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THERMAL STABILITIES OF SOME MAGNETIC CHROMIUM CHALCOGENIDES WITH SPINEL AND HEXAGONAL STRUCTURES

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ABSTRACT

The thermal stabilities of magnetic chromium chalcogenides having the spinel structure, MCr_2X_4 and $CuCr_2X_3Y$ ($M = Cu$, Zn, Cd or Hg; $X = S$, Se or Te; and $Y = Cl$ or Br), and those having a hexagonal structure, MCr_2X_4 ($M = Ba$, Pb or Eu; $X = S$ or Se), have been determined both in vacuum ($< 10^{-5}$ torr) and in air. Of the materials studied, $HgCr_2Se_4$ was found to be the most unstable and $ZnCr_2Se_4$ the most thermally stable. The decomposition processes in vacuum were deduced.

INTRODUCTION

Thermogravimetric analysis provides a useful means for investigating chemical reactions occurring in the solid state at elevated temperatures especially if the results are combined with the results obtained with some other technique such as X-ray diffraction, for detecting the constituents. The thermogravimetric data provide information associated with the pyrolytic behavior of a substance such as the thermal stability and the composition of intermediates and final products. These informations are very useful to understand their single crystal growth and solid state chemistry. Therefore, thermogravimetry of the new classes of magnetic-semiconducting chromium chalcogenides, MCr_2X_4 and $CuCr_2X_3Y$ ($M = Cu$, Zn, Cd, Hg, Ba, Pb or Eu; $X = S$, Se or Te; $Y = Cl$ or Br), is particulary attractive as a method of acquiring information about their thermal properties about which little is known.

In the present paper, the thermal properties of magnetic materials synthesized in this laboratory are described.

EXPERIMENTAL PROCEDURE

The following materials, which were all synthesized in this laboratory, were studied: polycrystals of the magnetic chalcogenide spinels $CuCr_2S_4$, $CuCr_2S_3Cl$, $CuCr_2Se_4$, $CuCr_2Te_4$, $CuCr_2Se_{3.2}Cl_{0.8}$, $CuCr_2Se_{3.2}Br_{0.8}$, $ZnCr_2Se_4$, $HgCr_2S_4$, $HgCr_2Se_4$, $CdCr_2S_4$ and $CdCr_2Se_4$; magnetic materials with a hexagonal structure $BaCr_2S_4$, $EuCr_2Se_4$ and $PbCr_2Se_4$; and single crystals of $CuCr_2Se_{3.5}Cl_{0.5}$, $CuCr_2Se_{3.5}Br_{0.5}$, $CdCr_2Se_4$ and $HgCr_2Se_4$. All polycrystalline samples were ground in an agate mortar and screened through a 400-mesh sieve (particle size 50–10 μ). Single crystals 2–3 mm in size were used without crushing. In all samples, except $CuCr_2Te_4$, no significant second phases were observed in the X-ray diffraction diagram. $CuCr_2Te_4$ contains some impurities of chromium telluride (5–10%).

A thermobalance was constructed using a quartz helical spring which was made by winding a 0.2-mm quartz fiber into about 100 turns. The diameter of the spring was 15 mm with a maximum load carrying capacity of 1.5 g and a sensitivity of 4.2 mg/mm. The detailed dimensions of the complete thermobalance system are illustrated in Fig. 1. The displacement resulting from a change in sample weight was measured by a cathetometer with a measuring range of 180 mm and a detection limit of 0.01 mm. With this system the change in sample weight could be determined to better than 5%.

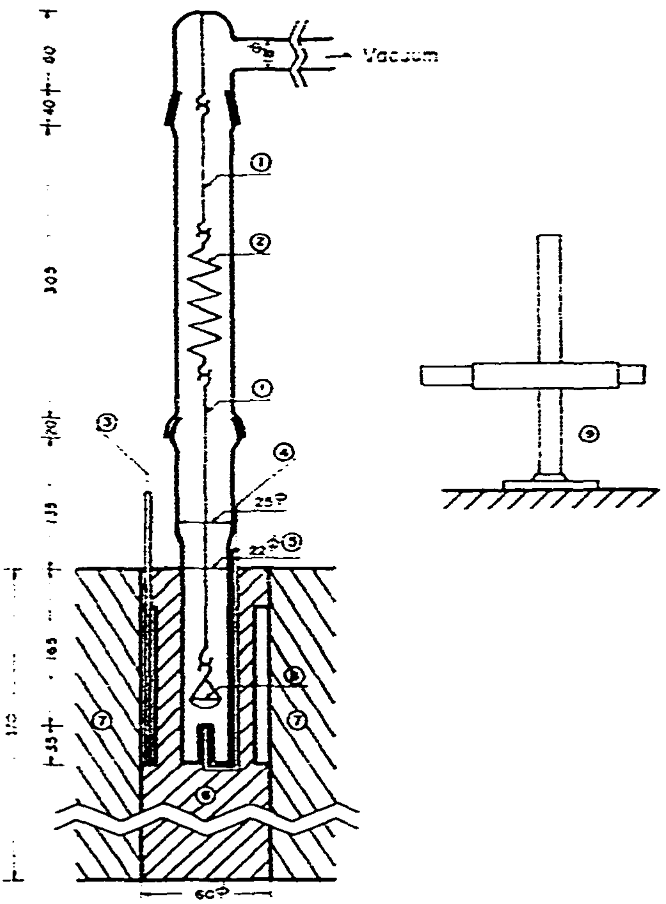

Fig. 1. Thermogravimetric apparatus. 1, quartz rod; 2, quartz spring; 3, thermocouple for temperature controller; 4, thermocouple for sample temperature; 5, quartz reaction tube; 6, refractory materials; 7, furnace; 8, quartz sample pan; 9, cathetometer.

The reaction temperature was measured with a platinum-platinum-13% rhodium thermocouple inserted into the furnace just below the sample pan. The furnace temperature was regulated by a PID type program controller with a SCR voltage regulator.

About 50 mg of material was precisely weighed by an analytical balance and placed into a quartz pan having a diameter of 12 mm and a depth of 7 mm suspended by a quartz fiber from the spring. The sample was first held at 150–200°C for about 45 min and then heated at a uniform heating rate of either 170°C/h in an initial vacuum of 10^{-5} torr or 250°C/h in air. After completion of the heating cycle the sample was reweighed using an analytical balance.

The thermograms obtained from commercially available $CaC_2O_4 \cdot H_2O$ using the present system were compared with those reported previously[1–8] in order to enable us to standardize the observed pyrolysis temperatures for the materials investigated. The use of $CaC_2O_4 \cdot H_2O$ as a thermogravimetric reference substance for determining the performance of a thermobalance has been previously investigated[6].

RESULTS AND DISCUSSION

Measurements made in vacuum

Some typical thermograms obtained in vacuum are shown in Fig. 2. The linear decrease in weight obtained in the absence of a sample, Curve 1, provides a base line for the measurements. The cause of this apparent weight decrease is not understood at present. No special corrections for this sloping base line on the measured thermograms were made since the slopes of both the initial and the final portions of the thermograms were mostly parallel with the base line.

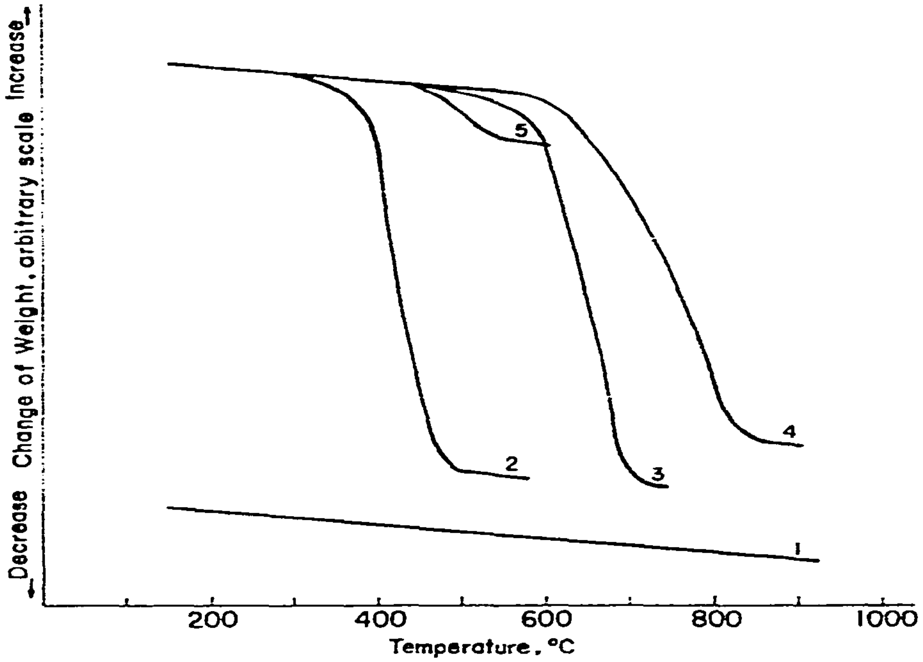

Fig. 2. Typical thermograms in vacuum (heating rate; 170°C/h). 1, base line; 2, $HgCr_2Se_4$; 3, $PbCr_2Se_4$; 4, $CdCr_2Se_4$; 5, $CuCr_2S_4$.

TABLE I

THERMAL DATA IN VACUUM

Sample	*Decomposition temperature range (°C)*	*Major decomposition process*	*Final product checked by X-ray*		*Sample weight (mg)*		*Molecular weight of final product*	
			Major	*Minor*	*Initial*	*Final*	*Obs.*	*Calc.*
$CuCr_2S_4$	$445 \rightarrow 550$	$\rightarrow CuCrS_2 + \frac{1}{2}Cr_2S_3 + \frac{1}{2}S\uparrow$	$CuCrS_2$, Cr_2S_3	[b]	50.70	47.80	278	280
$CuCr_2S_3Cl$	$668 \rightarrow 850$	$\rightarrow ?$	$CuCrS_2$, Cr_2S_3 Cr_3S_4	[b]	50.15	36.45	[c]	[c]
$CuCr_2Se_4$	$532 \rightarrow 560$	$\rightarrow CuCrSe_2 + \frac{1}{2}Cr_2Se_3 + \frac{1}{2}Se\uparrow$	$CuCrSe_2$, Cr_2Se_3	Cr_3Se_4	50.55	46.3[a]	443	444
$CuCr_2Se_{3.2}Cl_{0.8}$	$322 \rightarrow > 918$	$\rightarrow ?$	$CuCrSe_2$, Cr_3Se_4	Cr_2Se_3	51.00	37.65	[c]	[c]
$CuCr_2Se_{3.2}Br_{0.8}$	$518 \rightarrow > 888$	$\rightarrow ?$	$CuCrSe_2$, Cr_3Se_4	Cr_2Se_3	50.40	35.45	[c]	[c]
$CdCr_2S_4$	$528 \rightarrow 850$	$\rightarrow \frac{1}{2}Cr_2S_3 + \frac{1}{3}Cr_3S_4 + CdS\uparrow + \frac{1}{6}S\uparrow$	Cr_2S_3, Cr_3S_4	[b]	100.70	57.60	186	195
$CdCr_2Se_4$	$564 \rightarrow 864$	$\rightarrow \frac{2}{3}Cr_3Se_4 + CdSe\uparrow + \frac{1}{3}Se\uparrow$	Cr_3Se_4	CrSe	50.75	29.35	307	315
$HgCr_2S_4$	$395 \rightarrow 546$	$\rightarrow Cr_2S_3 + HgS\uparrow$	Cr_2S_3	[b]	50.80	25.60	218	200
$HgCr_2Se_4$	$300 \rightarrow 568$	$\rightarrow Cr_2Se_3 + HgSe\uparrow$	Cr_2Se_3	[b]	51.05	27.80	337	341
$ZnCr_2Se_4$	$650 \rightarrow > 1,000$	$\rightarrow 2CrSe + ZnSe\uparrow + Se\uparrow$	CrSe	[b]	50.45	28.85	277	262
$BaCr_2S_4$	$\rightarrow > 1,000$	$\rightarrow ?$	?		51.20	44.25	[c]	[c]
$EuCr_2Se_4$	$\rightarrow > 1,000$	$\rightarrow EuSe + 2CrSe + Se\uparrow$	CrSe, EuSe	[b]	50.55	43.15	488	493
$PbCr_2Se_4$	$525 \rightarrow 727$	$\rightarrow Cr_2Se_3 + PbSe\uparrow$	Cr_2Se_3	Cr_3Se_4	50.85	27.65	342	341

[a] Calculated from sensitivity of the quartz spring. [b] No other phases detected. [c] Not examined.

The results obtained for the decomposition temperature, final products, volatile and deposited materials, probable decomposition processes, and molecular weights of the final products for each of the samples studied are summarized in Table I. In the second column of this table, the decomposition temperature is given as the temperature interval from the initial temperature at which a change in weight was observed to that temperature at which no further appreciable change was observed.

Using the minimum TGA dissociation temperature as the criteria for determining thermal stability, the thermal stability of $CuCr_2X_4$ (X = S or Se) was observed to increase from S to Se. That of the halogen derivatives, $CuCr_2Se_{3.2}Y_{0.8}$ (Y = Cl or Br), increased in the order of $CuCr_2Se_{3.2}Cl_{0.8}$, $CuCr_2Se_{3.2}Br_{0.8}$, and $CuCr_2Se_4$. In the case of the sulfide and selenide homologues of MCr_2X_4 (M = Zn, Cd or Hg, X = S or Se), the thermal stability increased in the order of Hg, Cd and Zn. Among these spinels, $HgCr_2Se_4$ was thermally the most unstable, and started to decompose at 300°C. Lehmann and Emmenegger[9], however, found thermogravimetrically that in an argon atmosphere this compound decomposes into Cr_2Se_3 and HgSe above 450°C. Attempts at annealing $HgCr_2Se_4$ between 300°C and 600°C under a Se atmosphere failed due to decomposition of the compound into HgSe and Cr_2Se_3, and in a Hg atmosphere, however, the sample did not decompose, regardless of the pressure of Hg in the ampoule[10]. It was found in the present study that $CdCr_2Se_4$ decomposed into CdSe and Cr_3Se_4 at about 560°C in vacuum. Wehmeier[11] observed in an annealing study that an excess of selenium vapor (20 mg/ml ampoule volume) prevents $CdCr_2Se_4$ from decomposing into CdSe and Cr_2Se_3 at temperatures less than 870°C.

The ternary chalcogenides $BaCr_2S_4$, $PbCr_2Se_4$ and $EuCr_2Se_4$, which have a hexagonal structure, were also subjected to thermogravimetric analysis. The thermograms of $BaCr_2S_4$ and $EuCr_2Se_4$ monotonically decreased over the entire temperature range from 200 to 1,000°C and were poorly defined. Accordingly, the decomposition temperatures of these materials could not be determined although the thermal stability of $PbCr_2Se_4$ was observed to be comparable to that of $CdCr_2Se_4$.

The final products, after completion of decomposition, were weighed with an analytical balance. The final products and also the intermediate products obtained by heating the sample up to a given intermediate temperature and then cooling to room temperature were identified qualitatively by X-ray powder diffraction. The material deposited on the vessel wall was subjected to qualitative chemical analysis. The analytical results obtained are tabulated in Table II. From these measurements the major decomposition processes and final products for each sample were deduced and these are shown in the third and fourth columns of Table I. As is seen in Table I the decomposition process of the $CuCr_2X_4$ (X = S or Se) spinels was determined to be

$$CuCr_2X_4 \rightarrow CuCrX_2 + \tfrac{1}{2}Cr_2X_3 + \tfrac{1}{2}X\uparrow$$

For the halogen derivatives of the copper-spinels, $CuCr_2X_{3.2}Y_{0.8}$ (X = S or Se Y = Cl or Br), the formation of $CuCrX_2$ and of the chromium chalcogenides as fina products is similar to that for $CuCr_2X_4$. However, the data obtained for the com-

TABLE II

IDENTIFICATION OF DEPOSITED MATERIALS AND INTERMEDIATE PRODUCTS IN VACUUM

Sample	*Heating*		*Element in the deposited materials (Detected by wet-chemical analysis)*	*Species in the heating residue Checked by X-ray*		
	Temp. (°C)	*Time (min)*		*Temp. (°C)*	*Major*	*Minor*
$CuCr_2S_4$	300	30	free S	550	$CuCrS_2$, Cr_2S_3	spinel phase
	550	60	free S			
$CuCr_2S_3Cl$	350	40	Non-deposited S (free), material soluble in aq. reg.	450	spinel phase	$CuCrS_2$
	450	20				
$CuCr_2Se_4$	200	30	free Se	600	spinel phase	$CuCrSe_2$, Cr_2Se_3
	600	50	free Se			
$CuCr_2Se_{3.2}Cl_{0.8}$	200	50	Cl (trace), Se	600	spinel phase	$CuCrSe_2$
	350	40	Se, Cl			
	600	45	Se, Cl			
$CuCr_2Se_{3.2}Br_{0.8}$	300	45	Se, Br, Cu, Cr (?)	650	spinel phase	$CuCrSe_2$, Cr_2Se_3
	500	45	Se, Br			
	650	60	Se, Br, Cu, Cr (?)			
$HgCr_2Se_4$	300	70	Se, Hg, Cr (trace)	500	Cr_2Se_3	spinel phase
	500	90	Se, Hg, Cr			
$CdCr_2S_4$	200	45	free S	450	spinel phase	Cr_2S_3
	450	50	S, Cd			
$CdCr_2Se_4$	150	45	Se, Cd (?)	300	spinel phase	no
	300	30	Se, Cd (?)			

pounds $CuCr_2X_{3.2}Y_{0.8}$ was more complicated and the actual decomposition processes could not be determined with certainty.

Since the metal chalcogenides, MX, formed by the decomposition of MCr_2X_4 (M = Zn, Cd, Hg or Pb; X = S or Se) were generally volatile, the general decomposition process was *a priori* assumed to be

$$MCr_2X_4 \rightarrow MX\uparrow + Cr_2X_3$$

However, heating of all these materials did not always give Cr_2X_3 as a decomposition product, sometimes Cr_3X_4 or CrX was obtained. The actual phases of the chromium chalcogenides observed are shown in Table I. The experimental results suggest that the final state of the chromium chalcogenides is strongly dependent on the decomposition temperature of the given material. Actually, in the case of $HgCr_2Se_4$, which decomposed at the lowest temperature, the final phase was exclusively Cr_2Se_3, while in $ZnCr_2Se_4$, which decomposed at the highest temperature, the final phase observed was CrSe. Furthermore, for $CdCr_2Se_4$ and for $PbCr_2Se_4$, the final phases were a mixture of Cr_3Se_4 and CrSe, and of Cr_2Se_3 and Cr_3Se_4, respectively. In an attempt to understand the complicated decomposition scheme of these materials, γ-phase chromium selenide Cr_2Se_3, obtained from the decomposition of $HgCr_2Se_4$, was subjected to thermogravimetric analysis at a heating rate of 40°C/h under vacuum ($\sim 10^{-5}$ torr). The thermogram of this material was poorly defined and showed a continuous decrease over the wide temperature range from 600 to 1,000°C. From X-ray powder diffraction data the final phase was found to be CrSe. X-ray analyses of the same starting materials which were heated up to several intermediate temperatures definitely suggest the existence of a phase transformation $Cr_2Se_3 \rightarrow Cr_3Se_4 \rightarrow$ CrSe as the temperature is increased. The results obtained indicated that although the decomposition reactions overlapped considerably, Cr_2Se_3 was predominant up to 800°C, Cr_3Se_4 between 800 and 1,000°C, and CrSe above 1,000°C. A similar behavior would be expected for chromium sulfide. The rather complicated decomposition processes observed in $CdCr_2X_4$ (X = S or Se), $CuCr_2Se_4$ and $PbCr_2Se_4$ are thought to be due to the overlap of these phases.

Since the europium chalcogenides are not volatile, EuSe and CrSe are the final products for $EuCr_2Se_4$. The presence of CrSe at above 1,000°C in a final state is consistent with the results of thermal analysis of Cr_2Se_3. Neither X-ray analysis nor wet chemical analysis were performed on the final products from $BaCr_2S_4$ because thermal decomposition was apparently incomplete even at 1,000°C, which was practically the high temperature limit of our furnace.

It is assumed that the amount of chromium metal originally present remains without any loss during the heat treatment. The formula weights of the final products were then simply evaluated from the initial sample weight, its molecular weight and the weight of the final products, regardless of their molecular formula. The formula weights thus determined are listed in the last column of Table I under the notation "Obs.". These formula weights were then compared with those calculated theoretically on the basis of the molecular formula of the final products, as indicated by the decomposition processes, which were deduced from X-ray and chemical analyses data. The results were in fair agreement within the experimental error. Therefore, these results confirm that the decomposition processes deduced should be the most probable ones.

Single crystals of $HgCr_2Se_4$, $CdCr_2Se_4$, $CuCr_2Se_{3.5}Br_{0.5}$ and $CuCr_2Se_{3.5}Cl_{0.5}$ were also subjected to thermogravimetric analysis. The thermograms were essentially similar to those obtained from polycrystals, however, the single crystals tended to decompose at apparent temperatures higher than those for polycrystals by about 50–100°C.

Measurements made in air

Fig. 3 shows some typical thermograms obtained in air. In contrast to those obtained in vacuum, these thermograms, with the exception of $HgCr_2Se_4$, are poorly defined and spread over a considerable temperature range. In most cases a slight gain in weight in advance of a sudden decrease was observed. Although thermogravimetric analysis strongly depends on driving off an evolved vapor, under an atmospheric environment this vapor may bind to the residue. In the present case, either sulfur dioxide or selenium dioxide may be adsorbed on the surface of the residue because of the restriction in the immediate vicinity of the sample on the effluence. However, as soon as decomposition starts, a sudden change in weight occurs and simultaneously the ambient pressure of sulfur or selenium dioxide increases. This

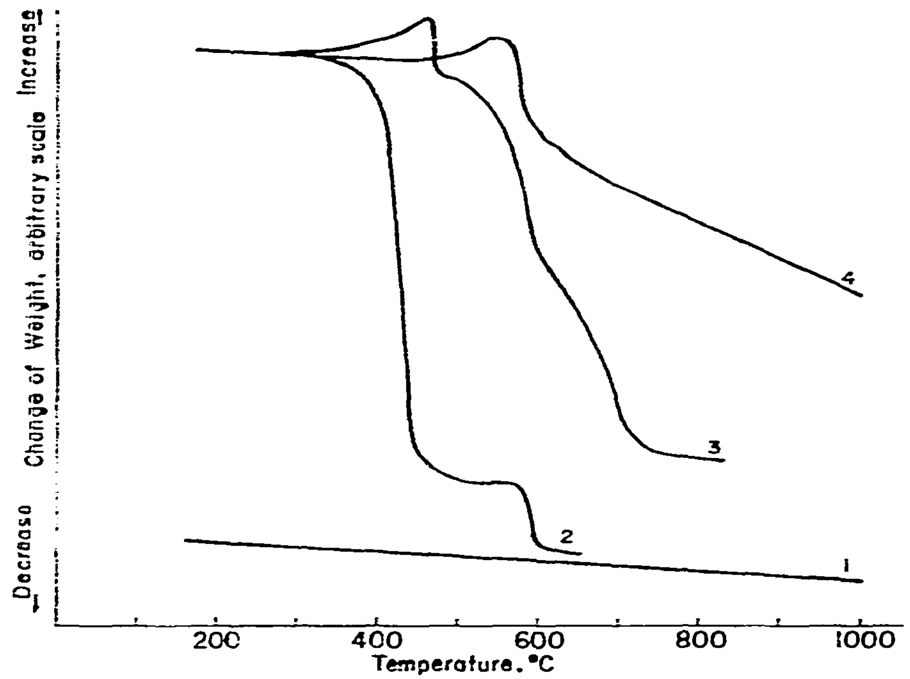

Fig. 3. Typical thermograms in air (heating rate; 250 C/h). 1, base line; 2, $HgCr_2Se_4$; 3, $CuCr_2S_3Cl$; 4, $CuCr_2S_4$.

in turn limits the reaction rate, but since the sulfur dioxide or the selenium dioxide diffuses gradually away, its ambient partial pressure is neither constant nor even reasonably predictable. As a consequence of all of these effects, the change in weight shown in a thermogram may be indistinct and spread over a considerable temperature range. The case of $HgCr_2Se_4$ is exceptional. Its thermogram was well defined and showed two distinct steps. The first step probably corresponds to the sublimation of HgSe which occurs in vacuum at a temperature close to that of the first step. The second step may be due to the oxidation reaction $Cr_2Se_3 \rightarrow Cr_2O_3$.

The results obtained in air for the decomposition temperature, final products, and volatile and decomposed materials are summarized in Table III. Although the thermograms obtained were too poorly defined to determine the detailed reactions which occurred, the relative thermal stabilities, in air, of the samples studied could be determined. The relative thermal stability of the $CuCr_2X_4$ (X = S, Se or Te) and of the $CuCr_2Se_{3.2}Y_{0.8}$ (Y = Cl or Br) systems was the same as was obtained in vacuum, that is the stability of $CuCr_2X_4$ increased from S to Te and that of $CuCr_2Se_{3.2}Y_{0.8}$ increased in the order of $CuCr_2Se_{3.2}Cl_{0.8}$, $CuCr_2Se_{3.2}Br_{0.8}$ and $CuCr_2Se_4$. In $CdCr_2X_4$, however, the sulfide was found to be more stable than the selenide.

TABLE III

THERMAL DATA IN AIR

Sample	*Decomposition temperature range (°C)*	*Final product checked by X-ray*		*Volatile and deposited material*
		Major	*Minor*	
$CuCr_2S_4$	562→1,000	$CuCrO_2$, Cr_2O_3	[a]	SO_2
$CuCr_2S_3Cl$	462→742	Cr_2O_3	[a]	CuCl, SO_2
$CuCr_2Se_4$	700→>948	$CuCrO_2$, Cr_2O_3	[a]	SeO_2
$CuCr_2Se_{3.2}Cl_{0.8}$	424→930	$CuCrO_2$, Cr_2O_3	[a]	CuCl, SeO_2
$CuCr_2Se_{3.2}Br_{0.8}$	620→1,040	$CuCrO_2$, Cr_2O_3	[a]	CuBr, SeO_2
$CuCr_2Te_4$	808→>1,055	[b]	[b]	[b]
$CdCr_2S_4$	800→>946	$CdCr_2O_4$	Cr_2O_3	SO_2
$CdCr_2Se_4$	542→>714	$CdCr_2O_4$	[a]	SeO_2
$HgCr_2Se_4$	340→612	Cr_2O_3	[a]	HgSe, SeO_2
$BaCr_2S_4$	→>1,000	$BaSO_4$, Cr_2O_3	[a]	SO_2
$EuCr_2Se_4$	650→>900	$EuCrO_3$, Cr_2O_3	[a]	SeO_2

[a] No other phases detected. [b] Not examined

For the compounds $CuCr_2X_4$ and its halogen derivatives, the final products observed were exclusively $CuCrO_2$ and Cr_2O_3 while for $CdCr_2X_4$ the final product observed was $CdCr_2O_4$. For $HgCr_2Se_4$, sublimation of HgSe was observed before the oxidation reactions. However, $CuCr_2X_4$ were attacked by oxygen before decomposition into chalcogenides of $CuCrX_2$ and Cr_2X_3. Oxidation of Cr_2S_3 in a stream of O_2 is significant at 500–600°C, and intense oxidation starts at 700°C[12]. In the ternary chalcogenides with a hexagonal structure, $BaCr_2S_4$ and $EuCr_2Se_4$, the final products were found from X-ray powder diffraction to be $BaSO_4$ and $EuCrO_3$.

respectively. Although the final products of the decomposition of $BaCr_2S_4$ in vacuum were not determined, the final product of the decomposition of $EuCr_2Se_4$ in air, $EuCrO_3$, was not the same as the EuSe which was obtained in vacuum.

The decomposition processes in air were not determined as were those in vacuum. To determine such processes from thermogravimetric measurements made in air is difficult since it is necessary to consider environmental influences as discussed by Garn and Kessler[13].

Further details on the thermal properties and on the kinetic parameters associated with thermal decomposition will be reported separately.

CONCLUSION

Most of the chalcogenide spinels presently studied decomposed between 300 and 700 °C in vacuum. They underwent decomposition mostly by the following two processes

$$MCr_2X_4 \rightarrow MCrX_2 + \tfrac{1}{2}Cr_2X_3 + \tfrac{1}{2}X\uparrow \qquad (1)$$

and

$$MCr_2X_4 \rightarrow MX\uparrow + Cr_2X_3 \qquad (2)$$

The copper containing spinels decomposed via Eqn. (1) and the rest via Eqn. (2). All the compounds MX produced in process (2) were vaporized at the decomposition temperature.

The thermal stability of $CuCr_2X_4$ ($X = S$, Se or Te) was observed to increase from S to Te. That of the halogen derivaties, $CuCr_2Se_{3.2}Y_{0.8}$ ($Y = Cl$ or Br), increased in the order of $CuCr_2Se_{3.2}Cl_{0.8}$, $CuCr_2Se_{3.2}Br_{0.8}$ and $CuCr_2Se_4$. In the case of the sulfide and selenide homologues of MCr_2X_4 ($M = Zn$, Cd or Hg; $X = S$ or Se), the thermal stability increased in the order of Hg, Cd and Zn. Chromium chalcogenides were always formed as final products in both cases. However, the compositional ratio of chromium to chalcogen in the chromium chalcogenides varied depending on the decomposition temperature of the original spinel. Cr_2Se_3 was the predominant product for decompositions carried out up to 800 °C, Cr_3Se_4 from 800 to 1,000 °C, and above 1,000 °C CrSe was observed as the main phase. Most of the spinels, except the cadmium chalcogenides, decomposed in air by a process similar to that in vacuum and then finally changed into their corresponding oxides, *i.e.* into $CuCrO_2$ and Cr_2O_3 in the case of copper containing spinels and into just Cr_2O_3 in the case of $HgCr_2Se_4$. Cadmium compounds formed the corresponding oxide, $CdCr_2O_4$. On the other hand, the final decomposition products from hexagonal chalcogenides were quite different from those in vacuum; $BaSO_4$ and Cr_2O_3 were formed from $BaCr_2S_4$, and $EuCrO_3$ and Cr_2O_3 from $EuCr_2Se_4$.

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