

X-RAY DIFFRACTION STUDY OF THE FORMATION OF SPINEL STRUCTURE OF HgCr_2Se_4

BY H. BRODA, D. KONOPKA AND I. KOZŁOWSKA

Institute of Physics, Silesian University, Katowice*

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On preparing the MeCr_2X_4 type compounds, with Me being either Hg or Cd, and X either S or Se, the compound HgCr_2Se_4 was seen to exhibit lattice distortions which depend on the duration of heat treatment. It was found that the lattice constant a changes from 10.725 Å to 10.752 Å and the parameter u from 0.387 to 0.390.

1. Introduction

The small number of studies [1-5] on the crystallographic and magnetic properties of selenospinel carried out up to now concerned the MeCr_2Se_4 type compounds, with Me being Cd, Hg, Ni, Zn, Fe, or Co. It was established that HgCr_2Se_4 has a normal spinel structure and lattice parameters [4] of $a = 10.753$ Å and $u = 0.390$. The effect of the heat treatment duration on the formation of the spinel structure had not been analyzed yet, and this was the aim of the present work.

2. Preparation of the samples

The compound HgCr_2Se_4 was prepared from metals of the following classes of purity:
Hg — analytically pure, manuf. P. O. Ch. (Gliwice),
Cr — pure, manuf. Schuchardt (München),
Se — analytically pure, manuf. P. O. Ch. (Gliwice).

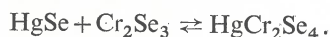
The mixture of the elements in stoichiometric quantities were pulverized in an agate mill, then samples were sealed in quartz tubes at 10^{-5} torr. The sealed samples were heated under the following conditions:

- 1) Sample A: 9 days at 350°C
10 days at 500°C
5 days at 600°C;
- 2) Sample B: 10 days at 350°C,
10 days at 500°C,
13 days at 600°C;

* Address: Instytut Fizyki, Uniwersytet Śląski, Katowice, Bankowa 12, Poland.

- 3) Sample C: 12 days at 350°C,
12 days at 500°C,
15 days at 600°C.

During preparation the heating process was interrupted, the samples were cooled with the furnace, pulverized, mixed and re-sealed. X-ray diffractograms were taken, and the obtained results show the intermediate reaction products that are forming during the formation of spinel. The reaction occurs *via* the formation of selenides HgSe and Cr₂Se₃ which then react according to the scheme:



The process of formation of this compound commences at 350°C but the long-time heating at this temperature does not lead to the complete synthesis of the initial substances.

3. X-ray diffraction analysis

The diffraction patterns of the three samples were obtained by the powder method at use of a DRON-1 diffractometer employing CuK_{αv} radiation, the angular velocity of the counter being 2 degrees/min. The lattice constants were determined by the internal etalon method at use of extrapolation to the Nelson-Riley function (Table I). NaCl was

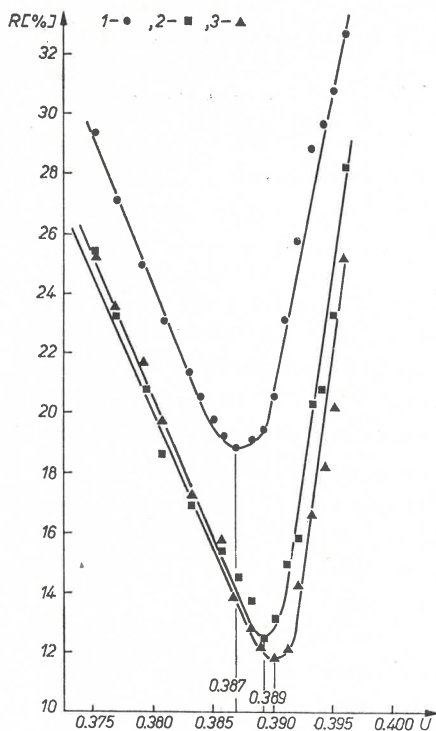


Fig. 1. Dependence between R-factor and anion parameter u for samples: A-1; B-2; C-3

the etalon substance. The parameter u was found by the minimizing of the $R(u)$ function (Fig. 1) [4]. The R -factor was calculated for 18 of the initial reflections within the 14° – 68° range. The relative values of total intensities were put into the formula for the R -factor

$$R = \frac{\sum_{hkl} |I_t^{hkl} - I_{\text{exp}}^{hkl}|}{\sum_{hkl} I_{\text{exp}}^{hkl}},$$

with

$$I_t^{hkl} = \frac{I_t^{hkl}}{I_{t_{\text{max}}}} 100\% \quad \text{and} \quad I_{\text{exp}}^{hkl} = \frac{I_{\text{exp}}^{hkl}}{I_{\text{exp}_{\text{max}}}} 100\%.$$

Here, I_{exp} are the experimental values of total intensities determined by means of the scintillation counter and a scaling unit with a printer at the DRON-1 diffractometer

TABLE I
The lattice constant a , the anion parameter u and the R -factor for three samples of HgCr_2Se_4 compound

Sample	a Å	u	R %
A	10.725 ± 0.002	0.387 ± 0.001	18.8
B	10.741 ± 0.001	0.389 ± 0.001	12.2
C	10.752 ± 0.002	0.390 ± 0.001	11.9

TABLE II
Theoretical and experimental intensities of three samples of the HgCr_2Se_4 compound

hkl	Sample A		Sample B		Sample C	
	$I_{tu=0.387}$	I_{exp}	$I_{tu=0.389}$	I_{exp}	$I_{tu=0.390}$	I_{exp}
111	8.1	0.8	7.4	2.0	5.6	2.2
220	82.1	56.0	81.8	69.7	89.7	79.2
311	86.3	69.6	83.3	83.2	87.4	95.5
222	30.9	29.3	33.4	30.9	30.6	33.0
400	17.0	21.4	18.3	20.9	16.6	23.2
331	25.7	25.9	28.6	30.2	31.9	32.9
422	34.1	29.9	32.7	32.5	34.6	33.2
333/511	57.1	65.5	60.4	70.1	66.6	69.5
440	100	100	100	100	100	100
531	3.3	2.4	3.0	2.0	2.7	1.9
600/442	0.4	0.9	0.5	0.7	0.9	0.8
620	13.3	10.6	12.8	8.4	12.5	10.1
533	12.9	11.5	12.6	11.5	13.9	8.0
622	8.3	9.3	9.9	6.7	6.8	5.8
444	2.5	4.5	2.7	2.3	2.0	1.1
551/711	5.9	7.4	7.0	5.5	7.7	4.4
642	22.4	15.5	23.3	14.2	25.5	17.4
731/553	18.7	15.0	18.2	11.5	19.2	19.9

($\text{CuK}_{\alpha\text{v}}$ radiation), the angular velocity of the counter being 1/8 deg/min. and the primary beam stability 1.7%. I_t are the theoretical values of relative intensities calculated at the assumption of a normal type of the structure. Computations were programmed in the MOST language and carried out on an ODRA 1003 computer. The program was written by M. Popielowa, M. Sc.

4. Results and interpretation

The results are presented in Tables I and II.

At the first stage, a lattice with defects is formed. This is implied by smaller dimensions of the elementary cell, the small u parameter and the high R -factor. During formation of the structure the diffusion of bivalent cations to the tetrahedral sites and trivalent cations to the octahedral sites occurs, which results in a broadening of the lattice and improves an agreement between the predicted and observed intensities.

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