JOURNAL OF SOLID STATE CHEMISTRY 97, 29–35 (1992)

Structure and Properties of a New Compound $AgTaS_3$

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Received November 13, 1990; in revised form July 31, 1991

A new silver tantalum sulfide $AgTaS_3$ was prepared by heating in a sealed silica tube at 500°C for 4 days. The X-ray powder diffraction patterns of $AgTaS_3$ were indexed on the basis of an orthorhombic cell (space group $Cmc2_1$) with lattice constants of $a = 3.3755(2)$ Å, $b = 14.0608(11)$ Å, and $c = 7.7486(7)$ Å. The measured density was 6.82(3) g cm^{-3}, which is consistent with $Z = 4$. A structure model being built up with TaS_3 chain blocks was proposed, and the refinement was performed using intensity data of X-ray powder diffraction. Electrical resistivity measurements show this material to be semiconducting. © 1992 Academic Press, Inc.

Introduction

The silver tantalum sulfides have been paid considerable attention in recent years in terms of intercalation chemistry. Four ternary compounds, Ag_xTaS_2 ($P6_3/mmc$, $0 < x < 0.08$), $Ag_{1/3}TaS_2$ ($R\bar{3}m$), $Ag_{2/3}TaS_2$ ($P6_3/mmc$), and $Ag_xTa_{1+y}S_2$ ($R\bar{3}m$), are known in the Ag–Ta–S system (*1–6*). All of their crystal structures are closely related to the host 2H–TaS_2 and/or 6R–$Ta_{1+x}S_2$, where the metal atoms of TaS_2 sandwiches are characterized by the trigonal prismatic coordinations of S atoms. Except for these intercalation compounds, however, little is known about the phase relations of the ternary compounds in the Ag–Ta–S system at higher temperatures.

In the course of investigation of the Ag–Ta–S system we have recently discovered the new ternary compound $AgTaS_3$ with an orthorhombic cell, $a \simeq 3.38$ Å, $b \simeq 14.06$ Å, and $c \simeq 7.75$ Å (*7*). In this paper we report the phase relations, the crystal structure, and the electrical properties of $AgTaS_3$.

Experimental

For the preparation of silver tantalum sulfides, tantalum (3*N*6), sulfur (6*N*), and Ag_2S (3*N*) powders were used as starting materials. Initially $TaS_{1.97}$ was prepared from the elements at 600°C and employed as a source material. Ternary sulfide samples were prepared by mixing Ag_2S, $TaS_{1.97}$, and S powders in the stoichiometric ratios. The ingredients were mixed in an agate mortar, pressed into pellets (radius: 7 mm), and sealed in evacuated silica tubes at less than 10^{-3} Torr. The heat treatments were carried out at 500–600°C for 1–4 days and then the tubes were quenched in water. The composition of the pure tantalum sulfides was determined by oxidizing them in air to Ta_2O_5 at 1000°C. Density measurements were carried out by the flotation method, using CCl_4.

Powder samples were identified using

0022-4596/92 $3.00

TABLE I

RESULTS OF PHASE IDENTIFICATION OF SILVER TANTALUM SULFIDES

Composition Ag : Ta : S	Temperature (°C)	Time (days)	Phase found
1 : 2 : 6	500	5	$AgTaS_3 + TaS_3 + TaS_2$
1 : 1 : 3	500	4	$AgTaS_3$
	600	1	$AgTaS_3$
	650	1	unknown phase
3 : 1 : 4	500	4	$AgTaS_3 + Ag_7TaS_6$
29 : 9 : 32	500	4	$Ag_7TaS_6 + AgTaS_3$
7 : 1 : 6	500	4	Ag_7TaS_6
11 : 1 : 8	500	4	$Ag_7TaS_6 + Ag_2S$
23 : 7 : 20	500	5	$Ag + Ag_2S + Ag_{2/3}TaS_2$

X-ray powder diffraction methods. The X-ray diffraction intensity data were collected with a step scan procedure on a Rigaku diffractometer (Geigerflex, RAD-B system) using graphite-monochromated Cu*Kα* radiation. In order to examine the crystal symmetry, electron diffraction patterns were taken from the crushed particles using a 100-KV electron microscope (Hitachi-500-type). The lattice parameters were calculated by a least-squares method. The structure refinement of the compound was performed using the total pattern fit program RIETAN (*8*) based on the Rietveld method (*9*).

Electrical resistivity and Hall effect of $AgTaS_3$ were measured on a sintered pellet using a standard dc four-probe method in a helium atmosphere. Electrical contacts were made by Au paste.

Results and Discussion

Phase Relations and Thermal Stability

Several kinds of silver tantalum sulfides with different compositions were prepared. Some of the representative experimental results are listed in Table I. An isothermal section of the tentative phase diagrams of the Ag–Ta–S system at 500°C is shown in Fig. 1. This diagram was constructed on the basis of our experimental results and from the binary Ta–S and Ag–S phase relations (*10–12*). At 500°C we found two new compounds; one is a face-centered cubic phase, Ag_7TaS_6, and the other is an orthorhombic phase, $AgTaS_3$. The compound Ag_7TaS_6 with a lattice constant of $a \simeq 10.51$ Å has been shown to belong to the argyrodite family, which was first designated by Khus *et al.* (*13*). A detailed description of the crystal structure of Ag_7TaS_6 is given elsewhere (*14*). The compound $AgTaS_3$ was obtained as a sintered pellet after heating at 500°C for 4 days. With respect to thermal stability, however, $AgTaS_3$ was not stable above 650°C. It transformed to an unknown high-temperature phase. The equilibriated sulfur pressure of this phase was estimated to be 1.74 atm at 675°C from the weight of sulfur deposited on the wall of the silica tube after quenching.

Structure Determination

The X-ray powder diffraction patterns of $AgTaS_3$ were refined to give an orthorhombic unit cell with a = 3.3755(2) Å, b = 14.0608(11) Å, c = 7.7486(7) Å, and V = 367.77(4) $Å^3$, where standard deviations in units of the last decimal are given in brack-

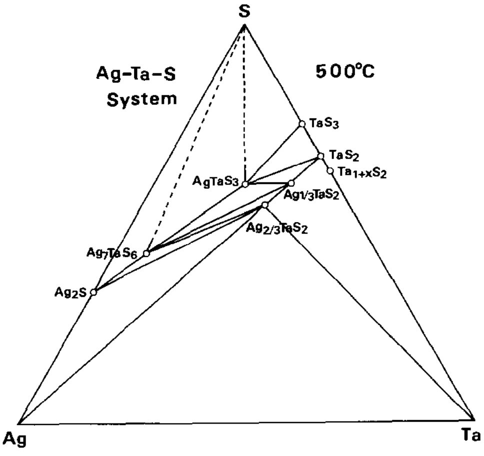

FIG. 1. Isothermal section of the tentative phase diagram of the Ag–Ta–S system at 500°C.

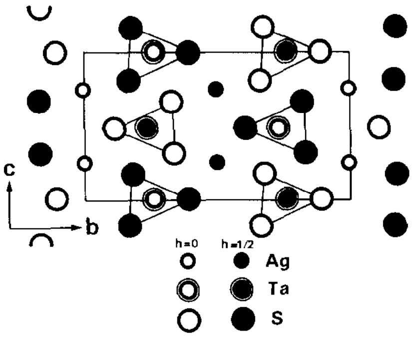

FIG. 2. Structure of orthorhombic $AgTaS_3$ projected on the (100) plane.

ets. A series of electron diffraction photographs indicated the following systematic reflection conditions:

hkl; $h + k = 2n$, $0kl$; $k = 2n$,
$h0l$; $h = 2n, l = 2n$, $hk0$; $h + k = 2n$,
$h00$; $h = 2n$, $0k0$; $k = 2n$,
$00l$; $l = 2n$.

These results uniquely determine the space group as $Cmc2_1$ (No. 36). The Laue group is mmm (D_{2h}). The measured density of this compound was $d_m = 6.82(3)$ g cm^{-3}, which means that the unit cell contains four formula units.

The crystal structure analysis was performed using X-ray powder diffraction data due to the difficulty in obtaining single crystals. As a first step, a structure model of $AgTaS_3$ was embodied after some trials. As shown in Fig. 2, the starting structure was constructed on the basis of the combination of TaS_3 units with a trigonal prismatic coordination by sulfur and Ag atoms occupying the octahedral interstices of sulfur packings. Intensity data in the range of d-spacings from 4.2267 to 1.0055 Å were used and nine positional parameters, three isotropic thermal parameters (for Ag, Ta, and S), and one scaling factor were refined from the initial parameters. A preferred orientation correction (*15*) was made, because this material showed strong (010) preferred orientation. The equation for the preferred orientation factor P in the program RIETAN is represented as $P = P_1 + (1 - P_1)\exp[-P_2q^2]$, in which q is the acute angle in radians between the diffraction plane and the selected preferred orientation plane (010). After several cycles, P_1 and P_2 converged to 0.61 and 2.26, respectively. The agreement of observed and calculated patterns was satisfactory: $R_{wp} = 13.03\%$, $R_p = 10.26\%$, $R_I = 10.65\%$, and $R_F = 5.13\%$ for $B(Ag) = 2.8(3)$, $B(Ta) = 0.6(2)$, and $B(S) = 0.3(5)$. This result indicated the correctness of the structure model. Further refinement was attempted tentatively by employing the anisotropic thermal parameters for Ag and Ta atoms. The resulting agreement factors were improved as follows: $R_{wp} = 9.61\%$, $R_P = 7.65\%$, $R_I = 6.59\%$, and $R_F = 3.73\%$, with $U_{11}(Ag) = 0.093(8)$, $U_{22}(Ag) = 0.022(8)$, $U_{33}(Ag) = -0.004(71)$, $U_{23}(Ag) = -0.020(12)$, $U_{11}(Ta) = 0.029(4)$, $U_{22}(Ta) = 0.011(4)$, $U_{33}(Ta) = -0.008(3)$, $U_{23}(Ta) = 0.004(11)$, and $B(S) = 0.8(4)$. However, it should be noted that structure analyses of single crystals are absolutely necessary in order to obtain the correct information on the temperature factors relating to anisotropic properties of Ag and Ta atoms. The observed and calculated X-ray powder diffraction profiles of $AgTaS_3$ are shown in Fig. 3, where the experimental data are plotted by dots and Bragg positions are indicated as vertical lines. The difference of ΔY between the observed and calculated profiles is also shown in the bottom of the figure. Final values of all structural parameters are given in Table II. The calculated intensities without the preferred orientation correction are listed in Table III, in comparison with the observed ones. The interatomic distances are listed in Table IV.

The crystal structure of $AgTaS_3$ is quite different from that of a similar kind of IB metal compound $CuTaS_3$ (*16*). As shown in

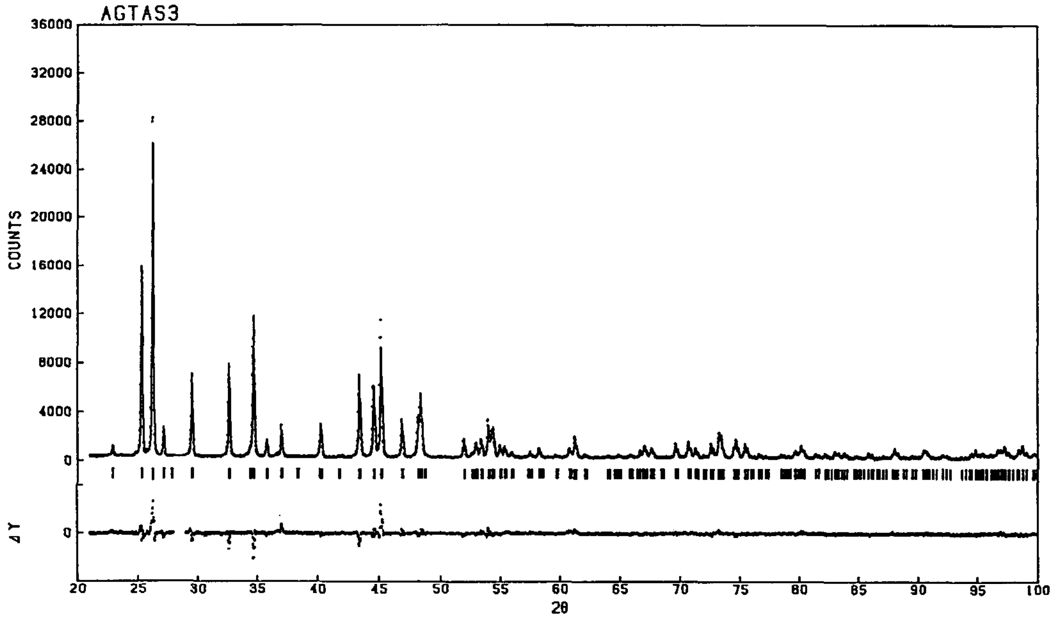

FIG. 3. The observed (dots) and calculated (solid line) X-ray powder diffraction patterns of $AgTaS_3$. The difference between the observed and calculated profiles is plotted below on the same scale. Intensity data in the Cu$K\alpha$ 2θ range from 28 to 29 are omitted for calculation due to the presence of a small amount of impurity phase.

Fig. 2, all the atoms of $AgTaS_3$ lie in the mirror planes at $x = 0$ and $\frac{1}{2}$. The Ta atoms are surrounded by eight S atoms forming bicapped trigonal prisms. There exist four chains of sulfur trigonal prisms stacked on top of each other by sharing triangular faces in the unit cell. These chains are running along the **a** direction and linked together through interchain Ta–S bonds to form slabs parallel to the **a**-**c** plane by shifting all neighboring prisms by half the unit-cell height. A van der Waals gap seems to lie between these slabs, and the Ag atoms occupy the octahedral sites between S atoms in the gap. With respect to the structural dimensionarity, it could be said from the presence of strong (010) preferred orientation that $AgTaS_3$ is a two-dimensional compound. Furthermore, it should be noted that the mutual arrangement of MX_3 coordination polyhedra of $AgTaS_3$ is quite different from those of quasi one-dimensional $ZrSe_3$, $NbSe_3$, and $TaSe_3$ (*17–19*).

The triangular face of the trigonal prism is formed by the following S–S pairs: S(1)–S(2) = 3.28 Å, S(1)–S(3) = 3.52 Å, and S(2)–S(3) = 2.76 Å. The former two distances are approximately the same as for those in TaS_6 prisms of 2H–TaS_2, 3.315 Å, implying that the sulfurs are not bonded to each other (*20*). On the contrary, the latter one reflects a slightly different situation. A distance of 2.76 Å is significantly larger than those of the usual polysulfide anion $(S_2)^{2-}$, such as 2.171 Å in FeS_2 (*21*) and 2.05 Å in NbS_3 (*22*), but is slightly shorter than the ordinary one, like 3.315 Å. Probably, the occurrence of such an intermediate S–S distance could be interpreted as a weakening of the S–S bond due to a bond formation between S and Ta atoms in a higher valence

TABLE II

STRUCTURE PARAMETERS OF AgTaS$_3$

Space group: $Cmc2_1$; a = 3.3755(2) Å, b = 14.0608(11) Å,
c = 7.7486(7) Å

Atom	Position	x	y	z	B_{eq} (Å^2)
Ag	4a	0.000	−0.002(7)	0.250[a]	3.0(6)
Ta	4a	0.000	0.2621(3)	−0.012(4)	0.8(2)
S(1)	4a	0.000	0.893(1)	−0.015(12)	1.0(4)
S(2)	4a	0.000	0.675(6)	0.164(11)	1.0
S(3)	4a	0.000	0.668(6)	0.814(12)	1.0

[a] Fixed on the least squares refinements. R_{wp} = 9.61%, R_p = 7.65%, R_I = 6.59%, R_F = 3.73%; Numbers of reflections used in the refinement = 126.

$$R_{wp} = \left\{ \frac{\left[\sum w_i \{ Y_{obs} - Y_{calc} \} \right]^2}{\sum w [Y_{obs}]^2} \right\}^{1/2}, R_p = \frac{\sum |Y_{obs} - Y_{calc}|}{\sum Y_{obs}},$$

$$R_I = \frac{\sum |I_{obs} - I_{calc}|}{\sum I_{obs}}, R_F = \frac{\sum |[I_{obs}]^{1/2} - [I_{calc}]^{1/2}|}{\sum [I_{obs}]^{1/2}},$$

where I = integrated Bragg intensity, Y = number of counts at angle 2, and w = weights.

state. If we assume a perfect pentavalent Ta atoms as a first approximation, the ionic charge of AgTaS$_3$ is expected to be formulated as Ag$^+$Ta^{5+}3S^{2-}. In this connection, however, XPS studies would be necessary for better understanding of the bonding nature of TaS$_3$ molecular blocks (*23*, *24*). The Ta atoms in the center of a trigonal prism are surrounded by the following six S atoms: two Ta–S(1) = 2.52 Å, two Ta–S(2) = 2.49 Å, and two Ta–S(3) = 2.53 Å. These values are in good agreement with those in TaS$_3$ (*20*). On the other hand, the Ag atoms are located near the center of the distorted octahedron of S atoms: two Ag–S(2) = 3.20 Å, two Ag–S(3) = 2.81 Å, and Ag–S(1) = 2.46 and 2.45 Å. It should be noted that the Ag atoms have a very large thermal factor of B_{eq} = 3.0 Å^2 (Table II). The same phenomenon has been reported for the octahedral Ag containing layered compound AgVP$_2$Se$_6$ (*25*). These results may suggest that there exists some instability of Ag atoms in certain lattices.

Electrical Resistivity of AgTaS$_3$

The electrical resistivity of a sintered polycrystalline sample of AgTaS$_3$ was measured from liquid N$_2$ temperature to 300 K. The uncertainty of the resistivity was estimated to be ±0.06 in logarithmic value due to the experimental limitation. As shown in

TABLE III

X-RAY POWDER DIFFRACTION DATA OF AgTaS$_3$

h	k	l	d_o	d_c	I_o	I_c[a]
0	2	0	7.041	7.030	37	45
0	2	1	5.208	5.207	8	7
0	0	2	3.874	3.874	4	5
0	4	0	3.516	3.515	53	41
0	2	2	3.393	3.393	100	100
1	1	0	3.283	3.282	10	11
1	1	1	3.023	3.022	27	38
1	3	0	2.739	2.739	30	33
0	4	2	2.603	2.603	1	1
1	3	1	2.583	2.583	46	59
1	1	2	2.504	2.504	7	7
0	2	3	2.4243	2.4244	10	7
0	6	1	2.2431	2.2431	1	1
1	3	2	2.2376	2.2366	14	11
0	4	3	2.0814	2.0814	28	33
1	5	1		2.0812		
1	1	3	2.0299	2.0298	29	32
0	6	2	2.0052	2.0052	45	33
0	0	4	1.9371	1.9371	15	12
1	5	2	1.8871	1.8870	16	16
1	3	3	1.8794	1.8792	24	24
0	2	4	1.8676	1.8676	1	2
0	8	0	1.7574	1.7576	8	5
0	6	3	1.7356	1.7356	1	1
1	7	0	1.7260	1.7262	7	6
0	8	1	1.7140	1.7141	7	4
0	4	4	1.6966	1.6966	15	11
2	0	0	1.6871	1.6878	15	21
1	7	1		1.6849		
1	1	4	1.6684	1.6683	5	4
1	5	3	1.6567	1.6572	4	6
2	2	0	1.6409	1.6412	3	2
0	8	2	1.6009	1.6006	2	2
1	3	4	1.5813	1.5816	5	3
2	0	2	1.5478	1.5473	3	1

[a] Intensities were calculated using the powder diffraction intensity program PPRG (*26*). I_o and I_c mean observed and calculated intensities, respectively.

Fig. 4, a plot of the resistivity ln ρ vs $1/T$ for $AgTaS_3$ reflects an extrinsic semiconducting behavior with an activation energy of approximately 6×10^{-2} eV at temperatures between 111 and 167 K. In this connection, the mobility of this material was determined by dc Hall voltage measurements. Negative Hall coefficients suggesting the presence of electronlike carriers were observed and R_H reached $-3.12\ cm^3/C$ at $T = 296$ K. Assuming a single carrier model, the number of carriers was calculated to be $5 \times 10^{-17}/cm^3$, which leads to a Hall mobility μ_H of about 1.2 cm^2/V sec. The observed electrical behavior could be explained as incorporation of additional atoms between slabs or the presence of S defects. However, further work on single crystals would be desirable to interpret the electrical property of the two-dimensional compound.

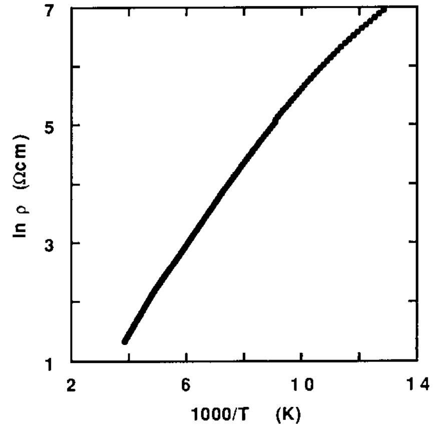

FIG. 4. Electrical resistivity ln ρ as function of the reciprocal temperature $1/T$.

Conclusion

The phase relations of the Ag–Ta–S system at 500–600°C were determined by sealed silica tube experiments. An orthorhombic new phase, $AgTaS_3$, was found together with a cubic phase, Ag_7TaS_6, which seemed to be a member of the "argyrodite" family. The compound $AgTaS_3$ has a lattice constant of $a \simeq 3.38$ Å, $b \simeq 14.06$ Å, and $c \simeq 7.75$ Å, with a space group $Cmc2_1$, and exhibits a type of layer structure. There exist one-dimensional TaS_3 chains running along the **a** axis. They are linked together through interchain S–Ta–S zig-zag bonds to form two-dimensional slabs parallel to the **a-c** plane. The Ag atoms are distributed statistically in the distorted octahedral sites of sulfur between these slabs. Resistivity measurement indicated that $AgTaS_3$ is an extrinsic semiconductor with an activation energy of 0.06 eV.

TABLE IV

Interatomic distances (Å) in $AgTaS_3$

Ta–Ta	2 × 3.376	S(1)–S(1)	2 × 3.376
–S(1)	2 × 2.52(2)	–S(2)	2 × 3.22(9)
–S(2)	2 × 2.49(2)	–S(3)	2 × 3.08(9)
–S(3)	2 × 2.53(2)	–S(2)	1 × 3.28(6)
–S(2)	1 × 2.57(3)	–S(3)	1 × 3.52(6)
–S(3)	1 × 2.78(3)		
		S(2)–S(2)	2 × 3.376
Ag–Ag	2 × 3.376	–S(3)	2 × 2.99(4)
–Ag	2 × 3.879	–S(3)	1 × 2.76(4)
–S(1)	1 × 2.46(9)		
–S(1)	1 × 2.45(9)	S(3)–S(3)	2 × 3.376
–S(2)	2 × 3.20(3)		
–S(3)	2 × 2.81(2)		

Acknowledgment

The authors thank Dr. F. Izumi for his help in the Rietveld analysis of X-ray diffraction data using the program RIETAN.

References

1. J. M. van den Berg, Thesis, University of Leiden (1966).
2. G. A. Scholz and R. F. Frindt, *Mater. Res. Bull.* **15,** 1703 (1980).
3. G. A. Wiegers, A. G. Gerards, H. Roede, R. J. Haange, and B. A. Boukamp, *Solid State Ionics* **28/30,** 1116 (1988).
4. J. Mahy, G. A. Wiegers, F. van Bolhuis, A. Diedering, and R. J. Haange, *Phys. Status Solidi A* **107,** 873 (1988).

5. G. A. Wiegers, R. J. Haange, and F. van Bolhuis, *Phys. Status Solidi A* **107**, 817 (1988).
6. B. Harbrecht and G. Kreiner, *Z. Kristallogr.* **178**, 81 (1987).
7. H. Wada and M. Onoda, *Chem. Lett.*, 705, (1990).
8. F. Izumi, *J. Cryst. Soc. Jpn.* **27**, 23 (1985) (in Japanese).
9. H. M. Rietveld, *J. Appl. Crystallogr.* **2**, 65 (1969).
10. F. Jellinek, *J. Less-Common Met.* **4**, 9 (1962).
11. M. Hansen and K. Anderko, "Constitution of Binary Alloys," McGraw–Hill, New York (1958).
12. F. C. Kracek, *Trans. Am. Geophys. Union* **27**, 364 (1946).
13. W. F. Kuhs, R. Nitsche, and K. Scheunemann, *Mater. Res. Bull.* **14**, 241 (1979).
14. H. Wada and M. Onoda, *J. Less-Common Met.* **175**, 209 (1991).
15. H. Toraya and F. Marumo, *Mineral. J.* **10**, 211 (1981).
16. S. A. Sunshine and J. A. Ibers, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **43**, 1019 (1987).
17. S. Furuseth, L. Brattas, and A. Kjekshus, *Acta Chem. Scand.* **A29**, 623 (1975).
18. A. Meerschaut and J. Rouxel, *J. Less-Common Met.* **39**, 197, (1975).
19. E. Bjerkelund, J. H. Fermor, and A. Kjekshus, *Acta Chem. Scand.* **20**, 1836 (1966).
20. A. Meerschaut, L. Guemas, and J. Rouxel, *J. Solid State Chem.* **36**, 118 (1981).
21. N. Elliot, *J. Chem. Phys.* **33**, 903 (1960).
22. J. Rijnsdorp and F. Jellinek, *J. Solid State Chem.* **25**, 325 (1978).
23. F. Jellinek, R. A. Pollak, and M. W. Shafer, *Mater. Res. Bull.* **9**, 845 (1974).
24. D. W. Bullett, *J. Phys. C: Solid State Phys.* **12**, 277 (1979).
25. G. Ouvrard and R. Brec, *Mater. Res. Bull.* **23**, 1199 (1988).
26. K. Kato, personal communication (1976).