, "SHELX-97: Program for tructure refinement." University of Goettingen, Germany, 1997.

29. E. Keller "SCHAKAL 92: A computer program for the graphical representation of crystallographic models." University of Freiburg, Germany, 1992.
30. J. Li, H.-Y. Guo, X. Zhang, and M. G. Kanatzidis, *J. Alloys Compounds* **218,** 1 (1995).
31. Z. Ban, and M. Sikirica, *Acta Crystallogr.* **18,** 594 (1965).
32. J. Li, H.-Y. Guo, R. A. Yglesias, and T. J. Emge, *Chem. Mater.* **7,** 599 (1995).
33. H. R. Heulings, J. Li, and D. M. Proserpio, *Main Group Metal Chem.* **21,** 225 (1998).
34. W. Bensch, P. Duerichen, and C. Weidlich, *Z. Kristallogr.* **211,** 932 (1996).
35. M. G. Kanatzidis and J.-H. Chou, *J. Solid State Chem.* **127,** 186 (1996).
36. W. Bensch and P. Duerichen, *Z. Kristallogr.* **212,** 1791 (1997).
37. K. O. Klepp and C. Weithaler, *Z. Natursch. B* **50,** 1791 (1995).
38. J. A. Hanko and M. G. Kanatzidis, *Angew. Chem. Int. Ed. Engl.* **37,** 342 (1998).
39. A. Pfitzner, *Z. Anorg. Allg. Chem.* **621,** 685 (1995).
40. A. Pfitzner, *Z. Kristallogr.* **209,** 685 (1994).
41. W. WM. Wendlandt and H. G. Hecht, "Reflectance Spectroscopy." Interscience, New York, 1966.
42. J. Li, unpublished results.