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The Preparation of Hot-Pressed Chalcogenide Spinels

D. PEARLMAN, E. CARNALL, JR., AND T. W. MARTIN

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

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The preparation of chalcogenide spinel powders is reviewed. Microcrystalline powders are formed by the thermal reaction of mixtures of anhydrous cadmium and chromium chlorides or coprecipitated cadmium and chromium hydroxides with H_2S, $Ar + CS_2$, or $H_2 + Se$. These spinel powders are hot pressed to form highly dense, polycrystalline disks. The effects of pressing variables on optical absorption coefficients are given. The spinel powders and hot-pressed disks are characterized and optical spectra, refractive index, and Faraday rotation data are given.

I. Introduction

The optical, electronic, and magnetic properties of the semiconducting ferromagnetic chromium chalcogenide spinels in the forms of single crystals, thin films, and compacts of powders have been investigated extensively (*1*, *2*).

The magnetic semiconducting chalcogenide spinels are potentially useful in information storage devices utilizing thermomagnetic writing (*3*, *4*), in magneto-optical recording (*5*), in devices for laser modulation (*1*), and as windows for optical devices (*6*).

The growth of single crystals and the properties of chromium sulfo- and seleno-spinels were reviewed recently (*1*, *2*, *7*). It has not yet been possible to grow chalcogenide spinel crystals more than a few millimeters long since these compounds do not melt congruently.

Hot pressing is carried out at a temperature a fraction of the melting point, and is appropriate for use with these chalcogenide spinels because they decompose before melting. The present paper reports the preparation of magnetic semiconducting chalcogenide and other spinels in microcrystalline form and the hot pressing of these powders to yield large pieces of high optical quality.

A. Spinel Powder Preparation

There are several methods for preparing thiochromites. Coprecipitates of zinc and chromium(III) hydroxides containing excess zinc have been heated with sulfur in hydrogen atmosphere (*8*, *9*). A somewhat similar method was used to prepare $CdCr_2S_4$ (*10*). The preparation of Ag, Pb, Cu, Cd, Zn, Co, Ni, Fe, Mn, and Zn thiochromites by metathesis of solutions of suitable salts with $NaCr_2S_2$ also has been described (*8*). This has been confirmed for the Zn, Ag, Cu, and Pb compounds (*11*, *12*).

Mercury, iron, and cobalt thiochromites have been prepared by heating the corresponding metal sulfide with chromium(III) sulfide (*13*), whereas the selenochromite spinels, $ZnCr_2Se_4$ and $CdCr_2Se_4$, were obtained from the selenides (*14*). $Zn_xCd_{1-x}Cr_2S_4$, where $x = 0$, 0.25, 0.50, 0.75, and 1.0, was prepared in a similar way (*15*) and from the elements (*16*).

Bouchard, Russo and Wold (*17*) have described the preparation of thiochromites of Mn, Co, Fe, Zn, and Cu by heating the elements together or by heating the corresponding chromites in H_2S. The compounds $CdCr_2X_4$, where X is S or Se, have also been prepared from CdX and $Cr + X$ (*18*). Finally, the Zn, Cd, Hg, Mn, Ni, and Co thiochromites have been prepared by heating $M(Py)_4Cr_2O_7$ in H_2S (*19*).

Close examination of the methods cited indicates that although both stoichiometry and intimate mixing are important (*20*), a large surface area is needed. At elevated temperature the growth of the crystals of the reacting species also is promoted (*21*). This increase in crystal growth, which can have an adverse effect on reactivity, can be minimized by heating at a lower temperature. In the case of the oxygen-containing reactants, the formation of refractory chromium(III) oxide may also be avoided.

The reaction of ZnS with Cr_2S_3 to form $ZnCr_2S_4$ has been shown to take place at about 490°C (*22*). In the absence of intermediates, the first step is the formation of the compound. When the ZnS and Cr_2S_3 become coated with thiospinel, diffusion through the spinel layer becomes rate determining.

B. Hot Pressing

The present state of the technology of hot pressing is such that one cannot completely stipulate *a priori* the powder properties required for the preparation of transparent pressings. However, for optical quality the powder should preferably have a cubic structure, be free of second-phase material, and be devoid of physically and chemically absorbed volatile contaminants.

The optical quality of a hot-pressed body depends upon reducing the porosity to levels below about 0.01%, depending upon the pore size distribution and concentration. Pores and any other second-phase impurities having a different refractive index will scatter light and cause reduced transmittance.

The three variables that can be manipulated to obtain low porosity and high transmittance are temperature, pressure, and time. For optimum magnetic properties, the chromium chalcogenide spinel microcrystals probably should be stoichiometric and free of impurities. In fact, our experience shows that the optical transparency of the hot-pressed member is the best measure of the stoichiometry and purity of the powder.

The mechanism by which densification in hot pressings takes place is still a subject of considerable interest. One school favors plastic flow (*23*) by dislocation motion and the other favors a diffusional creep (*24*) mechanism for final-stage densification. The choice as to which mechanism predominates appears to depend on (a) crystal structure and the number of available slip systems, (b) temperature of pressing, and (c) pressure. At high temperatures and pressures, additional slip systems can become activated and cause a change in densification mechanisms.

$MgAl_2O_4$ spinel has been studied by Rummler and Palmour (*25*). At temperatures below 1350°C and pressures of 3500 psi densification occurs by diffusion whereas above 1350°C plastic flow by dislocation motion is the operative mechanism. The chalcogenide spinels would be expected to be less refractory than the oxide material, so that plastic flow would be more likely to occur at moderate temperatures and pressures.

The hot-pressing technique has found use as a method of preparation of optical materials and a variety of compounds have been hot pressed (*26–40*). Hot pressing of the magnetic spinels $CuCr_2S_3Br$, $CuCr_2Se_{4-x}Br_x$, $ZnCr_2S_4$, $CdCr_2S_4$, and $CdCr_2Se_4$ has been reported previously (*41–46*) but optical-quality samples apparently were not obtained.

We report the preparation of hot-pressed 25-mm diam polycrystalline disks which have been found suitable for magneto-optical studies and devices (*5*, *45*, *46*).

II. Experimental Procedures

A. Powder Preparation

For the most part, experiments were made with mixtures of anhydrous cadmium and chromium chlorides or with coprecipitates of cadmium and chromium hydroxides. The chloride mixture represents a possible means of working with an oxygen-free system. The hydroxide mixture was used in an attempt to obtain a homogeneous preparation in a finely divided state.

The mixtures or coprecipitates were converted to the chalcogenides by heating either in an atmosphere of H_2S, $Ar + CS_2$, or $H_2 + Se$. Two different heating regimens were used: constant temperature or a series of incremental temperature increases. The chalcogenides were handled in the hood without further precautions.

1. Preparation of Chloride Mixture

Mechanical mixtures of stoichiometric amounts of $CrCl_3 \cdot 6H_2O$ and $CdCl_2 \cdot 2\frac{1}{2}H_2O$ were dehydrated according to Pray (*47*) and transferred to a quartz firing boat. For comparison, a control of hydrated material also was used.

2. Preparation of Hydroxide Coprecipitates

Hydrazine quantitatively converts Cr(VI) to Cr(III) (*48*) as a voluminous precipitate (*49*). Hydrazine, which forms a weak base with water, can be oxidized to form NH_4^+, e.g.,

$$N_2H_5^+ + Fe^{3+} \rightarrow Fe^{2+} + \tfrac{1}{2}N_2 + H^+ + NH_4^+$$

(*50*). We therefore explored the feasibility of coprecipitating a mixture of hydroxides, uncontaminated by salts, etc., from a solution of metal oxide in chromic acid. An aqueous solution of cadmium oxide in chromic acid, in a molar ratio of 1:2, was treated with a dilute solution of hydrazine, whereupon the Cr(VI) was reduced to Cr(III) and the hydroxides were precipitated. The product was filtered and dried at 105–110°C. It was amorphous. A sample heated to 650°C was identified as $CdCr_2O_4$. Analysis: calcd for $CdCr_2O_4$: Cd, 40.1; Cr, 37.1; found: Cd, 40.1; Cr, 37.2.

3. Spinel Formation

a. Constant temperature. A quartz firing tube arranged for cooling the sample rapidly in the firing atmosphere was used. Samples, contained in a quartz boat, were inserted into the hot, argon-purged tube. For conversion to sulfides, the samples were heated for 1, 3, 6, or 9 hr in H_2S at 400, 500, 600, 700, 800, and 925°C. For selenide formation, Se was mixed with the precursor material and the mixture was fired in H_2. The maximum temperature investigated was 800°C. At the end of each time period, the product was cooled to room temperature, ground, sampled for analyses, and the remainder was processed further.

b. Incremental temperature increase. The coprecipitated hydroxides were heated in H_2S for 1.5 hr at 350°C; the temperature was quickly raised to 500°C, and firing was continued for an additional 3 hr. The product was cooled to room temperature under H_2S. It was removed from the furnace, ground, a sample was removed for analyses, and the remainder was refired at 925°C for 1.5 hr.

After preparation, the aggregated crystals were ground again so that the material used for hot pressing would pass through a 100-mesh sieve.

c. Powder characterization. Elemental analysis for the cation constituents and for oxygen was performed by neutron activation techniques. Sulfur and selenium were determined by a weight-loss procedure (*16*). The powders were identified by X-ray diffraction. Surface areas were measured by the BET method (*52*) using a model 2100 surface area analyzer (Micrometrics Inst. Corp. Norcross, GA). Powders were examined in the scanning electron microscope.

B. Hot Pressing

1. Apparatus

The vacuum hot-pressing apparatus is shown in Fig. 1. The pressing is carried out in a vacuum maintained at 5×10^{-4} to 5×10^{-3} Torr during the heating cycle. The plunger and cylinder are

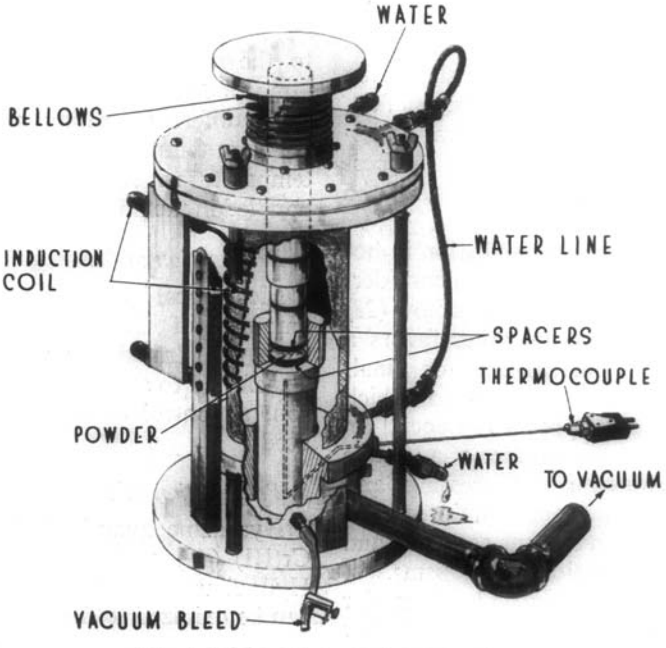

FIG. 1. Vacuum hot-pressing apparatus.

constructed of a molybdenum titanium–zirconium alloy (TZM Climax Molybdenum Corp.). The dies are coated with Aquadag which serves as a mold release. Pyrolytic graphite disks placed above and below the powder help maintain uniform temperature within the powder and also serve as a release material. The temperature is measured by a thermocouple placed in the pressing base, within $\frac{1}{16}$ in. of the bottom graphite disk. The temperature is controlled automatically. Uniaxial pressure is applied through a 4-column hydraulic press and the pressure read on 6-in. diam gauges (Marsh Master gauge). The mold is heated by direct coupling using a 10 kW, 9600-cycle induction heater.

2. *Pressing Procedure*

The powder, placed in the pressing cylinder between the pyrolytic graphite disks, is pressed at room temperature with 4000 psi. The pressing cylinder is then placed in the hot-pressing apparatus and the apparatus is evacuated to 5×10^{-4} Torr. At this time 5000 psi clamping pressure is applied to the powder and this pressure is maintained until the end of the soak period. The heating is then begun and the temperature is raised to the desired value over a 20-min period (900°C for $CdCr_2S_4$, 700°C for $CdCr_2Se_4$). This temperature is maintained for 10 min. The soak period permits temperature equilibration and outgassing. Next the pressure is slowly increased at a rate of 2500 psi/min to the maximum pressure, which is maintained for 20 min. At the end of the run, the induction heating is shut off but the pressure is maintained until the temperature has fallen to 600°C, at which time the pressure is allowed to fall slowly. Simultaneously with the release of the vacuum, the hot-pressing apparatus is backfilled with an inert gas and the apparatus cooled to room temperature.

C. Product Characterization

The density of the samples was measured by a hydrostatic weighing method with hexachloro-1,3-butadiene (*52*) as the liquid. Weighings were carried out on 1-g samples with a semimicrobalance.

Samples for optical measurements were ground and polished using conventional glass-finishing techniques and reduced to thickness between 0.04 and 2.0 mm.

Near-infrared measurements were obtained with a Beckman DK-2 and a Cary 14 RI spectrophotometer and infrared measurements between 2.5 and 40 μm with a Beckman 21A spectrophotometer. The index of refraction was determined from the interference pattern seen in the transmission spectrum of thin samples, and the reflectivity was calculated using the Fresnel reflectivity formula for normal incidence. The absorption coefficient α was calculated from $I = I_0 e^{-\alpha t}$, correction being made for reflection loss. At short wavelengths α includes both true absorption and scatter.

Faraday rotation measurements were made on $CdCr_2S_4$ as a function of wavelength, magnetic field, and temperature.

Polished samples were etched with boiling HNO_3, then examined and photographed using a Unitron metallograph. Scanning electron micrographs were prepared from fractured surfaces.

III. Results

A. Spinel Powder Formation

1. *Constant Temperature*

a. Chlorides. Because of the high volatility of $CdCl_2$, it was not possible to run a meaningful firing series at constant temperature using the chloride mixture.

b. Hydroxides. The effect of heating the coprecipitated hydroxides for 1, 3, and 6 hr in H_2S at 400, 500, 600, 700, 800, and 925°C is summarized in Table I. The data are presented only by way of an example.

The data indicate that almost complete conversion to sulfospinel takes place at about 500–600°C. Yet traces of second-phase material are not completely removed even after 10.5 hr of firing at 925°C. As shown below, the decrease in oxygen content is only partly due to the sulfiding treatment. Note also the change of surface area with duration and with increased temperature of firing. These preparations yielded poorly transparent pressings.

2. *Incremental Temperature Increase* (*ITI*)

a. Anhydrous chlorides. Table II summarizes the data obtained from samples prepared by the ITI procedure.

The results, presented here for the anhydrous chlorides, are also typical of those obtained for the chloride hydrate or for the hydroxide-derived products, with only slight differences.

When anhydrous chlorides were used with the ITI regimen, conversion was rapid and essentially

TABLE I

SPINEL POWDER FORMATION, CONSTANT TEMPERATURE, HYDROXIDES

Sample	H_2S treatment: Duration (hr)	H_2S treatment: Temp (°C)	Composition[a]: $CdCr_2S_4$	Composition[a]: CdS	Composition[a]: Unknown	Composition[a]: Cr_2S_3	Analysis (%): O_2	Analysis (%): S	Surface area (m^2/g)
71A	1	400	Poorly crystallized;				10.4	34.6	25.09
B	3	400	no X-ray				8.07	35.4	23.34
C	6	400	identification				4.01	37.1	
72A	1	500	100	Poorly defined			9.58	34.7	
B	3	500	100	3½	0	1½	2.34	36.3	
C	6	500	100	3	0	1½	1.52	36.6	10.78
73A	1	600	100	5	0	½	1.92	35.6	8.73
B	3	600	100	3	½	1½	1.89	36.7	8.07
C	6	600	100	2½	½	1½	1.71	37.1	5.88
75A	1	700	100	4	<2	2	4.16	34.7	6.45
B	3	700	100	3	½	2	1.46	36.9	3.75
C	6	700	100	<2	< ½	2	1.34	36.9	2.95
76A	1	800	100	<2½	1	<2	1.35	33.1	2.42
B	3	800	100	<1	<1	1½	1.03	36.7	2.26
C	6	800	100	½	0	<1½	0.71	37.0	1.37
78A	1	925	100	<2	½	1½	0.86	36.9	1.82
B	3	925	100	<1	< ½	< ½	0.65	37.1	1.2
C	6	925	100	0	0	1½	0.53	37.3	0.94
D	10.5	925	100	0	2	1	0.46	37.8	

[a] Estimated from X-ray diffraction intensity measurement.

complete at 500°C, as can be seen from Table II. The most transparent pressings were obtained from the 925°C treatment.

b. Hydrated chlorides. As indicated by X-ray diffraction, almost complete conversion was obtained when mixtures of stoichiometric amounts of cadmium and chromium chloride hydrates were heated in H_2S using the ITI regimen (Table III). Transparent pressings could not be obtained, however. During the

TABLE II

SPINEL FORMATION, INCREMENTAL TEMPERATURE INCREASE, ANHYDROUS CHLORIDES

Sample	H_2S treatment: Duration (hr)	H_2S treatment: Temp (°C)	Relative peak height; composition: $CdCr_2S_4$	Relative peak height; composition: CdS	Relative peak height; composition: Unknown	Relative peak height; composition: Cr_2S_3	Analysis (%): O_2	Analysis (%): S	Surface area (m^2/g)
125-1	1.5	350							
-2	3	500	100	3.3	5.3	1	0.24	42.0	7.42
-3	3	800	100	0	0	0	0.05	38.6	2.32
-4	2	925	100	0.2	0	2	0.04	37.2	1.68

TABLE III

SPINEL FORMATION, INCREMENTAL TEMPERATURE INCREASE, HYDRATED CHLORIDES

	H_2S Treatment		Composition						Analysis (%)		Surface area
Sample	Duration (hr)	Temp (°C)	$CdCr_2S_4$	CdS	Cr_2S_3	Unknown	$CdCl_2$	Cr_3S_4	O_2	S	(m^2/g)
194D	1	350	—	35	—	—	65	—	10.8	—	2.31
18	3	500	100	21	9	0	—	35	0.41	39.2	6.86
19C	3	800	100	0	2	½	—	—	0.15	36.8	0.67
19D	1.5	925	100	—	3	—	—	—	0.06	37.8	0.74

TABLE IV

SPINEL FORMATION, INCREMENTAL TEMPERATURE INCREASE, HYDROXIDES

		H_2S treatment		Relative peak height; composition:				Analysis (%)		Surface area
Sample		Duration (hr)	Temp (°C)	$CdCr_2S_4$	CdS	Unknown	Cr_2S_3	O_2	S	(m^2/g)
128-1		1.5	350	Poorly crystallized						
-2		3	500	100	2.6	1.4	1.6	1.79	36.8	10.477
-3	Grind	3	800	100	0	0	0	0.30	37.2	2.992
-4	Grind	2	925	100	0	0	1.1	0.18	37.3	1.990

initial dehydration, a voluminous mass was formed which overflowed the combination boat. It was impossible, therefore, to maintain the initial cadmium–chromium ratio of the reactants.

c. Coprecipitated hydroxides. Again, the X-ray diffraction data indicated the reaction to be almost completed at 500°C (Table IV).

In this series, two starting materials were used: One batch of material was handled only in Pyrex vessels, the other only in plastic containers. They were similar in every respect except the residual oxygen, as determined by neutron activation analysis. In Table V we present the data obtained with both chloride- and hydroxide-derived powders and from pressings made from these powders. The 925°C-fired products yielded good transparent pressings.

d. Sulfide powders. Cr_2S_3 powders, prepared by firing $CrCl_3$ or $Cr(OH)_3$ in H_2S below 600°C, mixed with precipitated CdS, and then fired in H_2S by the ITI procedure also yielded the spinel. Moderately transparent pressings were obtained. Sulfides, prepared from the elements, were not converted completely to the spinel under the same conditions; neither did they yield transparent pressings.

The data presented here are merely examples. We stress that we did not find it possible to relate the absorption coefficient of a hot-pressed piece directly to the analysis of the starting powder. Although we believe that some lack of repeatability stems from small deviations in

TABLE V

OXYGEN CONTENT POWDERS AND PRESSINGS

			Oxygen content (%)	
Prep. no.	Reactants	Vessel	Powder	Pressing
117	Hydroxides	Pyrex	0.149	0.100
149	Hydroxides	Plastic	0.079	0.038
118	Chlorides	No solution used	0.048	0.001
127	Chlorides	No solution used	0.072	0.004

stoichiometry, we are only now in the process of refining our analytical techniques.

$FeCr_2S_4$, $ZnCr_2S_4$, $Co_xCd_{1-x}Cr_2S_4$, $CdCr_2Se_4$, and $HgCr_2Se_4$ and other mixed chalcogenide spinels have been prepared in a similar manner. The procedures for preparing these have not yet been optimized.

B. Hot Pressing

1. Effect of Temperature on Density and Absorption Coefficient

In Table VI are shown the results of pressing $CdCr_2S_4$ at temperatures of 750–900°C, where pressure and time were held constant at 50 000 psi and 20 min.

From the value of density and absorption coefficient it is seen that higher pressing temperature permits greater densification. However, 900°C appears to be the upper limit. Samples which have been hot pressed at 1000°C have a reduced transmittance level, apparently owing to the partial decomposition of the spinel. Thermal gravimetric measurements (*53*) show that decomposition in the $CdCr_2S_4$ begins at about 528°C under vacuum. During hot pressing the thermal decomposition is apparently suppressed by the applied pressure. Pressings made at 1000°C when examined by X-ray diffraction show no evidence of decomposition products. The level present is probably too low to be detected by X-ray diffraction although the amount is sufficient to cause light scattering.

2. Effect of Pressure on Absorption Coefficient

In these experiments pressure was varied from 1275 to 33 700 psi and the temperature and time were held constant at 900°C and 20 min. These results are presented in Table VII.

TABLE VI

EFFECT OF PRESSING TEMPERATURE ON PERCENTAGE DENSITY AND ABSORPTION COEFFICIENT OF $CdCr_2S_4$

Pressing temp (°C)	Density[a] (%)	Absorption coefficient (cm^{-1}) 1.3 μm	2.0 μm
750	99.69	68	43
800	99.82	16	16
850	99.87	13	15
900	99.99	5	8

[a] Based on 4.2590 g/cm^3 as theoretical density of $CdCr_2S_4$.

TABLE VII

EFFECT OF APPLIED PRESSURE ON ABSORPTION COEFFICIENT OF $CdCr_2S_4$

Applied pressure (psi)	Absorption coefficient (cm^{-1}) at 3.0 μm	at 10.0 μm
1 275	55	9
2 250	29	4
3 800	22	4
5 100	17	3
16 850	10	5
33 700	8	4

The sulfide spinel can be hot pressed at very low pressures with little effect of applied pressure on the absorption coefficient at long wavelengths, but with a greater influence at 3 μm. This increase of absorption coefficient at shorter wavelengths is probably due to optical scattering by residual pores. The scattering increases at shorter wavelengths, and is indicative of a uniformly fine scattering center.

3. Effect of Pressing Time on Absorption Coefficient

In these experiments, time at maximum pressure was varied from 3 to 40 min. Pressure and temperature were held constant at 50 000 psi and 900°C. Those results are presented in Table VIII.

In hot-pressed $CdCr_2Se_4$ the effects of time, temperature, and pressure on the absorption coefficient follow the same pattern.

4. Microstructure

Hot-pressed $CdCr_2S_4$ samples have been etched and examined for pores but none have

TABLE VIII

EFFECT OF PRESSING TIME ON ABSORPTION COEFFICIENT OF $CdCr_2S_4$

Time (min)	Absorption coefficient (cm^{-1}) 3.0 μm	10.0 μm
3	10	5
10	17	6
20	17	6
40	20	7

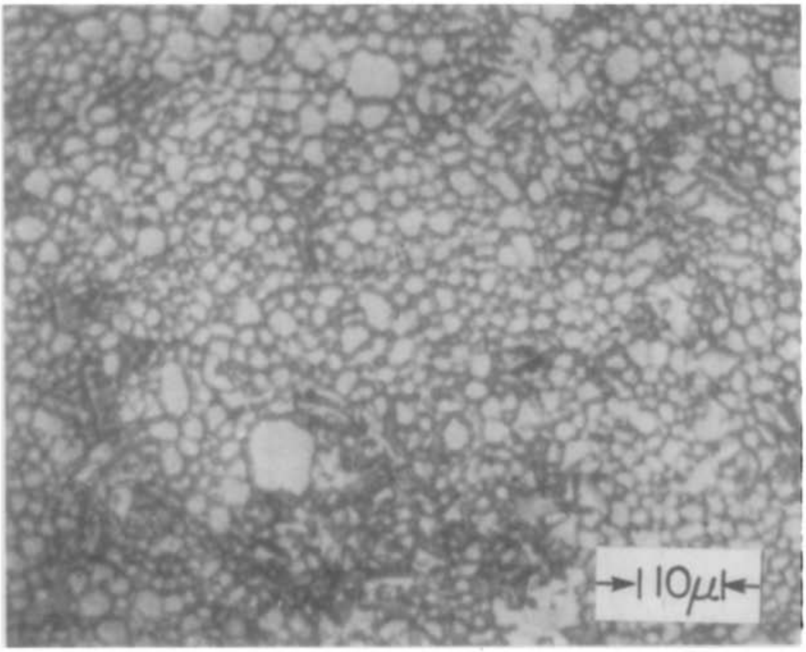

FIG. 2. Photomicrograph of chemically etched hot-pressed $CdCr_2S_4$.

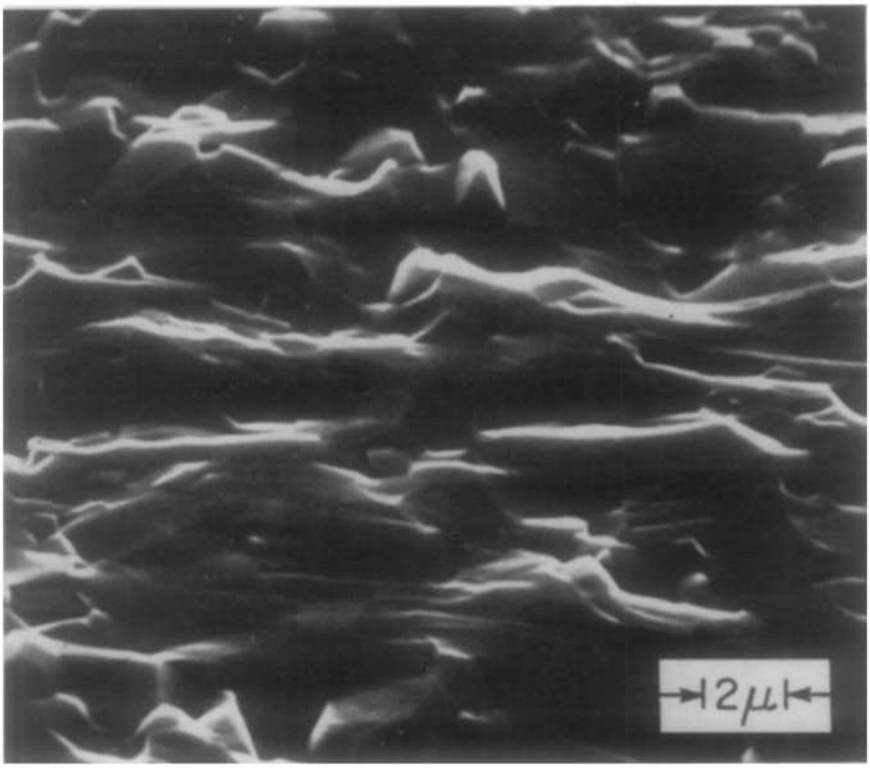

FIG. 3. Scanning electron micrograph of $CdCr_2S_4$ showing porosity.

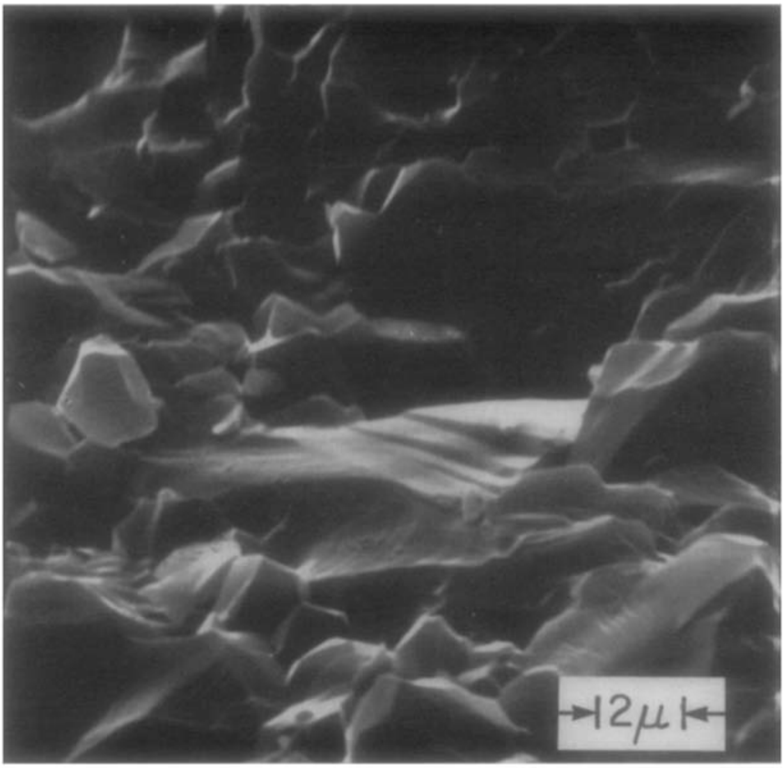

FIG. 4. Scanning electron micrograph of pore-free $CdCr_2S_4$.

been found. A typical micrograph is reproduced in Fig. 2. However, examination of fractured surfaces in a scanning electron microscope reveals porosity at the interfaces of crystals in more poorly transmitting samples, such as that shown in Fig. 3, which has an absorption coefficient of 22 cm^{-1} at 2.5 μm. None were found in better samples such as that shown in Fig. 4, which has a coefficient of 13 cm^{-1} at 2.5 μm.

Most of the pores observed are not connected. Frequently, the pores contain what appear to be foreign particles.

C. Optical Data

1. Optical Spectra

The optical spectra of hot-pressed $CdCr_2S_4$ and $CdCr_2Se_4$ are presented in Fig. 5. The complete optical spectra are presented elsewhere (*46*). Assignment of phonon parameters for both $CdCr_2S_4$ and $CdCr_2Se_4$ has been made (*54*).

The strong absorption bands at 570 and 620 cm^{-1} have been tentatively attributed to Cr_2O_3 based on the spectrum of Cr_2O_3 in KBr. Four additional weak bands found in Cr_2O_3 at 745,

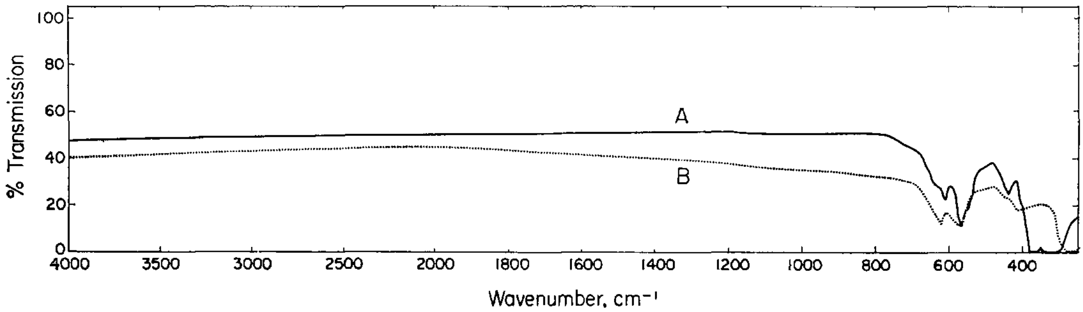

FIG. 5. Infrared spectra of (A) $CdCr_2S_4$ and (B) $CdCr_2Se_4$.

TABLE IX

REFRACTIVE INDEX VS WAVELENGTH FOR $CdCr_2S_4$ AND $CdCr_2Se_4$

$CdCr_2S_4$		$CdCr_2Se_4$	
Wavelength (μm)	Index	Wavelength (μm)	Index
0.633	3.57	1.18	3.33
0.800	3.86	1.22	3.30
0.850	3.75	1.45	3.23
0.900	3.58	1.70	3.20
0.950	3.46	2.56	3.15
1.00	3.37	2.97	3.14
1.20	3.13	3.33	3.14
1.50	2.97	4.45	3.14
2.00	2.89	5.33	3.14
2.50	2.86	6.68	3.14
5.00	2.84	8.94	3.16
10.00	2.84	13.53	3.18
15.00	2.84	15.01	3.17
		22.62	3.18
		26.95	3.17

440, 415, and 300 cm^{-1} have also been observed in samples of suitable thickness of both $CdCr_2S_4$ and $CdCr_2Se_4$. These strong bands are seen even in pressings which have been analyzed to contain 0.001 % oxygen.

2. *Refractive Index*

The refractive indices vs wavelength are presented in Table IX.

The refractive index at shorter wavelengths could not be measured for the $CdCr_2Se_4$ because of the high absorption in this region. Some index variation between samples has been observed in selenide spinels between 1.0 and 2.5 μm, possibly due to a variation in stoichiometry.

3. *Faraday Rotation*

The wavelength dependence of the Faraday rotation of hot-pressed $CdCr_2S_4$ has been determined from 750 to 15 000 nm at different field strengths and at different temperatures (*5*, *45*, *46*). A figure of merit of about 7.5 K/dB at 10.6 μm and 80 K can readily be obtained.

IV. Conclusions

The reaction system, consisting of one gaseous and two solid components, is complex and not immediately capable of kinetic study. Yet, from the data we infer the following course of the reaction: The component chlorides (or hydroxides) react at 350–400°C to form the individual sulfides, which are so finely divided that in most instances they cannot be detected by X-ray diffraction. Table III, for example, shows the presence only of CdS. At about 500°C, the finely divided sulfides interact to form the spinel.

Preliminary experiments on heating a composite pressing of CdS and Cr_2S_3, prepared from individual hot-pressed pieces of CdS and Cr_2S_3, show that both cations migrate in opposite directions across the boundary layer.

The interaction of the component sulfides to yield the spinel depends on good homogeneity. X-ray microprobe examination shows some deviation from stoichiometry on a microscopic scale; however, on a macroscopic scale, the spinel is obtained.

The results presented, particularly in conjunction with the optical data taken from the hot-pressed blanks, definitely demonstrate the efficacy of the method of using finely divided materials and low reaction temperature to obtain a spinel phase which can be hot pressed into an optically transparent material.

The results show that hot pressing can be carried out above the reported decomposition temperature for the chalcogenide spinels and can yield high-relative-density, small-grain-size blanks of useful size for device fabrication.

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