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Ternary Chalcogenide Compounds AB_2X_4: The Crystal Structures of $SiPb_2S_4$ and $SiPb_2Se_4$*

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The crystal structures of $SiPb_2S_4$ and $SiPb_2Se_4$ were determined from three dimensional X-ray diffraction data collected with Mo radiation. Both structures are monoclinic with space group $P2_1/c$ and 4 formula units per unit cell. Lattice dimensions for $SiPb_2S_4$ are $a = 6.4721(5)$ Å, $b = 6.6344(9)$ Å, $c = 16.832(1)$ Å, and $\beta = 108.805(7)°$. For $SiPb_2Se_4$, $a = 8.5670(2)$ Å, $b = 7.0745(3)$ Å, $c = 13.6160(3)$ Å, and $\beta = 108.355(3)°$. The Si is tetrahedrally coordinated to S and Se with Si–S about 2.10 Å and Si–Se about 2.27 Å. The structural framework can be described as consisting of trigonal prisms of S or Se atoms which form a prismatic tube by sharing the triangular faces. These tubes in turn share edges to form corrugated sheets, with the unshared edges projecting alternately on each side of the sheet. The structures are very similar but not identical. In the sulfide one Pb is in sevenfold coordination and the other crystallographically independent Pb is in eightfold coordination. The Pb–S distances range from 2.82–3.50 Å. In $SiPb_2Se_4$ both Pb atoms are in sevenfold coordination. Pb–Se distances range from 2.97 to 3.54 Å. In the sulfide the Pb atoms form a zig-zag chain within the channels formed by the prismatic tubes while in the selenide they are in a straight line.

Introduction

In an ongoing program of research on the crystal chemistry of ternary chalcogenide compounds of stoichiometry AB_2X_4 we previously described the structures of $GePb_2S_4$ and $SnBa_2S_4$ (*1*, *2*). We have synthesized $SiPb_2S_4$ and $SiPb_2Se_4$, which represent new structures, in addition to other compounds of this stoichiometry which turned out to be isostructural with olivine and K_2SO_4. This paper discusses the two structures and the subtle differences between them.

Sample Preparation

$SiPb_2S_4$ was prepared by direct reaction of the corresponding stoichiometric quantities of Si, and S in an evacuated, sealed vycor tube at 800°C for about 2 days. The crystals were transparent, yellow prisms with relatively easy cleavage along the prismatic faces. $SiPb_2Se_4$ was prepared by heating the elements in the stoichiometric proportions. The mixture was fired in a vacuum sealed vycor ampoule until the product looked homogeneous. A single-phase material was obtained after heating at 700°C for 4 days. The product was highly crystalline and crystals 5 mm and longer were found. The crystals were deep ruby red in transmitted light and showed semi-metallic luster when viewed by reflected light. Very easy cleavage parallel to $(\bar{1}02)$ was apparent, and was made use of when selecting a specimen for single crystal study.

Crystal Structure of $SiPb_2S_4$

X-ray diffraction photographs showed that the crystal quality was relatively poor due to lineage structure. After several trials a crystal was found which was acceptable for data collection and oscillation, zero and upper level Weissenberg, and precession photographs were taken. The diffraction symmetry was $2/m$ and the systematic absences were $h0l$ $(l = 2n + 1)$ and $0k0$ $(k = 2n + 1)$, uniquely determining the space group as

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$P2_1/c$. This crystal, 0.098 × 0.258 × 0.061 mm, was then mounted on an XRD-5 single-crystal diffractometer, and aligned so that the ϕ axis was parallel to the unique b axis (0.258 mm) of the crystal. The 2θ values of about 30 reflections between 29° and 48° were accurately measured at room temperature using K_{α_1} and K_{α_2} radiation from a molybdenum target ($\lambda_1 = 0.70926$ Å, $\lambda_2 = 0.71354$ Å), with the instrument at a 1° takeoff angle, and a 0.05° slit in front of the scintillation counter tube. The data were used in a least-squares calculation to determine the lattice parameters $a = 6.4721(5)$ Å, $b = 6.6344(9)$ Å, $c = 16.832(1)$ Å, and $\beta = 108.805(7)°$. Hagenmuller and Perez (*3*) report lattice constants of $a = 6.50$ Å, $b = 6.65$ Å, $c = 17.68$ Å, and $\beta = 115.5°$ obtained from single-crystal photographs. The values reported here are not reconcilable with Hagenmuller's by a transformation of axes.

The intensity data were collected by using the stationary crystal–stationary counter technique, balanced filters, the diffractometer at a 5° takeoff angle and a wide-open aperture in front of the counter. The intensities were measured by counting for 10 sec with the Zr filter and then for 10 sec with the Y filter. The data were collected to a cutoff value of $\sin\theta/\lambda = 0.68$ for a total of 1823 independent reflections. The intensities were transformed into a set of structure amplitudes by applying Lorentz, polarization, and absorption corrections. The absorption correction, $\mu = 581$ cm^{-1}, was calculated assuming the formula $SiPb_2S_4$ and using the values of the mass absorption coefficients tabulated in Ref. (*4*). The crystal shape was approximated by seven planes, and the transmission factor varied between 0.03 and 0.08. Reflections with a net intensity of more than 4 counts were considered as observed, and 1431 reflections satisfied this condition. Standard deviations were assigned using the formula:

$$\sigma(|F|) = \tfrac{1}{2}\left[K\left(1 + \frac{I_Y}{I_{Zr}}\middle/1 - \frac{I_Y}{I_{Zr}}\right)\right]^{1/2},$$

where K is the product of all correction factors and I_Y and I_{Zr} are the counts with the respective filters in the diffracted beam path.

Four molecules of $SiPb_2S_4$ per unit cell were assumed and from an interpretation of a three-dimensional Patterson map, a set of heavy atom positions was obtained and a structure factor calculation gave $R = 0.30$. An electron density map, computed using the phases from these two Pb atoms, showed clearly five peaks with approximately the same intensity. The Si atom could be located because it was tetrahedrally coordinated by the other peaks which were the sulfur atoms. An iterative least-squares structure factor refinement with all atoms, isotropic temperature factors and all reflections had a final value of $R = 0.17$. A refinement with anisotropic thermal parameters gave $R = 0.095$ and $wR = 0.088$, for 1431 observed reflections. No physical significance can be attached to the anisotropic thermal parameters because of the large absorption corrections. The differences in the positional parameters obtained from refinements with isotropic and anisotropic parameters were within 1 SD except for the x parameters of S4 and Si which differed by 3σ and 2σ, respectively. For all 1823 reflections, the corresponding values were $R = 0.123$ and $wR = 0.093$ ($R = \sum||F_0| - |F_c|| / \sum|F_0|$, $wR = [\sum w(F_0 - |F_c|)^2/\sum wF_0^2]^{1/2}$, $w = 1/\sigma^2$). The scattering factors used were those from the "International Tables for X-ray Crystallography" (*4*) for neutral atoms corrected, in the case of Pb, for the real and imaginary part of the dispersion term. The standard deviation of a reflection of unit weight is 1.534. The final atomic parameters and their standard deviations are shown in Table I, and the observed and calculated structure amplitudes are available[1]. A difference electron density map showed no peaks greater than 1.85 e/Å^3.

Crystal Structure of $SiPb_2Se_4$

A single crystal 0.16 × 0.24 × 0.04 mm was selected, and oscillation, zero and upper level Weissenberg, and precession photographs exhibited the diffraction symmetry $2/m$, with the systematic absences $h0l$ ($l = 2n + 1$); $0k0$ ($k = 2n + 1$) which uniquely characterize the space group $P2_1/c$. The $h0l$ photograph of $SiPb_2Se_4$ was almost identical with that of $SiPb_2S_4$, indicating a similarity in the corresponding ($h0l$) projections. The labelling of the axes in the selenide, however, would have to be interchanged for the superpositions of the photographs so that the resulting space group for $SiPb_2Se_4$ would then be $P2_1/a$.

The crystal was mounted on a XRD-5 single crystal diffractometer and 20 reflections with 2θ

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TABLE I

ATOMIC PARAMETERS AND THEIR STANDARD DEVIATIONS IN PARENTHESES ($\times 10^4$) FOR $SiPb_2S_4$[a]

	x	y	z	B(11)	B(22)	B(33)	B(12)	B(13)	B(23)
Pb1	2363(2)	2494(3)	223(1)	115(4)	294(6)	19(0)	21(4)	12(1)	5(1)
Pb2	2631(2)	3117(3)	2854(1)	132(4)	149(4)	19(0)	26(3)	12(1)	0(13)
S1	52(16)	−7(12)	1355(7)	153(26)	−61(16)	40(5)	1(15)	43(9)	−6(6)
S2	−8(15)	14(13)	3612(6)	123(25)	−10(19)	25(4)	−1(16)	15(8)	−11(6)
S3	5791(14)	2279(16)	1768(5)	100(22)	132(27)	14(3)	57(19)	19(6)	4(7)
S4	6221(18)	2398(29)	4773(6)	142(29)	576(66)	14(3)	53(38)	11(8)	3(14)
Si	7939(16)	2483(21)	1064(6)	102(27)	191(33)	16(4)	−3(25)	12(8)	−7(10)

[a] The temperature factor is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

values between 91 and 146° were centered on the CuK_{α_1} ($\lambda_1 = 1.54071$ Å) and CuK_{α_2} ($\lambda_2 = 1.54433$ Å) radiations. The resulting 2θ values, measured at room temperature, were used in a least-squares calculation to find the lattice parameters $a = 8.5670(2)$ Å, $b = 7.0745(3)$ Å, $c = 13.6160(3)$ Å, and $\beta = 108.355(3)°$.

An ω scan of several reflections showed that the peak width measured from background to background averaged 1.2° and therefore integrated intensities were obtained using the stationary counter-moving crystal technique with a Norelco automatic diffractometer, PAILRED. The crystal was aligned so that the spindle axis of the diffractometer was parallel to the b axis, and intensity data were collected with MoK_{α_1} radiation, monochromatized with a graphite single crystal. For each reflection the intensity was integrated at the rate of 1°/min. The integration interval within a given layer was fixed, but ranged from 3 to 3.6° for reflections having $\Upsilon > 15°$, and from 3 to 6° for those having $\Upsilon \leqslant 15°$ as the inclination angle (μ) increased. Background intensities at both ends of the interval of integration were counted for 60 sec. When the integrated intensity was less than 20,000 counts, the ω scan was repeated once more. The intensities were measured using a 3° circular receiving aperture. Nine layers of reciprocal space, $h0l$ to $h8l$, were explored. The maximum Υ angle was set at 60° and 2282 independent reflections were measured. Pairs of the type $hk0$ and $\bar{h}k0$ were measured and they were averaged after absorption-corrected $|F|$'s were obtained. During the course of the data collection, three standard reflections were checked every time a new reciprocal lattice layer was started, and the intensities were constant within 4%. The intensities were transformed into structure amplitudes through the application of Lorentz, polarization, and absorption corrections ($\mu = 624$ cm^{-1}). The shape of the crystal was described by six faces for the absorption correction and the transmission factor varied from 0.017 to 0.106. The basis (*5*) for accepting a reflection as statistically nonzero was $\Delta I/I < 0.6$, where

$$\Delta I/I = [(T + t^2 B)^{1/2}]/(T - tB),$$

with T = total counts in time t_T for the omega scan, B = total background counts, $t = t_T/(t_1 + t_2)$, where t_1 and t_2 are background counting times (in this case, $t_1 = t_2 = 60$ sec). Of the 2282 reflections collected, about 1500 satisfied this criterion. The comparatively large number of unobserved reflections was due to a superstructure along the a axis which makes complete rows in reciprocal space very weak. The standard deviation for a structure factor was estimated by the formula

$$\sigma(|F|) = \left\{\left(\frac{F}{2I}\right)^2 \left[I + \frac{Bt}{2} + 0.0004(I)^2\right]\right\}^{1/2},$$

and $1/\sigma^2(|F|)$ was used as the weight in the least-squares calculations.

The Patterson function could be interpreted on the basis of two sets of independent Pb atom positions and structure factor calculations for each set produced R values of 0.437 and 0.446, so that the ambiguity could not be resolved. Consequently, two Fourier maps, each phased on one of the two sets of heavy atoms were computed, and in both of them four peaks with the approximate weight to be expected for Se atoms could be found. No attempt was made at this point to locate the Si atom because at these values of R the Fourier maps were too noisy. Two structure factor calculations were then carried out for each set of 2Pb and 4Se atoms. In one of them all the atomic parameters converged and the *R* factor was 0.19 after the positional and isotropic thermal parameters were refined. In the other the convergence was poor, and the *R* factor was 0.31. A new Fourier map, phased on the 2Pb and 4Se atoms corresponding to the first set was calculated, and the Si atom was easily located. Its inclusion in a new structure-factor calculation for all reflections produced an *R* value of 0.18. Refinement with anisotropic thermal parameters brought the *R* factor to 0.053 for 1501 observed reflections and *wR* was 0.044. Two reflections which were suspected of being affected by extinction were not included in the refinement. The standard deviation of a reflection of unit weight was 2.40. With the parameters obtained in this refinement, the *R* factor for all 2282 reflections was 0.101, while $wR = 0.046$. The scattering factors for neutral atoms were taken from the "International Tables for X-ray Crystallography" (*4*) and were corrected for the real and imaginary part of the dispersion term for Pb and Se. A difference Fourier map was computed and it showed no peaks greater than 1.2 e/A^3. The final atomic parameters and their standard deviations are shown in Table II. The observed and calculated structure amplitudes are available.[1]

Discussion

A projection of the structure of $SiPb_2S_4$ on the (010) plane is shown in Fig. 1(a). A list of the most important interatomic distances is given in Table III. As expected, the Si atom is tetrahedrally coordinated by sulfur atoms, with Si–S distances between 2.09 and 2.10 Å and values of the tetrahedral angle ranging from 105 to 112°. Pb(2) is in sevenfold coordination with respect to S, and the coordination polyhedron is a distorted trigonal prism (the triangular bases are not parallel) capped on one of the lateral faces. The Pb(2)–S distances vary between 2.80 and 3.35 Å, with the next nearest approach equal to 4.00 Å. Pb(1), however, lies almost exactly on the glide plane, and this has the effect of making it close to one more S atom. The coordination number is thus 8, with distances between 2.82 and 3.50 Å. The configuration is again a distorted trigonal prism with two lateral faces capped. The structure can be described in terms of zig-zag rows of Pb atoms running parallel to the *c* axis, each surrounded by a trigonal prism of S atoms in such a way that the prisms share triangular faces. The resulting prismatic "tubes" share edges, thereby forming corrugated sheets, with the unshared edges projecting alternately on each side of the sheet. The plane of the sheet is parallel to the (100) plane. The structure can be imagined as a stacking of these sheets with the stacking direction along the *a** axis. Two consecutive sheets are mutually displaced in the direction of the *c* axis by one half of the height of the trigonal prism. This arrangement has tetrahedral voids, and some of them are occupied by the Si atoms.

The structure of $SiPb_2Se_4$ is very similar to that of $SiPb_2S_4$, although this is not evident from the appearance of the respective powder patterns. Si is tetrahedrally coordinated by Se with Si–Se distances ranging from 2.25 to 2.28 Å and tetrahedral angles from 105 to 113° (Table IV). The coordination polyhedron around Pb1 is a distorted trigonal prism with an extra Se atom in

TABLE II

ATOMIC PARAMETERS AND THEIR STANDARD DEVIATIONS IN PARENTHESES ($\times 10^4$) FOR $SiPb_2Se_4$[a]

	x	*y*	*z*	B(11)	B(22)	B(33)	B(12)	B(13)	B(23)
Pb1	543(1)	1581(1)	3715(1)	51(1)	96(1)	16(0)	−8(1)	7(0)	2(1)
Pb2	5602(1)	1479(1)	3672(1)	51(1)	104(1)	19(0)	15(1)	7(0)	−5(1)
Se1	2737(2)	4779(2)	2640(2)	56(3)	45(3)	12(1)	−5(2)	4(1)	−4(2)
Se2	7437(2)	4726(2)	2603(2)	50(3)	42(3)	16(1)	−1(2)	6(1)	−2(2)
Se3	3668(2)	2626(3)	420(1)	41(2)	97(4)	12(1)	−1(3)	6(1)	−3(2)
Se4	9313(2)	2602(3)	557(1)	32(2)	80(3)	15(1)	−6(3)	2(1)	−3(2)
Si	2037(6)	2400(7)	1449(4)	32(7)	44(8)	10(3)	3(6)	4(3)	2(4)

[a] The temperature factor is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

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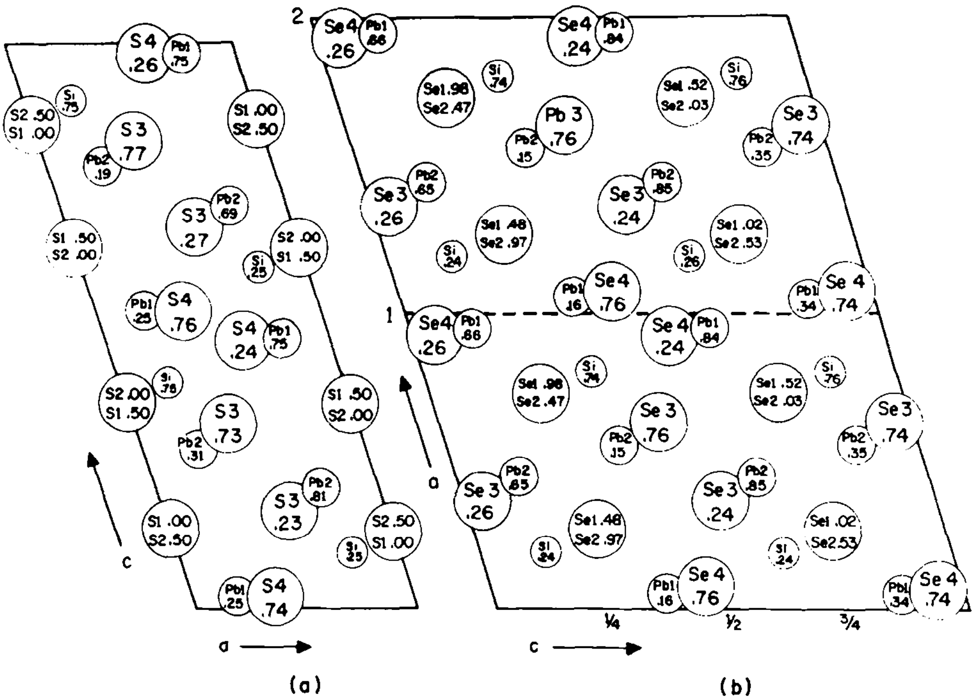

FIG. 1. (a) The projection of the structure of $SiPb_2S_4$ on (010). (b) The projection of the structure of $SiPb_2Se_4$ on (010). The unit cell of the latter is shown doubled along the *a* axis to emphasize the relationship between the two structures.

TABLE III

INTERATOMIC DISTANCES AND ANGLES IN $SiPb_2S_4$[a]

Distances (Å)

Pb1-S1	3.09(1)	Pb2-S1	2.80(1)	S1-S2	3.33(2)
S1	3.23(1)	S1	3.28(1)	S1-S3	3.41(2)
S2	3.12(1)	S2	2.80(1)	S1-S4	3.46(3)
S2	3.30(1)	S2	3.19(1)	S2-S3	3.50(2)
S3	2.82(1)	S3	2.94(1)	S2-S4	3.41(3)
S4	2.83(2)	S3	3.20(1)	S3-S4	3.46(3)
S4	3.38(2)	S4	3.35(2)		
S4	3.50(2)	Si-Pb1	3.42(2)		
Si-S1	2.09(2)	Si-Pb2	3.52(2)		
S2	2.10(2)	Pb1-Pb2	4.066(4)		
S3	2.10(2)				
S4	2.10(2)				

Angles (°)

S1-Si-S2	105(1)
S1-Si-S3	108(1)
S1-Si-S4	111(1)
S2-Si-S3	112(1)
S2-Si-S4	108(1)
S3-Si-S4	111(1)

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[a] Standard deviations are shown in parentheses.

TABLE IV

INTERATOMIC DISTANCES AND ANGLES IN $SiPb_2Se_4$

		Distances (Å)			
Pb1–Se1	3.108(4)	Pb(2)–Se1	2.875(4)	Se1–Se2	3.588(5)
Se1	3.539(4)	Se1	3.358(4)	Se1–Se3	3.689(5)
Se2	3.146(4)	Se2	2.913(4)	Se1–Se4	3.712(5)
Se2	3.433(4)	Se2	3.362(4)	Se2–Se3	3.736(5)
Se3	2.992(4)	Se3	2.977(4)	Se2–Se4	3.711(5)
Se4	2.974(4)	Se3	3.361(4)	Se3–Se4	3.794(5)
Se4	3.064(4)	Se4	3.460(4)		
Si–Pb1	3.607(8)	Si–Se1	2.282(9)		
Si–Pb2	3.557(8)	Se2	2.254(9)		
Pb1–Pb2	4.215(2)	Se3	2.274(9)		
		Se4	2.271(9)		
		Angles (°)			
		Se1–Si–Se2	104.5(3)		
		Se1–Si–Se3	108.1(3)		
		Se1–Si–Se4	109.2(3)		
		Se2–Si–Se3	111.1(3)		
		Se2–Si–Se4	110.2(3)		
		Se3–Si–Se4	113.1(3)		

front of one of the rectangular faces. Pb1–Se distances range from 2.97 to 3.54 Å. For Pb2 the coordination is the same, with Pb2–Se distances varying from 2.87 to 3.46 Å.

The structure can be described by the packing of triangular prisms, in the same way as for the structure of $SiPb_2S_4$. The main difference is that in $SiPb_2Se_4$, the Pb atoms are almost exactly in straight lines running parallel to the *a* axis, while they are arranged in a zig-zag fashion in $SiPb_2S_4$. To facilitate the comparison between the corresponding projections on the (010) plane, a left-handed coordinate system has been used in Fig. 1(a). Approximate superposition between the two structures can be achieved by placing the origin of the unit cell of $SiPb_2S_4$ at the point $(0,0,\frac{1}{4})$ with respect to the origin of the unit cell of $SiPb_2Se_4$. Cleavage parallel to $(\bar{1}02)$ occurs because no Si–Se bonds need to be broken across this plane [Fig. 1(b)]; in $SiPb_2S_4$ this orientation corresponds to $(\bar{1}01)$.

The crystal structure of $GeSr_2S_4$ has recently been published (*6*). The values of the *b* axes and of the monoclinic angle β for this compound are very similar to the values observed for $SiPb_2S_4$ and $SiPb_2Se_4$. Moreover, the *a* parameter of the unit cell of this compound is very close in value to the *a* parameter of $SiPb_2Se_4$, while the *c* parameter is very similar to the *a* parameter of $SiPb_2S_4$ (or to the *c* parameter, if the space group is chosen as $P2_1/a$). The space group of $GeSr_2S_4$ is reported to be $P2_1/m$. Thus a close relationship exists between the structures of $GeSr_2S_4$, $SiPb_2S_4$, and $SiPb_2Se_4$. In fact, the packing of the anions is extremely similar in the three structures, with severe distortions imposed by the different symmetries; the positions occupied by the Sr atoms in $GeSr_2S_4$ are similar to those occupied by the Pb atoms in $SiPb_2S_4$ and $SiPb_2Se_4$. It should be noted, however, that the set of tetrahedral voids occupied by Ge in $GeSr_2S_4$ is not the same which is occupied by Si in $SiPb_2S_4$ and $SiPb_2Se_4$, and this is probably the reason for the doubling of one of the axes in $SiPb_2S_4$ and $SiPb_2Se_4$.

The structure for $SiPb_2S_4$ bears no relationship to that of $GePb_2S_4$ (*2*), even though the space group is the same. The coordination numbers for Ge and Pb are the same but the configuration around Pb is a very distorted octahedron capped on one face instead of a capped trigonal prism.

References

1. K. KUGIMIYA AND H. STEINFINK, *Inorg. Chem.* **7**, 1762 (1968).
2. K. SUSA AND H. STEINFINK, *J. Solid State Chem.* **3**, 75 (1971).
3. P. HAGENMULLER AND G. PEREZ, *C. R. Acad. Sci.* **260**, 167 (1965).
4. "International Tables for X-ray Crystallography," Vol. III. Kynoch Press, Birmingham, England (1962).
5. M. MACK, *Norelco Rep.* **12**, 40 (1965).
6. E. PHILIPPOT, M. RIBES, AND M. MAURIN, *Rev. Chim. Min.* **8**, 99 (1971).