Table V. Ratios of Effective Ionic Radii[37] of A^+ (CN 12) and X^- (CN 6) for $AScX_3$ Compounds

($KScCl_3$)[a] 0.906	($KScBr_3$) 0.837	($KScI_3$) 0.745
$RbScCl_3$ 0.950	$RbScBr_3$ 0.878	($RbScI_3$) 0.782
$CsScCl_3$ 1.039	$CsScBr_3$ 0.959	$CsScI_3$ 0.855

[a] Compounds in parentheses are unknown.

$RbScI_3$ were not obtained. This may be because of an inability to obtain good two-dimensional packing within the AX_3 layers when cations and anions are of very unequal size. Qualitative support for this consideration might be the radius ratios given in Table V for A^+ and X^- ions. Here effective ionic radii[37] for A^+ and X^- with CN 12 and 6, respectively, were chosen because their sums are close to the interatomic distances observed or estimated. In this point of view, the best packing should occur for a ratio of 1.00, which is approximately the case for $CsScCl_3$. If either the A^+ radius becomes smaller or the X^- radius enlarges, the radius ratio decreases and $AScX_3$-type compounds become less stable or do not exist. However, the case of $KScCl_3$, which therefore should exist, makes it clear that the radius ratio can not be the only reason for stability or instability of these compounds. A significant contribution of van der Waals energy to the lattice stability for the heavier elements may be a factor. The inability to reduce yttrium in $Cs_3Y_2Cl_9$ is surprising in view of the stability of other reduced phases such as Y_2Cl_3 and YCl.[10] Although the Y^{2+} ion may be too large for the $CsNiCl_3$-type structure, this should not be true in a $CsCdCl_3$ analogue. Perhaps reduced yttrium is stable only when strongly metal–metal bonded and not as the dipositive ion.

On the other hand, it is striking that only those ternary trihalides were observed that form a corresponding enneahalide, independent of the structure type for the latter. Additionally, only $AScX_3$-type compounds with the $CsNiCl_3$ structure type were observed, with all scandium–scandium distances equal and as short as possible. Whether this implies some kind of metal–metal interaction cannot be decided from structural data alone. However, it should be noted that the shared octahedra(trigonal antiprisms) are always elongated along the threefold axis and that the Sc–Sc distance ($=c/2$) seems to be quite normal in comparison with other $CsM^{II}Cl_3$ compounds of the first transition series. With the exceptions of Cr^{2+} and Cu^{2+}, where Jahn–Teller type elongations occur, the observed M–M distances decrease slightly for heavier metals as far as the known experimental data allow such a comparison. Unfortunately no special efforts have yet been made to determine lattice constants of these compounds systematically and with high precision, which makes a detailed structural comparison much more difficult.

Acknowledgment. G.M. is indebted to Deutsche Forschungsgemeinschaft, Bonn, for support which made this work possible.

Registry No. $CsScCl_3$, 65545-44-0; $CsScCl_2Br$, 77648-22-7; $CsScClBr_2$, 77648-23-8; $CsScBr_3$, 77648-24-9; $CsScI_3$, 77648-25-0; $RbScCl_3$, 77648-26-1; $RbScBr_3$, 77648-27-2; $Rb_3Sc_2Cl_9$, 12272-72-9; $Rb_3Sc_2Br_9$, 12431-62-8; $Cs_3Sc_2I_9$, 74472-54-1; $Cs_3Sc_2Br_9$, 12431-61-7; $Cs_3Sc_2Cl_9$, 12272-71-8; CsI_3, 12297-72-2.

---

(37) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751.

Contribution from the Department of Chemistry, Brown University, Providence, Rhode Island 02912,
the Army Materials and Mechanics Research Center, Watertown, Massachusetts 02172,
and the Exxon Research and Engineering Company, Linden, New Jersey 07036

Preparation and Properties of Poorly Crystallized CoS_2 and RuS_2

J. D. PASSARETTI, K. DWIGHT, A. WOLD,* W. J. CROFT, and R. R. CHIANELLI

Received November 11, 1980

Amorphous or poorly crystallized samples of RuS_2 and CoS_2 were made by sulfurizing $(NH_4)_2RuCl_6$ and $[Co(NH_3)_6]Cl_2$ at low temperatures with H_2S. The amorphous products were annealed under various conditions, and the resulting degree of crystallinity was determined. For RuS_2, the average crystallite sizes ranged from 26 Å for the poorly crystallized material to greater than 2000 Å for the well-crystallized material. CoS_2 average crystallite sizes ranged from 130 Å to greater than 2000 Å. The stoichiometry, appearance of the crystalline pyrite phases, cell parameters, and magnetic properties were studied as a function of annealing temperature.

Introduction

There has recently been reported[1] a technique for the preparation of a number of poorly crystallized platinum metal dichalcogenides. These materials were prepared by the reaction of the ammonium hexachlorometalate complex with hydrogen sulfide. X-ray diffraction patterns of these compounds resemble those obtained for materials which might be classified as being almost amorphous.[2,3] The presence of only a small degree of short-range order, as evidence by the shape of the X-ray diffraction pattern obtained, forms the basis for the term "poorly crystallized". This work describes the synthesis of amorphous CoS_2 from hexaamminecobalt(II) chloride, as well as a study of the properties of poorly crystallized CoS_2 and RuS_2 as a function of annealing temperature. The characterization methods employed were X-ray powder diffraction analysis, thermogravimetric analysis, scanning electron microscopy, and magnetic susceptibility.

Experimental Section

Preparation of RuS_2. Poorly crystallized RuS_2 was prepared from the reaction between hydrogen sulfide and ammonium hexachlororuthenate(IV) as reported previously.[1]

Preparation of CoS_2. Anhydrous $CoCl_2$ was prepared[4] from $CoCl_2 \cdot 6H_2O$ (Baker). The anhydrous $CoCl_2$ was ground thoroughly under nitrogen with use of an agate mortar and pestle. The sample

---

* To whom all correspondence should be addressed at Brown University.

(1) Passaretti, J. D.; et al. *Inorg. Chem.*, in press.
(2) Brill, R. *Z. Kristallogr.* **1928**, *68*, 387.
(3) Jones, F. W. *Proc. R. Soc. London, Ser. A* **1938**, *166*, 16.
(4) *Inorg. Synth.* **1957**, *5*, 154.

0020-1669/81/1320-2631$01.25/0 © 1981 American Chemical Society

Table I. Annealing Conditions and Cell Parameters for RuS_2

temp of anneal,[a] °C	a, Å	crystallite size, Å	temp of anneal,[a] °C	a, Å	crystallite size, Å
350	5.625 (2)	26 (5)	500	5.609 (2)	64 (6)
400	5.617 (2)	32 (6)	570	5.607 (2)	109 (11)
450	5.612 (2)	44 (6)	800	5.602 (2)	>2000

[a] Four days.

Table II. Annealing Conditions and Cell Parameters for CoS_2

temp of anneal,[a] °C	a, Å	crystallite size, Å	temp of anneal,[a] °C	a, Å	crystallite size, Å
250	5.520 (2)	133 (10)	500	5.532 (2)	500 (19)
320	5.522 (2)	156 (14)	800	5.533 (2)	>2000
360	5.525 (2)	176 (18)			

[a] Four days.

was transferred to a silica boat which was held in place by means of a clamshell furnace. The system was purged at a flow rate of 55 cm^3/min, first with nitrogen for 30 min and then with ammonia for 2 h, both at room temperature. Anhydrous cobalt(II) chloride reacts with ammonia gas to form hexaamminecobalt(II) chloride $[Co(NH_3)_6Cl_2]$.[5] The hexaamminecobalt(II) chloride is then treated with hydrogen sulfide for 2 h at room temperature to form poorly crystallized CoS_2. The hexaamminecobalt(II) chloride must be treated immediately with hydrogen sulfide because the complex oxidizes in air.[6] The reaction between hexaamminecobalt(II) chloride and hydrogen sulfide also produces ammonium chloride which is removed by extracting the product in a Soxhlet extractor with methanol for 24 h. The materials were extracted subsequently with carbon disulfide to remove any sulfur that may have been deposited onto the products. After extraction with carbon disulfide, the products were dried under vacuum.

Annealing Experiments. The products obtained after the extractions with methanol and carbon disulfide were annealed with excess sulfur (10 wt %) in evacuated sealed silica tubes at temperatures ranging from 250 to 800 °C. The excess sulfur was required to minimize formation of metal-rich sulfides. The temperatures and times of annealing are outlined in Tables I and II. After annealing, the samples were quenched to room temperature.

X-ray Analysis and Characterization. Powder diffraction patterns were obtained with a Norelco diffractometer using monochromated high-intensity Cu $K\alpha_1$ radiation ($\lambda = 1.5405$ Å). Initially, all products were examined by fast scans at 1° (2θ)/min in order to determine the presence of obvious impurities. Slow scans of 0.25° (2θ)/min were obtained for all single-phase samples in the range $12° \leq 2\theta \leq 120°$. Lattice parameters for the annealed samples of poorly crystallized RuS_2 and CoS_2 were determined by least-squares analysis with use of 2θ values from 45 to 90°.

Crystallite sizes were calculated from the peak widths by using the Scherrer equation[7-9]

$$D = k\lambda/(\beta \cos \theta)$$

where D = crystallite size, k = shape factor (a value of 0.9[7] was used in this study), λ = X-ray radiation wavelength (Cu $K\alpha_1$ wavelength = 1.5405 Å), and β = half-height width expressed in radians for the peak at 2θ (corrected for $K\alpha_2$ and instrumental broadening).

Thermogravimetric Analysis. The sulfur to metal ratio in the poorly crystallized and well-crystallized materials was determined by thermogravimetric analysis with use of a Cahn electrobalance (Model R.G.). Approximately 30 mg of finely powdered samples of each of the amorphous products was placed in a silica bucket and then subjected to thermogravimetric analysis. The thermogravimetric analysis of poorly crystallized RuS_2 was carried out under vacuum, but it was necessary to do thermogravimetric analysis of crystallized RuS_2 and both poorly and well-crystallized CoS_2 in a stream of argon/15% hydrogen to ensure complete reduction to the metal. The maximum temperature reached during the heating of the sample was 900 °C, and the rate of heating was 30 °C/h. The sample was kept at 900 °C until its weight was constant (10 h). After 10 h, the furnace was shut off and the sample was allowed to cool to room temperature. The weight lost by the sample could then be read from the recorded chart with an accuracy of 0.001 mg.

Table III. Preparation, Composition, and Magnetic Properties of RuS_2 and CoS_2

material	prepn	compn S:metal	magnetic properties
poorly crystallized RuS_2	as prepared from $(NH_4)_2RuCl_6$ at 250 °C	2.19:1	diamagnetic
crystallized RuS_2	annealed at 800 °C for 4 days	2.06:1	diamagnetic
poorly crystallized CoS_2	as prepared from $Co(NH_3)_6Cl_2$ at room temp	1.93:1	paramagnetic
crystallized CoS_2	annealed at 800 °C for 4 days	1.99:1	ferromagnetic

Magnetic Measurements. Magnetic susceptibility data were obtained with a Faraday balance equipped with a Cahn R.G. electrobalance, described elsewhere,[10] over a temperature range of 77–300 K for poorly crystallized and crystalline RuS_2. Measurements were performed at field strengths between 6.25 and 10.30 kOe. The balance was calibrated with the use of a platinum wire ($X_g = 0.991 \times 10^{-6}$ emu/g at 275 K). No corrections were made for core diamagnetism of the samples measured.

Magnetization measurements of CoS_2 were made with a Foner type vibrating-sample magnetometer manufactured by Princeton Applied Research, Princeton, N.J. Field-dependent measurements were made with fields up to 8.0 kOe. The magnetometer was calibrated relative to a sphere of high-purity nickel. Temperature-dependent magnetization curves were obtained from 77 to 200 K. The temperature was measured with a Chromel-P vs. gold–0.07 atom % iron thermocouple. The thermocouple was located within 6.5 mm of the sample outside the sample chamber.

Results

A sample of poorly crystallized RuS_2 was prepared by the sulfurization of $(NH_4)_2RuCl_6$ at 250 °C. Portions of the sample were annealed in sealed evacuated silica tubes with 10% by weight of excess sulfur. The annealing temperatures and conditions are given in Table I together with the cell parameters and calculated crystallite sites for the pyrite phase which was observed to form at annealing temperatures greater than 350 °C. Sulfur to ruthenium ratios were determined by thermogravimetric analysis for both the poorly crystallized and most crystallized forms of RuS_2 and are given in Table III, which also summarizes the magnetic susceptibility data obtained for these two samples.

A sample of poorly crystallized CoS_2 was prepared by the sulfurization of $[Co(NH_3)_6]Cl_2$ at room temperatures. Portions of the sample were annealed in sealed evacuated silica tubes with 10% by weight of excess sulfur. The annealing temperatures are given in Table II together with the cell parameters and calculated crystallite sizes for the pyrite phase which was observed to form at annealing temperatures greater than 250 °C. Sulfur to cobalt ratios were determined by thermogravimetric analysis for both the poorly crystallized and well crystallized forms of CoS_2 and are given in Table III, which also summarizes the magnetic susceptibility data obtained for these two samples.

---

(5) Brauer, G. "Handbook of Preparative Inorganic Chemistry", 2nd ed.; Academic Press: New York, 1965; Vol. 2, p 1516.
(6) Blitz, W.; Fetkehewer, B. *Z. Anorg. Allg. Chem.* **1914**, *89*, 97.
(7) Klug, H. P.; Alexander, L. E. "X-ray Diffraction Procedures"; Wiley: New York, 1974.
(8) Snell, F. D.; Hilton, C. L. "Encyclopedia of Industrial Chemical Analysis"; Wiley: New York, 1966; Vol. 3.
(9) Croft, W. J. *Ann. N.Y. Acad. Sci.* **1956**, *62*, 464.
(10) Morris, B.; Wold, A. *Rev. Sci. Instrum.* **1968**, *39*, 1937.

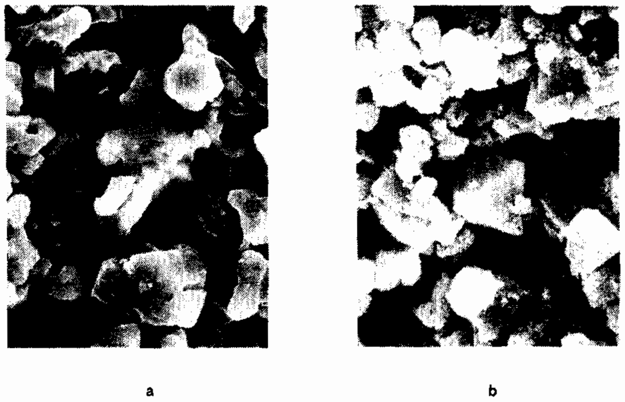

Figure 1. Photomicrographs of RuS_2 at 5000×: (a) before anneal; (b) after annealing at 800 °C/4 days.

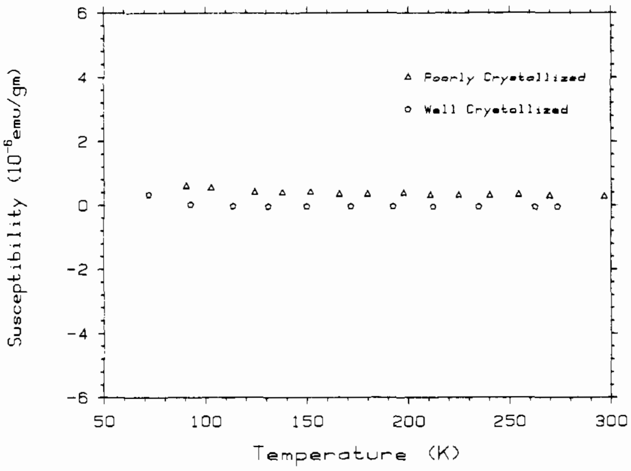

Figure 2. Magnetic susceptibility of well-crystallized and poorly crystallized RuS_2.

Discussion

Thermogravimetric analysis of the poorly crystallized RuS_2, as prepared from the sulfurization of $(NH_4)_2RuCl_6$ with H_2S, indicated a composition having the sulfur to ruthenium ratio of 2.19:1. The sample annealed at 800 °C gave a sulfur to ruthenium ratio of 2.06:1. These results are consistent with the decrease in the cell parameters of RuS_2 observed for samples annealed at different temperatures. At 350 °C, RuS_2 begins to crystallize with a pyrite structure [a = 5.625 (2) Å]. As the annealing temperature is increased, the samples become more crystalline, as evidenced by sharper powder X-ray diffraction patterns and the photomicrographs shown in Figure 1. The sample annealed at 800 °C shows clearly the development of octahedral faces. It can be seen from Table I that the average crystallite size of RuS_2 annealed at 350 °C was found to be 26 Å and increased as a function of temperature, reaching a value of over 2000 Å for the sample annealed at 800 °C. The magnetic properties of poorly crystallized and well-crystallized samples of RuS_2 are given in Figure 2. The results indicate that the samples are diamagnetic, which is expected for low-spin state d^6 Ru.

Thermogravimetric analysis of the poorly crystallized CoS_2 indicated a composition having a sulfur to cobalt ratio of 1.96:1. The sample annealed at 800 °C gave a sulfur to cobalt ratio of 1.99:1. The increase in the sulfur ratio is consistent with an increase in the cell parameters observed for samples annealed at different temperatures, as indicated in Table II.

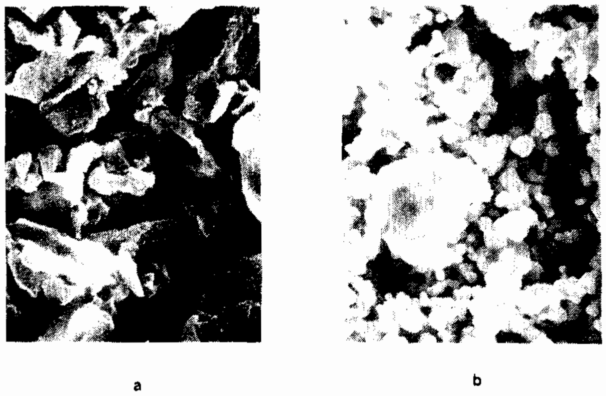

Figure 3. Photomicrographs of CoS_2 at 5000×: (a) before anneal; (b) after annealing at 800 °C/4 days.

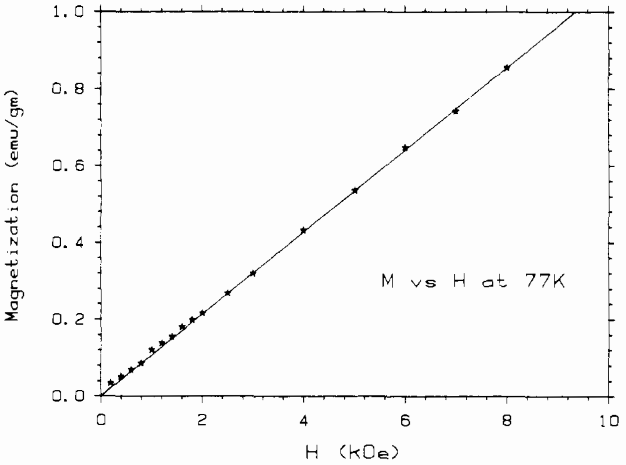

Figure 4. Field dependence of the magnetization of CoS_2 before annealing, showing paramagnetic behavior.

Table IV. Comparison of the Curie Temperature of CoS_2 Prepared in This Study with Other Reported Values

prepn	compn S:Co	T_C, K	ref
from $Co(NH_3)_6Cl_2$ annealed at 800 °C	1.99:1	128	this study
from CoS + S	1.97:1	122	11
from Co + S		124	12
from Co + S		130	13

At 250 °C, CoS_2 began to crystallize with a pyrite structure [a = 5.520 (2) Å]. From Table II, it can be seen that the average crystallite size of CoS_2 prepared at 250 °C was found to be 133 Å and increased as a function of temperature, reaching a value of over 2000 Å for the sample annealed at 800 °C. The photomicrographs of CoS_2 shown in Figure 3 indicate the development of octahedral faces on samples which were annealed at 800 °C.

The results of the magnetic measurements indicate that crystallized CoS_2 has a Curie temperature of 128 K. A comparison of the Curie temperature and comparison of crystallized CoS_2 prepared in this study, with values obtained by previous investigators, is given in Table IV. It can be seen from the results that the reported Curie temperatures are in good agreement. The results of the magnetic measurements for the amorphous CoS_2 samples, as seen in Figure 4, indicate paramagnetic behavior and hence the absence of long-range magnetic order. When a poorly crystallized CoS_2 sample is annealed at 250 °C (average crystallite size = 133 Å), there is an onset of ferromagnetic behavior but with an anomalous Curie temperature. A residual magnetism is observed at 200

---

(11) Morris, B.; Johnson, V.; Wold, A. *J. Phys. Chem. Solids* **1967**, *28*, 1565.
(12) Adachi, K.; Sato, K.; Takeda, M. *J. Appl. Phys.* **1968**, *39*, 900.
(13) Miyahara, S.; Teranishi, T. *J. Appl. Phys.* **1968**, *39*, 896.

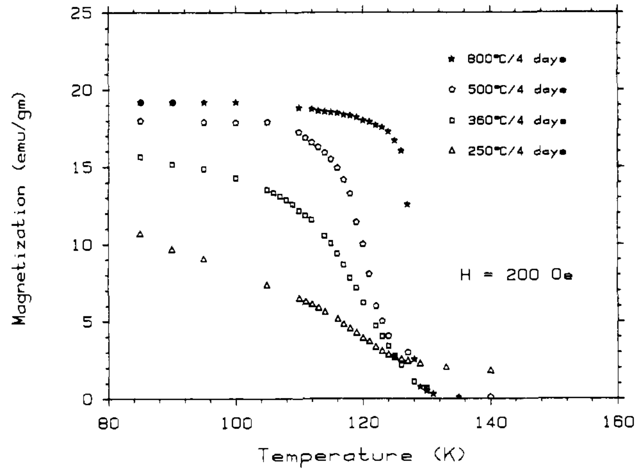

Figure 5. Temperature dependence of the magnetization of annealed CoS_2, showing the variation with annealing condition.

Oe as well as a higher Curie temperature than observed for well-crystallized CoS_2.

When CoS_2 is annealed at higher temperatures, the stoichiometry more nearly approaches a sulfur to cobalt ratio of 2:1, and the observed anomolies in the magnetic behavior disappear. These results are shown in Figure 5. It is clear that the metal to sulfur ratios must undoubtedly influence the relative strengths of the ferromagnetic and antiferromagnetic interactions present in the different annealed samples studied. It was shown previously[14] that selenium substitution for sulfur in CoS_2 increases the cell size and reduces the strength of the ferromagnetic interactions with respect to the antiferromagnetic interactions. It is, therefore, not surprising that the poorly crystallized samples of CoS_2, which are rich in cobalt, would have smaller cell constants, and, as a result, the ferromagnetic interactions would increase in strength. This is consistent with the higher Curie temperatures and residual magnetism measured at low field for the cobalt-rich samples.

Conclusions

Poorly crystallized RuS_2 and CoS_2 were prepared by the reaction of hydrogen sulfide with anhydrous ammonium hexachlororuthenate(IV) at 180 °C and hexaamminecobalt(II) chloride at room temperature, respectively. Both materials crystallize with the pyrite structure upon annealing. The onset of crystallization is observed at 350 °C for RuS_2 and 250 °C for CoS_2. Physical characteristics such as sulfur to metal stoichiometry, crystallite sizes, lattice parameters, and magnetic properties as a function of annealing temperatures were studied. As samples are annealed, the lattice parameters of the products as well as their composition approach those obtained for the well-crystallized sulfide. Magnetic studies show poorly crystallized and well-crystallized RuS_2 to be diamagnetic, which indicates low-spin d^6 ruthenium.

Amorphous CoS_2 is sulfur deficient. As samples are annealed as a function of temperature, the values of the lattice parameter approach that reported for well-crystallized CoS_2,[15] having a sulfur to cobalt ratio of 1.99:1. Magnetic studies indicate that poorly crystallized CoS_2 is paramagnetic. However, as the annealed CoS_2 samples begin to crystallize, ferromagnetism is observed to occur but with a higher Curie temperature compared to that observed for well-crystallized CoS_2. As the crystallinity increases, the Curie temperature approaches the value for pure CoS_2, i.e., 128 K.

Acknowledgment. The authors wish to thank the Exxon Research and Engineering Co., Linden, NJ, for the support of J.D.P. Also, acknowledgement is made to the National Science Foundation, Washington, D.C., Grant No. DMR-79-23605, for support of K.D. The Materials Research Laboratory Program at Brown University is also acknowledged.

Registry No. CoS_2, 12013-10-4; RuS_2, 12166-20-0; $Co(NH_3)_6Cl_2$, 13874-13-0; H_2S, 7783-06-4.

---

(14) Johnson, V.; Wold, A. *J. Appl. Phys.* **1969**, *40*, 1287.

(15) Kuznetsov, V. G.; et al. *Inorg. Mater.* (*Engl. Transl.*) **1965**, *1*, 617.