

The Preparation of Hot-Pressed Chalcogenide Spinel. II. Stoichiometry and Optical Transparency in CdCr_2S_4 and CoCr_2S_4

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The compounds CdCr_2S_4 and CoCr_2S_4 have been hot pressed into disks that are highly transparent in the infrared. Stoichiometry has been altered by varying the $\text{Cr}^{3+}/\text{M}^{2+}$ ratio, where M^{2+} is Cd^{2+} or Co^{2+} . The effects of nonstoichiometry on optical transmission were determined. Excess M^{2+} attenuates the transmission much more than excess Cr^{3+} .

I. Introduction

A general method for preparing microcrystalline thiocromites was described recently (1). These were hot pressed to form very dense, polycrystalline, 0.5 in. diameter disks, many of which were highly transparent in the infrared. However, it was not possible to relate the transparency directly to the material preparation.

We describe here the preparation of CdCr_2S_4 and CoCr_2S_4 of high optical transmittance. Compositional variations were made where $1.95 \leq \text{Cr}^{3+}/\text{M}^{2+} \leq 2.04$. The Cr and Cd or Co present in both powders and pressings were determined by classical chemical methods. Pressings having excess Cr^{3+} are ir transparent, whereas those with excess Cd^{2+} or Co^{2+} are not.

This investigation was part of a program seeking magneto-optical materials usable around room temperature. The ir transmission and magneto-optical properties of these and other hot-pressed materials have already been reported (2, 3).

II. Experimental Methods

A. Analysis

Before use, the CP-grade starting materials, CdO , CrO_3 , and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, were analyzed for metal content. Cd was determined as CdSO_4 (4), Co as the EDTA complex using a standardized Cu solution (5) and a fluorochromic indicator (6), and Cr iodometrically (7).

B. Preparation

The analyzed starting materials were dissolved together and the aqueous solution was filtered through an 0.8- μm Millipore filter, giving stoichiometric solutions approximately 0.8 M in CrO_3 . To these were added sufficient 5-10% solution of hydrazine to simultaneously reduce Cr(VI) to Cr(III) and raise the pH of the resulting suspension to 9-10.5 (1). The precipitated products, comprising intimate mixtures of Cr(III) oxide hydrate and divalent hydroxides, were filtered without washing and dried at 110°C overnight. The filtrates were analyzed by atomic absorption to determine any losses.

The dried precipitates were converted to the sulfides by the ITI method (1). The following regimens of H_2S were used: for CoCr_2S_4 , 350°C for 1.5 hr, 500°C for 3 hr, 800°C for 3 hr; CdCr_2S_4 , 350°C for 1.5 hr, 500°C for 3 hr, and 925°C for 3 hr. Although CdCr_2S_4 could be handled without precautions, the Co compounds, particularly CoCr_2S_4 , slowly react with moisture. Therefore, all grinding and transfer operations were carried out in a protective atmosphere of dry argon. The powders were also stored in argon. Hot-pressed pieces, which have very low surface areas, did not require this protection.

C. Hot Pressing

Molybdenum-alloy dies were used in the vacuum hot-pressing apparatus as before (1). CoCr_2S_4 powder was cold pressed at 17,000 psi.

TABLE I
 VOLATILIZATION OF M²⁺ SULFIDES^a

Sample	Material	Cr ³⁺ :M ²⁺ Precursor hydroxides	Cr ³⁺ :M ²⁺ Produce sulfide	M ²⁺ loss (%)
A	CdCr ₂ S ₄	1.999	2.006	0.35
B		1.997	2.012	0.75
C		2.015	2.031	0.80
D	CoCr ₂ S ₄	1.996	1.996	0.00
E		2.005	2.005	0.00
F		2.027	2.033	0.30

^a M²⁺ = Cd²⁺ or Co²⁺.

The temperature was then raised to 800°C and maintained for 10 min. The pressure was increased at a rate of 8500 psi/min to a maximum of 50,000 psi, and held for 20 min. Then the sample was cooled to 600°C while the pressure was reduced stepwise to 17,000 psi. The pressure was released and the sample was cooled to room temperature under a nitrogen atmosphere. The procedure for pressing CdCr₂S₄ has already been described (1).

D. Characterization

The coprecipitated hydroxides, thiochromite powders, and thiochromite pressings were analyzed for metal content. The hydroxide precipitates were dissolved in HCl, the sulfides in HNO₃ (see below). Aliquots were taken for analysis. In the case of the Cd-Cr compounds,

Cd(II) was separated from Cr(III) as the sulfide (4) and determined as the sulfate. Cr was determined iodometrically in the presence of Cd. The Co-Cr compounds were treated in a similar manner. Both Co and Cr were determined in the presence of each other.

Strictly speaking, the sulfide samples are not completely soluble in nitric acid. The powdered samples dissolved rapidly in the acid, but a residue, always observed in a diluted solution as a Tyndall cone, could be collected on a Millipore filter (0.1 μm). This residue, identified as Cr₂O₃ by X-ray diffraction, was determined by X-ray fluorescence to be about 0.005 wt % of the sample, too low to influence the analytical results. The pressings, particularly CdCr₂S₄, proved to be refractory. The pressings were ground in an automatic mortar for approximately 45 min and

 TABLE II
 LONG-WAVELENGTH IR ABSORPTION COEFFICIENT AS A FUNCTION OF STOICHIOMETRY

Sample	Material	Cr ³⁺ :M ²⁺ Pressing	Cr ³⁺ :M ²⁺ Powder	Absorption coefficient (cm ⁻¹)		
				9.0 μm	10.0 μm	11.0 μm
1	CdCr ₂ S ₄		1.953	44.3	34.6	30.2
2			1.982	4.7	4.6	5.3
3			2.002	3.0	2.7	3.2
4			2.030	1.9	2.1	2.6
5			2.040	3.0	2.7	3.2
6	CoCr ₂ S ₄	1.951	1.950	47.7	45.0	47.6
7		1.977	1.975	43.0	41.7	41.3
8		1.993	1.993	17.0	16.1	16.2
9		2.008	2.005	9.0	8.3	8.7
10		2.034	2.034	11.3	9.8	10.3

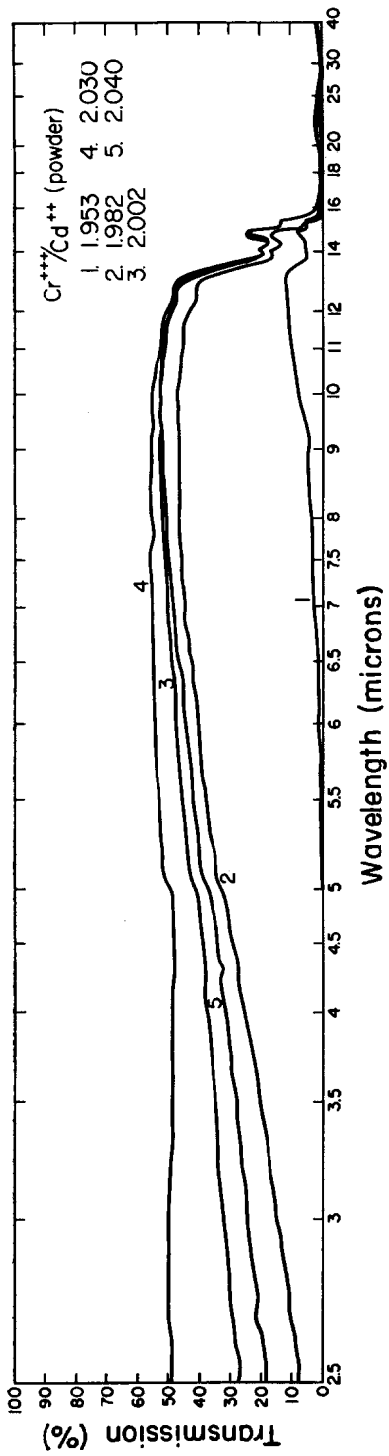


FIG. 1

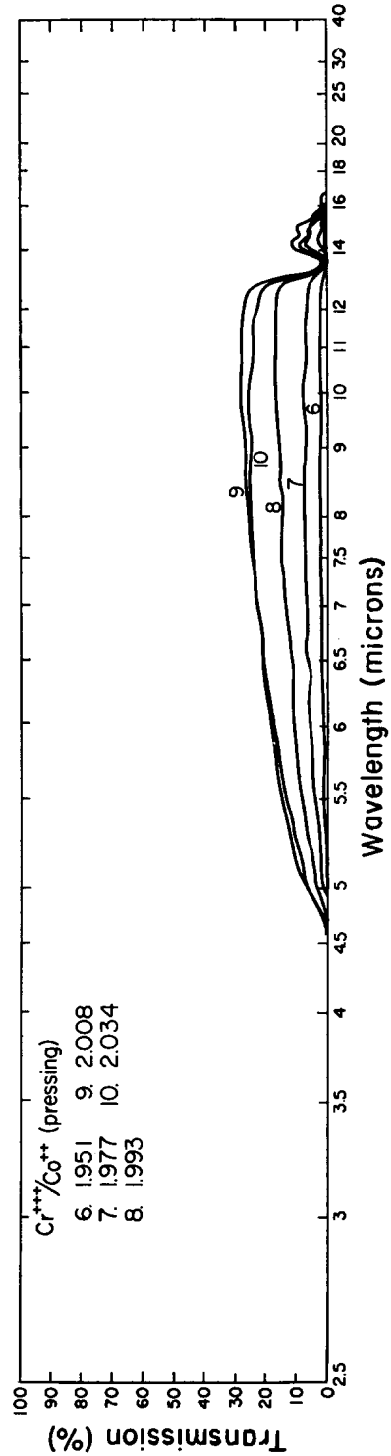


FIG. 2

treated in HNO_3 for 5 and 25 hr at 125°C in a Parr bomb. Traces of residue remained even after the 25-hr treatment.

The structures of the thiochromite powders were identified and the lattice constants determined by X-ray diffraction. The infrared transmission of the pressings, which had been ground and polished to approximately 0.60-mm thickness, was measured between 2.5 and $40\ \mu\text{m}$ using a Beckman 21A spectrophotometer. The absorption coefficient, α , was evaluated from the relationship $T = (1 - r)^2 e^{-\alpha t} / (1 - r)^2 e^{-2\alpha t}$, where T is the measured value of transmission of a sample having the thickness t and reflectivity r .

III. Results

The analyses of the filtrates of the coprecipitated hydroxides showed that the soluble cations Co(II) , Cd(II) , and Cr(III) were present in amounts below what could be determined by the analytical procedures used with the solids.

In Table I, we present some of these analytical results, expressed as ratios of chromium to cadmium and chromium to cobalt, for both the coprecipitated hydroxides and the end-product thiochromites.

The spectral transmission curves for a family of CdCr_2S_4 samples in which the stoichiometry was purposely altered from chromium rich to chromium poor are presented in Fig. 1. The transmission curves for a similar set of CoCr_2S_4 samples are presented in Fig. 2. In all cases, the samples were approximately 0.60-mm thick.

The calculated absorption coefficients at 9.0, 10.0, and $11.0\ \mu\text{m}$ are presented in Table II along with the analytically determined ratios for the CdCr_2S_4 powders and for the CoCr_2S_4 powders and pressings.

IV. Discussion

The analytical procedures used to determine Cd, Cr, and Co are accurate to about 0.3%. Assuming the largest deviation, the ratios of $\text{Cr}^{3+}/\text{M}^{2+}$ should be accurate to $\approx 0.6\%$. The $\text{Cr}^{3+}/\text{Cd}^{2+}$ ratios were determined for many samples of hydroxide precursor and thiochromite. In every case, this ratio was greater for the thiochromite than for the hydroxide.

The results given in Table I indicate a loss of Cd as volatile CdS on conversion of the hydroxides to the thiochromites. This is most obvious in samples B and C. Comparison of A and B

shows an uncontrolled variation. The CdS loss depends upon experimental conditions such as the way the powder is compacted in the firing vessel and the constancy and rate of H_2S flow, as well as the temperature and duration of firing.

In the case of the CoCr_2S_4 , samples D, E, and F, CoS is not expected to volatilize during the synthesis. This is confirmed by the analysis. There is no difference in $\text{Cr}^{3+}/\text{Co}^{2+}$ ratio between hydroxide precursor and thiochromite product.

The transmission at long wavelength given in Figs. 1 and 2 has been converted to absorption coefficient, which is reported in Table I. For samples of approximately equal thickness, the lower values of transmission of the best CoCr_2S_4 compared to the CdCr_2S_4 are due, to a large extent, to the differences in refractive indices (3.58 for CoCr_2S_4 and 2.81 for CdCr_2S_4).

Table II shows no loss of Co on forming transparent pieces by hot pressing. The sample having the best transmission is the most stoichiometric. Excess Cr has a less adverse effect on transmission than excess Co, and a modest amount of excess Cr can be tolerated.

The interpretation of the results obtained with CdCr_2S_4 is not as clean-cut because of experimental difficulties. A small and variable fraction of CdCr_2S_4 decomposes and decomposition products boil off during the hot-pressing operation. Cadmium sulfide and/or oxide frequently is found on cold portions of the mold. This is confirmed by the analysis. The pressing almost always has a higher $\text{Cr}^{3+}/\text{Cd}^{2+}$ ratio than the powder. Moreover, paralleling the differences in reaction rates of CdCr_2S_4 and CoCr_2S_4 with moisture and water, the hot-pressed CdCr_2S_4 is far more difficult to dissolve in nitric acid than CoCr_2S_4 . In fact, the erratic analytical results obtained from the pressings of the CdCr_2S_4 probably are due to the variability in its decomposition, volatility of its decomposition products, and to its refractory solubility in HNO_3 . Although the $\text{Cr}^{3+}/\text{Cd}^{2+}$ ratios of only the powdered material are presented, in the pressings the ratios could be different and the amount volatilized randomly variable. Nevertheless, it can be seen that the best samples are those which approach stoichiometry. Again, excess Cr has less adverse effect than excess Cd, and, as with the CoCr_2S_4 , a modest amount of chromium can be tolerated.

Cr_2O_3 is always present in these preparations. It is seen in the infrared absorption spectra (Figs. 1 and 2) as a group of bands between 12.5

and 17 μm (1, 2). The Cr_2O_3 was also detected as an insoluble residue. Ideally, the best transmission should be obtained from a stoichiometric preparation. Actually, the best materials reported above contain more Cr than is indicated by the ratio $\text{Cr}^{3+}/\text{M}^{2+}$. Most of this additional Cr could be present in the form of Cr_2O_3 which, in the best pressings of CdCr_2S_4 , is almost balanced by the volatilization and loss of an equivalent amount of CdS. The transparency of the CoCr_2S_4 pressings will probably be improved by a more appropriate balancing of the $\text{Cr}^{3+}/\text{Co}^{2+}$ ratio.

In general, the powder used to prepare highly transmitting hot pressings must fulfil several requirements. Residual impurities, particularly foreign anions and adsorbed materials, must be absent. Those impurities that become entrapped on grain boundaries or cause the formation of pores cause optical scattering. In most hot pressings, transmittance falls off at short wavelengths because of scattering of the incident light by submicron pores or by second-phase impurities. This is clearly seen on the short-wavelength side in Fig. 1. Here, the attenuation in transmission roughly follows the increase in amount of second-phase material. The differences in the adverse effect on the short-wavelength transmission of excess Cr compared to excess Cd or Co might be due to differences in particle size. That is, the particle size of the Cr_2O_3 and/or Cr_2S_3 might be much smaller than the particle size of the CdS and CoS. It is known that the wavelength region over which scattering is observed and the degree of scattering are related to the particle-size distribution of the scattering particles and the quantity present.

A study of the mechanism of the reaction for

the coprecipitated hydroxides and oxide hydrates with H_2S might reveal how the thiochromite is formed and why traces of Cr_2O_3 are always present. Obviously, there is a competition in the reactions between these oxygen-containing components to form chromites, between the conversion of the hydrated chromium(III) oxide to form refractory Cr_2O_3 , and the reaction between all these species with H_2S to form sulfides and/or thiochromites. It is not clear whether the presence of Cr_2O_3 is due to incomplete conversion or to hydrolysis during sulfiding treatment.

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