JOURNAL OF SOLID STATE CHEMISTRY 14, 349–353 (1975)

Preparation of the $HgCr_2(Se_xS_{1-x})_4$ Type Compounds and the X Ray Control of the Process of Formation of their Spinel Structures

I. OKOŃSKA-KOZŁOWSKA, D. KONOPKA, M. JELONEK, J. HEIMANN,
J. PIETKIEWICZ, AND A. CHEŁKOWSKI

Uniwersytet Śląski, Instytut Fizyki, ul. Uniwersytecka 4, 40-007 Katowice, Poland

Received June 20, 1974; in revised form October 7, 1974

Compounds of the $HgCr_2(Se_xS_{1-x})_4$ type were prepared for $0.750 \leqslant x \leqslant 0.250$ by thermal synthesis from parent elements. Individual reaction stages were controlled röntgenographically. The values of electrical conductivity activation energy of the compounds have been calculated and chemical analyses of the substances prepared have been developed.

Die Substanzen $HgCr_2(Se_xS_{1-x})_4$ wurdem im Bereich $0.750 \leqslant x \leqslant 0.250$ aus stöchiometrischen Mischungen der Elemente in evakuierten Quarzampullen durch termische Synthese hergestellt. Der Reaktionverlauf wurde Röntgenographisch untersucht. Es wurde die Leitfähigkeitsaktivierungsenergie der hergestellten Substanzen bestimmt und die chemische Analyse bearbeitet.

1. Introduction

Investigations of anionic substituted mixed spinels have not been so far undertaken to a great extent (*1–4*). The works cited deal with $ZnCr_2(Se_xS_{1-x})_4$, $CdCr_2(Se_xS_{1-x})_4$, $ZnCr_2(Se_{1-x}Te_x)_4$, $CuCr_2(Se_xS_{1-x})_4$, and $CuCr_2(Se_{1-x}Te_x)_4$ compounds, from among which only $CdCr_2(Se_xS_{1-x})_4$ has been prepared throughout the whole substitution range. In our work attempts were made to prepare the compounds, the crystallographic data a, λ, and u, some of which have been recently published (*5*). The compounds investigated are presented in Table I.

2. Preparation of Compounds

The compounds presented in Table 1 were prepared from parent elements (Hg, Cr, S, Se) by thermal synthesis in quartz ampoules (d = 100–150 mm, $\varphi = 20$–30 mm) in an oxygen-free atmosphere. Since the process of formation of these compounds proceeds very slowly, their thermal treatment was carried out several times, grinding a compound each time in an agate mortar. The following sintering temperatures were used: for the samples with $0.500 \leqslant x \leqslant 1$, 400–650°C; for the samples with $0 \leqslant x \leqslant 0.375$, 600–800°C.

3. The X Ray Control

The phase analysis was carried out using the X ray diffractometer Dron-1 (Cu_K radiation) at a scintillation counter angular velocity of 2°/min.

The reaction was controlled röntgenographically after successive thermal treatments. Spectra of all the compounds in initial reaction stages revealed the presence of lines originating from intermediate reaction products HgS, HgSe, Cr_2S_3, and Cr_2Se_3. It was also noted that the lines originated from the spinel phase, and their intensity depended on the assumed stoichiometric composition. The number and intensity of the lines originating from the spinel phase diminished as x tended to about 0.500. The results of X ray analysis revealed that single phases were obtained for $x = 0$, 0.0625, 0.125, 0.750, 0.875, 0.9375, and 1. The compounds with $x =$ 0.250, 0.375, 0.500, and 0.625 were reacted in 70, 0, 20, and 60%, respectively. The compound for $x = 0.750$ was magnetically

TABLE I

THE ACTIVATION ENERGIES OF CONDUCTIVITY E (eV) FOR COMPOUNDS OF THE $HgCr_2(Se_xS_{1-x})_4$ TYPE

Number	X	Compound	E (eV)	Temperature range (°C)
1	1	$HgCr_2Se_4$	0.36	25–500
2	0.9375	$HgCr_2Se_{3.75}S_{0.25}$	0.45	30–550
3	0.875	$HgCr_2Se_{3.5}S_{0.5}$	0.53	50–550
4	0.750	$HgCr_2Se_3S$	0.68	50–600
5	0.125	$HgCr_2Se_{0.5}S_{3.5}$	1.3	125–600
6	0.0625	$HgCr_2Se_{0.25}S_{3.75}$	1.65	100–550
7	0	$HgCr_2S_4$	0.36	20–100
			1.2	100–400
			2.0	400–600

purified and a spinel content of about 80% was obtained.

4. Conclusions

It was found that the process of formation of anionic substituted compounds runs very slowly. In some cases ($x = 0.500$) even several long-term soakings did not result in the spinel formation. During the preparation of these compounds there both the anion and cation must occur. The diffusion and recrystallization processes in anionic substituted systems are additionally impeded with a small mobility of anions of large ionic radii (*6*). Difficulties encountered during their preparation can be attributed to differences between the radii of anions forming the spinel lattice which can be of considerable significance in diffusion processes.

All the $HgCr_2(Se_xS_{1-x})_4$ type compounds prepared, for which the spinel structure was obtained, were thermally instable above 650°C. Attempts to prepare the compounds with $x = 0.500$ using $HgCr_2Se_4$ and $HgCr_2S_4$ spinelas are continuing.

5. The Electric Properties of the $HgCr_2(Se_xS_{1-x})_4$ Type Compounds

The temperature dependence of the electric conductivity of the compounds obtained was investigated over the 20–500°C range. Measurements at higher temperatures have not been performed due to a strong thermal decomposition of these compounds. The measurements were carried out by the current-voltage method providing a linear increase of temperature with time (*7*). A sample compacted in a quartz capillary (diameter, 0.65; length, 10–20 mm) was placed in an evacuated quartz vessel. This system assured a good electric contact, maintained the form of the sample, and limited its evaporation during measurements at higher temperatures. Under such conditions the density of samples was 70–85% relative to X-ray density. Also, note that the total resistance of a sample is large enough to make possible the use of voltages eliminating the contact effects (2V).

The graphs of the dependence of $\ln\sigma$ on reciprocal temperature were plotted using the measurement results (Fig. 1) and the electrical conductivity activation energy values were calculated from the slopes of rectilinear sections. These values are compiled in Table I. It can be seen that values of the activation energy rise with the sulfur content. For $HgCr_2Se_4$ $E = 0.36$ eV. This value is less than the width of the forbidden band evaluated by the optical method (*8*). This indicates that $HgCr_2Se_4$ is an extrinsic semiconductor. However, this value is greater than that obtained in (*9*), which can be explained by the fact that the measurements were carried out in the higher temperature range, where levels of a greater activation energy are responsible for the

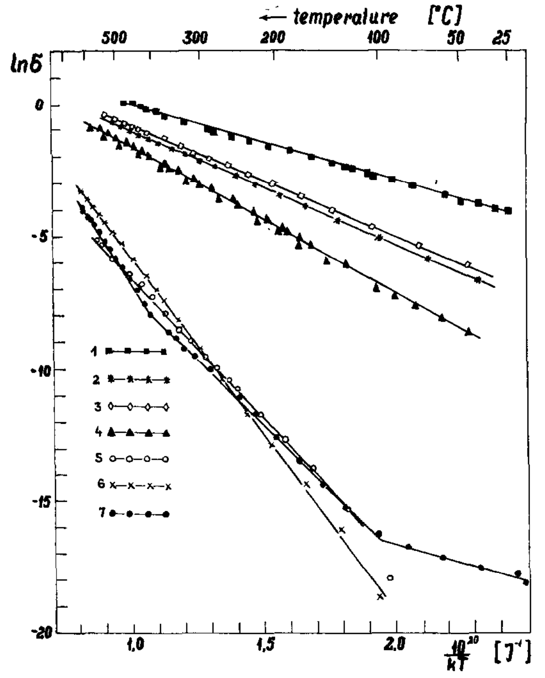

FIG. 1. The temperature dependence of lnσ for the compounds investigated.

conductivity. Electric contacts at grain boundaries also affect the activation energy E and can account for its increase. $HgCr_2Se_4$ differs from other compounds in that it shows three different E values in various temperature ranges (see Table I). The E value obtained for the 400–600°C range corresponds to a general trend of increase of E with x.

For the compounds 1–4, showing a sufficiently high electrical conductivity, $\sigma > 0.25 \times 10^{-5}$, the Seebeck effect was measured. The temperature of the copper vertical electrodes placed between the cylindrical samples was measured with Cu–(Cu–Ni) thermocouples. The thermoelectric force between an upper heated electrode and a lower one was measured using a Kipp and Zonen Mikrograph-BD6 recorder.

TABLE 2

RESULTS OF CHEMICAL ANALYSIS

Number	Se (% obs.)	Se (% calc.)	S (% obs.)	S (% calc.)	Cr (% obs.)	Cr (% calc.)	Hg (% obs.)	Hg (% calc.)
1	49.90	50.91	—	—	17.20	16.76	32.17	32.33
2	46.17	48.64	1.36	1.32	17.07	17.09	32.64	32.95
3	42.69	46.29	2.84	2.69	17.40	17.42	30.33	33.60
4	38.88	41.30	5.55	5.59	18.90	18.13	30.04	34.97
5	7.39	8.65	27.8	24.59	26.70	22.79	38.39	43.96
6	4.42	4.44	27.3	27.04	23.41	23.39	41.59	45.12
7	—	—	30.3	29.63	23.96	24.03	42.40	46.34

The mean calculated $\alpha = \Delta V/\Delta T$ mV/°K values for individual compounds are

$$\alpha_4 = +0.55$$
$$\alpha_3 = +0.47$$
$$\alpha_2 = +0.50$$
$$\alpha_1 = +0.56.$$

The investigations have been carried out over the 20–200°C range. The coefficients determined are positive, indicating the *p*-type conductivity of the compounds studied. This can be attributed to a creation of acceptor centres due to an insufficient amount of Hg (see Table II), which causes part of the Cr atoms to oxidize to Cr^{4+}, creating electron traps.

6. Chemical Analysis

The results of analysis of the compounds obtained are given below. The main difficulties encountered in the course of the analysis were the dissolution of compounds and volatility of some elements, e.g., Hg. The procedure employed permitted the use of known methods of determination, although some modifications were necessary.

The attempts to determine Cr by the versenate method (*10*) were unsuccessful. From among the methods of oxidation of Cr(III) (*11*, *12*), that employing $HC10_4$ (*13*, *14*) appeared to be the best.

It was very difficult to determine Hg due to the great volatility of this element. The attempts to apply the versenate method (*10*) failed. Moreover, the method of distillation of Hg (*14*) consisted in a conversion of this element into an amalgam, was unsuccessful.

The thio and seleno-spinels prepared were analyzed for Cr, Hg, S, and Se. The results are given in Table II. The samples were dissolved in aqua regia or in concentrated (70%) boiling perchloric acid.

Chromium (*13*)

The sample was treated with concentrate perchloric acid and kept boiling for about 20 min. The cooled solution was diluted with water and treated with 0.1 *N*-ferrous-ammonium sulfate. Unoxidized by dichromate ions, an excess of ferrous salt was then titrated with 0.1 *N* potassium permanganate using ferroin as an indicator.

Mercury (*16*)

The sample was dissolved as above. After the oxidation of Cr(III) to Cr(VI) and driving off perchloric acid fumes, the solution was diluted with water and treated with 2 *N* HNO_3 to pH ~ 5. HgS was precipitated with thioacetamide, also which precipitated sulfur and selenium. The precipitate was then purified through several washings with concentrated H_2SO_4 (the dissolution of Se) and concentrated carbon disulphide (the dissolution of S), and dried at 105°C.

Sulfur (*13*)

Sulfur was precipitated in the form of barium sulphate. This method was chosen because of the oxidation of S to S(VI) during the dissolution of spinels in aqua regia. To accelerate the precipitation, a barium salt solution was added to the hot reaction mixture. The filter was burnt slowly with a good access of the air and then calcinated at 800°C. To avoid the coprecipitation of Cr, the 0.1 *N* EDTA solution was added after the evaporation of samples with aqua regia and then with concentrated HCl. In the samples containing Se, it was filtered off after reduction with HCl.

Selenium (*15*)

The samples were dissolved in aqua regia and the solution was evaporated to dryness to drive off nitrogen oxides and mercury chloride. The dry residue was treated with about 100 ml of concentrated HCl. Then about 100 ml 10% hydrazine solution was added and the liquid was boiled for several minutes. The red precipitate was filtered off through a sintered filter G4, washed with water and alcohol, and dried at 40°C for 3 hr and then at 140°C for 30 min.

Acknowledgments

This work was supported by The Institute of Physics, Polish Academy of Science.

References

1. P. K. Wojtowicz, P. K. Baltzer, and M. Robbins, *J. Phys. Chem. Solids* **28**, 2423 (1967).
2. K. Obayashi, Y. Tominaga, and S. Iida, *J. Phys. Soc. Japan* **24**, 1173 (1968).
3. E. Riedel and E. Horvath, *Z. Anorg. Allgem. Chem.* **371**, 248 (1969).
4. E. Riedel and E. Horvath, *Z. Anorg. Allgem. Chem.* **399**, 219 (1973).
5. D. Konopka and I. Kozłowska, A. Chełkowski, *Phys. Letters*, **44a**, 289 (1973).
6. H. Schmalzried, *Z. Phys. Chem. (Frankfort)* **33**, 111 (1962).
7. I. Okońska-Kozłowska, J. Heimann, and A. Chełkowski, *Z. Anorg. Allgem. Chem.* **407**, 109 (1974).
8. H. W. Lehmann and F. P. Emmeneger, *Solid State Commun.* **7**, 965 (1969).
9. K. Minematsu, K. Miyatani, and T. Takahashi, *J. Phys. Soc. Japan* **31**, 123 (1971).
10. F. J. Welcher, "The Analytical Uses of Ethylenediamine Tetraacetic Acid," Polish translation, p. 247, WNT, 1968.
11. M. Struszyński, "Analiza ilościowa i techniczna (The quantitative and technical analysis," p. 288, PWT, 1954.
12. G. Charlot, "Les méthodes de la chimie analitique," Russian translation, (Khimiya, Ed.), p. 910, Moskwa, 1965.
13. J. Minczewski, Z. Marczenko, "Chemia analityczna (The analytical chemistry)," pp. 462, 408, PWB, 1965.
14. Ensslin, *Z. Anal. Chem.* **149**, 25 (1956).
15. G. Charlot, "Quantitative Inorganic Analysis," pp. 486, 559, London, 1957.
16. H. Flaschka and H. Jakobljevich, *Anal. Chim. Acta* **5**, 152 (1951).