450 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49(2), 450—456 (1976) [Vol. 49, No. 2

Composition of Single Crystals of Chromium Chalcogenide Spinels Grown by Chemical Vapor Transport

Kohei Ametani

RCA Research Laboratories, Inc., Zushi-machi, Machida-shi, Tokyo 194-02

(Received May 15, 1975)

Compositional analyses using atomic absorption spectrophotometry were carried out on the vapor-phase grown single crystals of copper-based spinels with the nominal formulas such as $CuCr_2S_3Cl$, $Cu_{1-x}Fe_xCr_2S_4$ ($x \leq 1$), $Cu_{0.5}In_{0.5}Cr_2S_4$, $CuCr_2Se_3Cl$, and $CuCr_2Se_3Br$, and the cadmium-based spinels of $CdCr_2S_4$ and $CdCr_2Se_4$, including crystals doped with indium, silver, and copper. The grown crystal usually had a composition different from the nominal formula and a tetrahedral-site deficiency of the copper-based spinels is reported for the first time. All crystals of $Cu_{1-x}Fe_xCr_2S_4$ and $Cu_{0.5}In_{0.5}Cr_2S_4$ were contaminated with a considerable amount of chlorine and some of the crystals had a substantial cation deficiency on the tetrahedral sites; the cation deficiency increases with increasing copper or chlorine content. For the $CuCr_2S_3Cl$ and $CuCr_2Se_3Br$ crystals, a large copper deficiency was also found while the halogen content was close to that expected for the nominal compositions, or somewhat higher. Of all the copper-based spinels, the least tetrahedral-site deficiency was observed in the $CuCr_2Se_3Cl$ crystals, but the chlorine content was much less than the stoichiometric content. The cadmium-based spinels usually satisfied the stoichiometric formula $CdCr_2S_4$ or $CdCr_2Se_4$.

The magnetic, electrical, and optical properties of chromium chalcogenide spinels have been extensively investigated. In spinels with the general formula ACr_2X_4, the A sites are usually filled with bivalent metal ions (M^{2+}) or a mixture of uni- and trivalent cations ($M^{+}_{0.5}M^{3+}_{0.5}$–). The X sites are occupied by a single chalcogen anion (–X^{2-}_4) or a combination of chalcogen with halogen anions (–$X^{2-}_3Y^-$; Y=halogen); in the latter case, the effective cation valence of the A sites is reduced to univalent. Single crystals are usually grown by the chemical vapor-transport method, using a halogen as a transport agent.[1—3] The crystals obtained are, at most, 3—4 mm on edge and weigh only several mg. A number of workers have spent a lot of time and effort to grow large single crystal using the chemical vapor-transport method and other methods, but the crystals obtained are size limited. Therefore, some of published papers reported the physical properties of the crystals without chemical analysis, or only a partial chemical analysis of impurities[4—11] and some of the main components[10—16] of the crystals has been made. Very little has been published about the compositional analysis of all the major constituents.[9,17] Most of the published papers described only the results of the analysis without details of the procedures for the analysis. In the present paper, we describe a method of chemical analysis to determine the composition of some single crystals of chromium chalcogenide spinels using AAS (Atomic Absorption Spectrophotometry) technique and present a serious problem regarding the composition of various samples; the grown crystals usually had compositions different from their nominal formula. The AAS technique provides a high sensitivity and selectivity so that the sample weight can be reduced to a minimum amount, and the major as well as minor constituents or impurities can be determined continuously or simultaneously from the same small sample. The use of the same sample would be recommended to obtain consistent analytical data. The present analytical method was developed from our previously reported procedures for chlorine[10] and sulfur.[15] Using 10 mg samples, the metallic elements were determined directly from their atomic absorptions. Chlorine and sulfur were determined indirectly from the silver and barium atomic absorptions after being captured in the form of silver chloride[10] and barium sulfate,[15] respectively.

The materials to be analyzed were the copper-based spinels with nominal formulas such as $CuCr_2S_3Cl$, $Cu_{1-x}Fe_xCr_2S_4$($x \leq 1$), $Cu_{0.5}In_{0.5}Cr_2S_4$, $CuCr_2Se_3Cl$, and $CuCr_2Se_3Br$, and the cadmium-based spinels of $CdCr_2S_4$ and $CdCr_2Se_4$, including crystals doped with indium, silver, and copper. Of these materials, the chlorine content for some of the copper-based and cadmium-based spinels,[10,11] the sulfur content of $CuCr_2S_3Cl$ and $CdCr_2S_4$ crystals,[15] and the content and site preference of dopants in $CdCr_2X_4$ crystals,[11] were reported previously. The single crystals, except for the halochalcogenides, were grown by the closed-tube vapor transport, where the starting materials with the above-described compositions were mixed with a solid transport agent $CrCl_3$, usually in ratio of 10 : 1. The halochalcogenide crystals were grown by transport either with an intrinsic copper halide present in the starting materials or an extra copper halide added as the halogen source. The details of the growth conditions can be found elsewhere.[1,11,18—20] All the crystals were prepared in these laboratories and the physical properties of some of the crystals have been reported.[18—23]

Experimental

Apparatus. Atomic absorption measurements were made in an air-acetylene flame using a Hitachi model 208 Atomic Absorption Spectrophotometer and Hitachi hollow-cathode lamps HLA-3, except the lamp used for the selenium measurement, which was obtained from Westinghouse. The analytical lines used were Cr 357.9 nm, Fe 372.0 nm, Cu 324.7 nm, Se 204.0 nm, Ag 328.1 nm, Cd 228.8 nm, In 303.9 nm, and Ba 553.5 nm.

Standard Solutions. (1) Solutions of metal chlorides: The chromium and iron solutions were prepared by dissolving metals (99.9%) in hydrochloric acid and diluting with deionized water. The copper, cadmium, and indium solutions were prepared by dissolving metals (99.9—99.99%) in nitric acid, removing the excess nitric acid by evaporation with hydrochloric acid, and then dissolving the residue in de-

Table 1. Confirmation of procedures using mixtures of standard solutions

Solution[a)]	Analyte, mg									
	Cu		Cd		Cr		S		Cl	
	added	obsd	added	obsd	added	obsd	added	obsd	added	obsd
1	2.00	2.00	—		3.50	3.48	3.00	3.01	—	
2	2.00	2.00	—		3.50	3.48	3.50	3.52	—	
3	2.00	2.00	—		3.50	3.49	4.00	3.95	—	
4	—		3.00	3.01	3.00	2.98	4.00	3.95	—	
5	2.00	1.98	—		3.50	3.53	—		1.50	1.50
6	2.00	1.98	—		3.50	3.53	—		1.00	0.99
7	2.00	1.98	—		3.50	3.53	—		0.500	0.492
8	0.150	0.150	3.00	2.96	3.00	2.99	—		0.100	0.102
9	0.100	0.100	3.00	2.96	3.00	2.99	—		0.050	0.052
10	0.050	0.051	3.00	2.99	3.00	3.03	—		0.025	0.026
11	—		3.00	2.99	3.00	3.02	—		0.010	0.010

a) Solutions (5—7) and (8—11) also contained 3.50 and 4.00 mg of S, respectively, as Na_2SO_4.

ionized water. All the solutions were stocked as 0.1 M hydrochloric acid solutions with a concentration of 1 mg analyte/ml. (2) Solutions of metal nitrates: The chromium and iron solutions were prepared by dissolving the respective nitrates in deionized water and then standardizing by chelatometry using EDTA. The copper, cadmium, and indium solutions were prepared by dissolving metals (99.9—99.99%) in nitric acid and diluting with deionized water. All the solutions were stocked as 0.1 M nitric acid solutions with a concentration of 1 mg analyte/ml. (3) Other solutions: The selenium solution was prepared by dissolving elemental selenium (99.9%) in nitric acid and diluting with deionized water. The stock solution had a concentration of 1 mg Se/ml with 0.1 M nitric acid. The silver solutions (1, 0.5, or 0.25 mg Ag/ml) were prepared by dissolving silver nitrate (dried at 110 °C) in a minimum amount of deionized water, and then diluting with concentrated nitric acid. The silver solutions were used to dissolve samples as described below. The solutions containing 1 mg Ag/ml were also prepared from silver nitrate and stocked as 0.1 M nitric acid solutions. The barium solution (5 mg Ba/ml) was prepared by dissolving barium chloride dihydrate in deionized water and standardizing by chelatometry using EDTA. The sulfur and chlorine solutions (1 mg analyte/ml) were prepared by dissolving sodium sulfate and sodium chloride (dried at 110 °C), respectively, in deionized water. Reagents used were of analytical reagent grade.

Procedure (A). Pulverized crystals weighing 10 mg (usually 5—6 crystals) were dissolved in nitric acid containing excess silver ions of a known quantity and chlorine was simultaneously precipitated as silver chloride. For a sample containing several hundred μg to about 1 mg of chlorine, 5 ml of nitric acid containing 1 mg Ag/ml was used, and the solution was then diluted to about 50 ml. However, if the expected chlorine content in the sample was less than 100 μg, 2 ml of nitric acid containing 0.5 or 0.25 mg Ag/ml was used and the solution diluted to about 20 ml. The solution was aged for 30 min over a hot water bath. After the solution was cooled in ice water, the precipitated silver chloride was filtered and washed with six 5-ml portions of cold nitric acid (1 : 50), and dissolved in an aqueous ammonia solution. Both the ammoniacal solution and the filtrate were diluted to an appropriate concentration of analytes and the atomic absorptions measured. For the measurements, the concentrations of nitric acid and ammonia were adjusted to 0.05—0.3 M and 3%, respectively, because the interference effects of coexisting foreign elements at these concentrations were found to be negligible.[10,11] The chlorine content, except for the silver-doped $CdCr_2S_4$ and $CdCr_2Se_4$ crystals, was determined indirectly from the silver content, usually, in both the ammoniacal solution and the filtrate. For the silver-doped crystals, chlorine was determined from the silver content in the ammoniacal solution. Metallic elements, such as chromium, iron, copper, cadmium, and indium, and also selenium, were determined from the filtrate. The silver content in the silver-doped crystals was determined by comparing the total amount of silver in both the filtrate and the ammoniacal solution with the amount of silver contained in the nitric acid solution used to dissolve the crystals. The results obtained were corrected by the blank test in all cases.

Procedure (B). This procedure is applicable for the sulfides only, and not for the selenides. Pulverized crystals weighing 10 mg were dissolved in 2 ml of concentrated nitric acid containing bromine in order to oxidize the sulfurs into sulfate ions. The sample solution was evaporated nearly to dryness. After removal of the nitric acid by evaporation with hydrochloric acid, the residue was dissolved in deionized water. The sample solution was diluted to about 20 ml and warmed to about 80 °C. If iron was present in the solution, the iron(III) ions were reduced to iron(II) ions by adding a minimum amount of ascorbic acid. The acidity of the solution was adjusted to 0.05 M hydrochloric acid, and 5 ml of the standard barium solution (5 mg Ba/ml) was slowly added to the solution. The precipitated barium sulfate was allowed to settle for 1 hr over a hot water bath. After aging more than 20 hr, the precipitate was filtered and washed with six 5-ml portions of boiling water. The filtrate was diluted to an appropriate concentration of analytes and the atomic absorptions measured. For the measurements, the concentration of hydrochloric acid was adjusted to 0.05—0.2 M because the interference effects of coexisting foreign elements are negligible at these concentrations.[11,15] Metallic elements, except for silver, were determined directly by their atomic absorptions, and sulfur, indirectly by the atomic absorption of an excess of barium in the filtrate. Silver was not determined by this procedure.

The procedures (A) and (B) were confirmed by using mixtures of the standard solutions. Table 1 shows typical results for procedures (A) and (B). The tabulated values

TABLE 2. RESULTS OF SINGLE-CRYSTAL ANALYSIS FOR COPPER-BASED CHROMIUM SPINELS

Sample, nominal composition	Analyte, mole ratio								Lattice constant, a_0(Å)[d)]
	Cu	Fe	In	Cr	X[a)]	Y[a)]	Cr/A[b)]	M/(X+Y)[c)]	
$CuCr_2S_3Cl$ (1)	0.87_3	—	—	2.04_3	2.97_5	1.10_6	2.33_8	0.71_4	9.902
$CuCr_2S_3Cl$ (2)	0.86_4	—	—	2.04_8	2.94_2	1.14_4	2.37_1	0.71_2	9.906
$CuCr_2S_3Cl$ (3)	0.85_2	—	—	1.99_6	2.78_5	1.18_6	2.34_1	0.71_7	9.907
$Cu_{0.8}Fe_{0.2}Cr_2S_4$	0.70_3	0.05_6		1.93_8	3.28_8	1.01_2	2.54_9	0.62_8	9.901
$Cu_{0.6}Fe_{0.4}Cr_2S_4$	0.81_3	0.07_3	—	2.01_1	3.34_1	0.76_0	2.26_9	0.70_6	9.880
$Cu_{0.4}Fe_{0.6}Cr_2S_4$	0.65_5	0.29_8	—	2.03_4	3.55_7	0.45_3	2.13_2	0.74_4	9.892
$Cu_{0.2}Fe_{0.8}Cr_2S_4$	0.32_0	0.69_5	—	2.04_5	3.70_2	0.23_5	2.01_2	0.77_7	9.936
$FeCr_2S_4$	—	0.96_8	—	2.01_1	3.95_2	0.06_6	2.07_6	0.74_1	10.083
$Cu_{0.5}In_{0.5}Cr_2S_4$ (1)	0.52_2	—	0.45_8	1.91_4	4.01_9	0.08_4	1.95_0	0.70_3	10.057
$Cu_{0.5}In_{0.5}Cr_2S_4$ (2)	0.57_3	—	0.35_9	1.94_3	3.85_5	0.26_6	2.08_1	0.69_5	10.089
$Cu_{0.5}In_{0.5}Cr_2S_4$ (3)	0.59_3	—	0.31_4	1.99_4	3.87_1	0.22_5	2.19_7	0.70_3	10.016
$CuCr_2Se_3Cl$	0.97_6	—	—	2.01_6	3.68_7	0.31_9	2.06_5	0.74_7	—
$CuCr_2Se_3Br$[e)]	0.77_8	—	—	1.99_9	3.19_4	1.02_7	2.56_9	0.65_8	—
$CuCr_2Se_3Br$[e)]	0.82_3	—	—	1.99_7	3.14_0	1.03_6	2.42_5	0.67_5	—

a) "X" designates S or Se and "Y" designates Cl or Br. b) The ratio expected for the formula is 2 for each sample, where "A" is Cu, Fe, and/or In. c) "M" designates cationic elements (Cu, Fe, In, and Cr) and the expected value of the ratio is 0.75 for each sample. d) Average of at least five determinations with the standard deviation 0.003—0.005 Å. e) Both sets of crystals were grown in the same batch. The first set was analyzed by procedure (A) of the present work and the second set was analyzed by the alternative method.[29)]

for chlorine are the average of values obtained from the filtrate and the ammoniacal solution. Most of the observed values are in agreement with the added amounts, within 1—2%.

Results and Discussion

The results of analyses are presented as mole ratios of the analytes, as calculated from the observed wt% values, in order to easily understand the chemical composition of the present materials. Most of the results for metallic elements are the average of values obtained by the procedures of both (A) and (B). Table 2 shows the results for the copper-based chromium chalcogenide spinels. Table 3 compares the compositions determined by chemical analysis with those estimated from lattice parameters for crystals of the system $Cu_{1-x}Fe_xCr_2S_4$ ($x \leq 1$). Table 4 gives the results for the cadmium-based spinels including crystals doped with indium, silver, and copper.

$CuCr_2S_3Cl$. Samples grown in three different batches were analyzed. As can be seen in Table 2, all the results indicate that the crystal did not have the stoichiometric formula $CuCr_2S_3Cl$; the chlorine content is much higher than the stoichiometric amount.[10)] The cation-to-anion ratio, (Cu+Cr)/(S+Cl), also shows that the total amount of the anionic elements was higher and that of the cations was lower than the expected amount. This is due to an insufficient amount of copper as shown in Table 2. Therefore, it can be concluded that the crystal has a copper deficiency on the tetrahedral sites in the spinel structure and the formula is written as $Cu_{1-x}\square_xCr_2S_{4-y}Cl_y$, where $\square$ designates the copper deficiency. When the mole ratios in Table 2 are normalized by the value of 2 for chromium, the empirical formulas for these crystals can be expressed as follows;

sample (1) $Cu_{0.86}\square_{0.14}Cr_2S_{2.91}Cl_{1.08}$,
sample (2) $Cu_{0.84}\square_{0.16}Cr_2S_{2.87}Cl_{1.12}$,
sample (3) $Cu_{0.85}\square_{0.15}Cr_2S_{2.80}Cl_{1.19}$.

Actually, Wada[24)] of these laboratories successfully prepared polycrystalline powders of the copper-deficient chlorosulfospinels, $Cu_{1-x}\square_xCr_2S_3Cl$ ($x \leq 0.3$), by firing mixtures of copper(I) chloride, copper(II) chloride, chromium metal, elemental sulfur at high temperatures. He found that compounds with x=0.2—0.3 were the most pure of all the compositions, whereas the stoichiometric compound (x=0) always had a minor second phase of hexagonal $CuCrS_2$ as determined by X-ray diffraction; the degree of contamination by the second phase increased with the decreasing x. Another example of such metal-deficiencies are the trivalent metal-based sulfospinels $M_{16/9}\square_{3/9}Cr_{8/9}S_4$ with M= Al or In.[25)]

The lattice constants of these crystals range from 9.902 to 9.907 Å, as given in Table 2. These values are nearly the same as those for single crystals with the composition close to $CuCr_2S_3Cl$ reported by Sleight and Jarrett.[12)] They used a chemical analysis to determine the composition of crystals, but did not give the data for elements other than chlorine nor did they present the details of their chemical analysis. Presumably the crystal composition is dependent on the growth conditions.

$Cu_{1-x}Fe_xCr_2S_4$. For the system, samples with the nominal composition x=0.2, 0.4, 0.6, 0.8, or 1.0 were analyzed. For all of the crystals analyzed, the copper content was higher and the iron content much lower than the nominal amount, especially for the lower values of x. Colorimetric methods[26)] also showed similar results. It seems that copper is transported more preferentially than iron during the vapor transport reaction, while, in the case of the $Cd_{1-x}Fe_xCr_2S_4$

system ($0 \leq x \leq 1$),[16] iron is incorporated more readily than the nominal content in the vapor-phase grown crystals. As can be seen in Table 2, a deficiency in the tetrahedral-site was also found for the crystals. For crystals containing the higher amount of iron, however, the degree of this deficiency was small; both ratios of chromium-to-copper and iron, Cr/(Cu+Fe), and cation-to-anion, (Cu+Fe+Cr)/(S+Cl), are closer to the expected values than those of crystals with the lower amount of iron. On the other hand, when the copper content increases or the iron content decreases, the tetrahedral-site cation deficiency increases when chlorine is easily incorporated in the crystals (see results for the $Cu_{0.8}Fe_{0.2}Cr_2S_4$ and $Cu_{0.6}Fe_{0.4}Cr_2S_4$ crystals). The $FeCr_2S_4$ crystal even seems to have a small deficiency on the tetrahedral sites as shown in Table 2. A similar result was reported by Goldstein *et al.*,[9] where the $FeCr_2S_4$ crystal was grown by use of $HCl+Cl_2$ gas as the transport agent. They found about 1% deviation in the chromium-to-iron ratio, Cr/Fe, but our result was about 3.5%. The discrepancy between the two results may be related to a variation of the chlorine content in the crystal; the mole ratio of chlorine presented in Table 2 corresponds to 0.8 wt%, whereas Goldstein *et al.*[9] reported only 0.01 wt%.

Haacke and Beegle[27] prepared polycrystalline samples in the entire composition range of the system $Cu_{1-x}Fe_xCr_2S_4$ ($0 \leq x \leq 1$), and found that the curve of lattice parameters *vs.* composition obeys Vegard's law. They used Vegard's law to determine the copper and iron content in single crystals grown by chemical vapor transport using HCl gas as the transport agent; the reported compositions ranged from $Cu_{0.59}Fe_{0.41}Cr_2S_4$ to $FeCr_2S_4$. However, the present results suggest that Vegard's law seems to be unsuitable for the determination of the copper and iron content in vapor-phase grown crystals of this system because of the tetrahedral-site deficiency and the observed higher incorporation of chlorine, (as described previously), which, in turn, cause the compositional variation of components other than copper and iron.

Table 3 compares the compositions determined by Vegard's law and our chemical analysis using this AAS technique for crystals of the system $Cu_{1-x}Fe_xCr_2S_4$. The compositions determined by chemical analysis are normalized by the value of 2 for chromium while those by Vegard's law are determined by the lattice constants, 9.819 and 9.989 Å for polycrystalline $CuCr_2S_4$ and $FeCr_2S_4$,[13] respectively. As can be seen in Table 3, the iron content determined by Vegard's law is usually much higher, particularly for crystals with a lower iron content than that obtained by chemical analysis. Banus[13] also obtained similar results for single crystals of this system by determining the copper, iron, and chromium content, using chemical analysis of crystals grown by transport with $CrCl_3$ as the transport agent. He found that the lattice constants of single crystals are 0.005 to 0.025 Å higher than those of polycrystals, assuming that both polycrystalline and single-crystal samples have the same value of *x*. This tendency indicates that the iron content determined by Vegard's law is apparently higher than the actual content because the lattice constant of $FeCr_2S_4$ is larger than that of $CuCr_2S_4$. In addition, Vegard's law does not suggest anything about components other than copper and iron. Our results for the $Cu_{0.2}Fe_{0.8}Cr_2S_4$ crystal showed that the composition of crystals of this system comes closer to the general formula $Cu_{1-x}Fe_xCr_2S_4$ when the iron content increases and the chlorine content decreases.

TABLE 3. COMPARISON OF COMPOSITIONS DETERMINED BY VEGARD'S LAW AND CHEMICAL ANALYSIS FOR SINGLE CRYSTALS OF THE SYSTEM $Cu_{1-x}Fe_xCr_2S_4$

Sample, nominal composition	Determined composition	
	by Vegard's law	by chemical analysis
$Cu_{0.8}Fe_{0.2}Cr_2S_4$	$Cu_{0.52}Fe_{0.48}Cr_2S_4$	$Cu_{0.73}Fe_{0.06}Cr_2S_{3.39}Cl_{1.04}$
$Cu_{0.6}Fe_{0.4}Cr_2S_4$	$Cu_{0.64}Fe_{0.36}Cr_2S_4$	$Cu_{0.81}Fe_{0.07}Cr_2S_{3.32}Cl_{0.76}$
$Cu_{0.4}Fe_{0.6}Cr_2S_4$	$Cu_{0.57}Fe_{0.43}Cr_2S_4$	$Cu_{0.64}Fe_{0.29}Cr_2S_{3.50}Cl_{0.45}$
$Cu_{0.2}Fe_{0.8}Cr_2S_4$	$Cu_{0.31}Fe_{0.69}Cr_2S_4$	$Cu_{0.31}Fe_{0.70}Cr_2S_{3.62}Cl_{0.23}$
$FeCr_2S_4$	——	$Fe_{0.96}Cr_2S_{3.93}Cl_{0.07}$

The reason Vegard's law gives apparent higher values for iron is due to the incorporation of chlorine in the crystals. Incorporating chlorine in the system $Cu_{1-x}Fe_xCr_2S_4$ will result in a chemical reduction of cationic species and give an increase in effective cation size so that there is an increase in unit cell volume. This tendency occurs because the lattice constant of crystals for the system $Cu_{1-x}Fe_xCr_2S_4$ decreases upon annealing in a sulfur atmosphere,[13] where the relative sulfur and chlorine content increases and decreases, respectively. Therefore, the present $FeCr_2S_4$ crystal has a lattice constant (10.083 Å) higher than that of the polycrystalline sample (9.989 Å),[13] where the former contains a substantial amount of chlorine, while the latter is believed to be a chlorine-free sample.

$Cu_{0.5}In_{0.5}Cr_2S_4$. The results for samples grown in three different batches showed that the anionic element content is higher than the expected content, as shown by the ratio of (Cu+In+Cr)/(S+Cl) in Table 2. The chlorine content is small when the indium content is large and/or the copper content is small. The copper-to-indium ratio, Cu/In, always exceeds unity, indicating a higher preferential incorporation of copper, as compared to indium, in crystals. This is consistent with the previous result obtained by X-ray fluorescence spectroscopy.[14] The ratio of chromium-to-copper and indium, Cr/(Cu+In), is lower than the expected value of 2 for the crystal with the relatively higher content of indium (sample (1)) but the ratio is higher than 2 for other crystals with a lower indium content (samples (2) and (3)). This indicates that indium in sample (1) may substitute partially for chromium on the octahedral sites in addition to occupancy of tetrahedral sites, just as was found for $CdCr_2S_4$ crystals heavily doped with indium.[11] For samples (2) and (3) a tetrahedral-site deficiency, as described earlier for $CuCr_2S_3Cl$ and $Cu_{1-x}Fe_xCr_2S_4$ crystals, was found. Among these crystals, sample (1) has the copper-to-indium ratio (Cu/In) nearest to unity and the lowest chlorine content. Samples (2) and (3) have a composition relatively similar to each other but the lattice constants of the samples differ as

shown in Table 2; the values of 10.089 Å (sample (2)) and 10.016 Å (sample (3)) bracket the 10.057 Å of sample (1), while the lattice constant of the polycrystalline sample is reported to be 10.065 Å.[28]

$CuCr_2Se_3Cl$ and $CuCr_2Se_3Br$. The $CuCr_2Se_3Cl$ crystal shows a tendency to have a different composition than the $CuCr_2S_3Cl$ crystal. The chlorine content is much less than the stoichiometric content, as shown in Table 2. This may be due to the difference between the chalcogenide elements sulfur and selenium. A comparison of the ionic radii of these elements indicates that the sulfur ionic size (S^{2-}; 1.84 Å) is nearly the same as chlorine (Cl^-; 1.81 Å) while selenium (Se^{2-}; 1.91 Å) is somewhat larger. This large difference in ionic radii is responsible for the reduced incorporation of chlorine in the $CuCr_2S_3Cl$ crystal, while chlorine is more easily incorporated in the $CuCr_2S_3Cl$ crystal as described previously, because the sulfur- and chlorine-ion sizes are comparable. However, the ratios of chromium-to-copper, Cr/Cu, and cation-to-anion, (Cu+Cr)/(Se+Cl), are close to the expected values as shown in Table 2. The formula, normalized by the value of 2 for chromium, is $Cu_{0.97}Cr_2Se_{3.66}Cl_{0.32}$. Similar results for crystals grown in different batches were found, while Miyatani *et al.*[19] reported without chemical analysis that the composition of crystals always ranged from $CuCr_2Se_{3.6}Cl_{0.4}$ to $CuCr_2Se_{3.5}Cl_{0.5}$. They determined the composition by comparing the lattice constant (Vegard's law) and the magnetic property of single crystals with those of polycrystalline samples having a known composition.

In the case of the $CuCr_2Se_3Br$ crystal, the compositional problem is expected to be similar to that of the $CuCr_2S_3Cl$ crystal because for both crystals the ionic size of the chalcogen is nearly equal to that of the corresponding halogen (Br^-; 1.96 Å). Although the present method of chemical analysis was established for materials containing chlorine, the use of procedure (A) to analyze the $CuCr_2Se_3Br$ crystal seems reasonable because the solubility of silver bromide in aqueous media is much smaller than that of silver chloride. For the analysis, 10 mg of the sample was dissolved in 5 ml of nitric acid containing 1 mg Ag/ml. The results showed that the total amount of the anionic elements is higher, and that of the cations lower, than the expected amount. As in the case of the $CuCr_2S_3Cl$ crystal, this is due to the tetrahedral-site deficiency of copper. An alternative method[29] showed a similar result for a crystal grown in the same batch as shown in Table 2. For another crystal grown in a different batch, the composition was found to be $Cu_{0.80}Cr_{2.01}Se_{3.06}Br_{1.13}$ by the alternative method.

The present crystal is one of samples for the system $CuCr_2Se_{4-x}Br_x$ reported by Miyatani *et al.*[19] The alternative method was used to analyze their both polycrystalline and single-crystal samples at that time. They reported that the actual compositions of their polycrystalline samples are found to be the same as those intended within 1% by chemical analysis but did not give the data of chemical analysis for single crystals; the composition of single crystals was determined by comparing the lattice constant (Vegard's law) and the magnetic property (the Curie temperature) of single crystals with those of polycrystalline samples. They concluded as follows: (1) No excess-bromine compounds ($x>1$) can be synthesized. (2) The ionic configuration assumed is $Cu^{2+}_{1-x}Cu^{+}_{x}Cr^{3+}_{2}Se^{2-}_{4-x}Br^{-}_{x}$. (3) The physical properties of crystals can be explained in terms of the x-value dependence; for example, both the Curie temperature and electrical resistivity vary drastically over the small range $0.98 \leq x \leq 1.0$.

From the present results, however, it is revealed that the physical properties of crystals cannot be explained in terms of the compositional (x-value) dependence. Near $x=1$, they considered that the Cu^{2+} ions concentration is negligibly small but the present results indicated that the Cu^{2+} ions concentration is larger than that of Cu^+ ions. When the values in Table 2 (the first set) are normarized by the value of 2 for chromium, taking into account the electroneutrality of crystal, the present crystal can be expressed by the ionic configuration $Cu^{2+}_{0.63}Cu^{+}_{0.15}Cr^{3+}_{2}Se^{2-}_{3.19}Br^{-}_{1.03}$, while they regarded the crystal as one of samples with the composition close to $CuCr_2Se_3Br$ and the effective copper valence as monovalent. Moreover, their experiments to determine the composition are clearly found to be very careless because the composition of the crystal with the lattice constant 10.414 Å was reported to be $CuCr_2Se_{3.5}Br_{0.5}$; the lattice constant for the system $CuCr_2Se_{4-x}Br_x$ increased linearly from 10.325 to 10.405 Å as x increased from 0 to 1. Therefore, we can now understand that their conclusions are very suspicious and a complete analysis for the composition is necessary to interpret the physical properties of crystals.

$CdCr_2S_4$ and $CdCr_2Se_4$. We have already described the chlorine contamination,[10,11] and the actual content and site preference of dopants such as indium, silver, and copper for the $CdCr_2S_4$ and $CdCr_2Se_4$ crystals.[11] To provide a review of all the constituents, data for the minor elements are summarized with the major constituents in Table 4. All the crystals are contaminated with chlorine, but the chlorine content is much less than that of the copper-based spinels. The chlorine content increases in the following order; indium-doped, undoped, silver-doped, and copper-doped crystals. The content of dopants is usually less than the nominal content, especially, in $Cd_{0.95}Ag_{0.05}Cr_2S_4$ and $Cd_{0.9}Ag_{0.1}Cr_2S_4$ crystals. There seems to be a solubility limit for dopants in the single crystals.[30] The tetrahedral-site deficiency was not usually observed, although the undoped $CdCr_2Se_4$ and $Cd_{0.99}Ag_{0.01}Cr_2Se_4$ crystals had a somewhat lower value for cadmium in comparison with the chromium content. The stoichiometric formula $CdCr_2X_4$ is more closely satisfied for $CdCr_2S_4$ than for $CdCr_2Se_4$.

In summary, for the copper-based spinels, single crystals with the nominal formula $Cu_{1-x}Fe_xCr_2S_4 (x \leq 1)$, $Cu_{0.5}In_{0.5}Cr_2S_4$, or $CuCr_2X_3Y$ (X=S or Se, and Y=Cl or Br) were not found. In crystals of the halochalocogenides, combinations such as S–Cl and Se–Br on the anionic sites caused a substantial cation deficiency on the copper sites, while the halogen content was close to stoichiometric, or somewhat higher, because in both cases chalcogens and halogens are of nearly the same ionic size. The combination of Se–Cl on the

Table 4. Results of analysis for $CdCr_2S_4$ and $CdCr_2Se_4$ single crystals

Sample, nominal composition	Analyte, mole ratio				
	Cd	M[a)]	Cr	X[a)]	Cl
$CdCr_2S_4$	0.99_4	—	1.99_3	4.00_6	0.00_5
$CdCr_2S_4$[b)]	1.00_9	—	1.99_7	3.98_4	0.00_8
$Cd_{0.99}In_{0.01}Cr_2S_4$	0.99_1	0.00_3	2.00_0	3.99_9	0.00_3
$Cd_{0.99}In_{0.01}Cr_2S_4$[b)]	0.98_6	0.00_4	2.01_8	3.98_7	0.00_1
$Cd_{0.95}In_{0.05}Cr_2S_4$	0.98_9	0.04_6	1.99_2	3.96_2	0.00_7
$Cd_{0.99}Ag_{0.01}Cr_2S_4$[c)]	0.98_6	0.01_6	1.99_7	—	—
$Cd_{0.95}Ag_{0.05}Cr_2S_4$	0.99_9	0.01_3	2.01_4	3.96_4	0.00_8
$Cd_{0.9}Ag_{0.1}Cr_2S_4$	0.98_6	0.01_5	2.00_9	3.97_4	0.01_3
$Cd_{0.95}Cu_{0.05}Cr_2S_4$	0.99_1	0.03_0	2.00_1	3.95_5	0.02_1
$Cd_{0.9}Cu_{0.1}Cr_2S_4$	0.95_1	0.06_4	2.01_5	3.93_4	0.03_3
$CdCr_2Se_4$	0.97_6	—	2.11_2	3.90_5	0.00_5
$Cd_{0.99}In_{0.01}Cr_2Se_4$	0.96_0	0.01_2	2.04_7	3.97_8	$<0.00_1$
$Cd_{0.95}In_{0.05}Cr_2Se_4$	0.96_0	0.05_1	2.01_7	3.96_4	0.00_4
$Cd_{0.9}In_{0.1}Cr_2Se_4$	0.93_8	0.05_8	2.01_9	3.97_5	0.00_7
$Cd_{0.99}Ag_{0.01}Cr_2Se_4$	0.97_4	0.00_9	2.08_7	3.91_8	0.00_8
$Cd_{0.9}Ag_{0.1}Cr_2Se_4$	0.96_3	0.04_4	1.99_1	3.97_5	0.02_3
$Cd_{0.95}Cu_{0.05}Cr_2Se_4$	0.95_7	0.03_3	2.00_8	3.97_9	0.02_0
$Cd_{0.9}Cu_{0.1}Cr_2Se_4$	0.94_7	0.05_3	1.99_7	3.98_0	0.02_1

a) "M" designates dopants (In, Ag, and Cu) and "X" designates S or Se. b) Annealed in vacuum at 600 °C for 48 hr. c) The crystal was dissolved in concd HNO_3 without Ag^+ ions. The intrinsic Ag and Cl present in the material were reacted with each other to form AgCl precipitates during the dissolution Only metals such as Cd, Ag, and Cr were determined subsequently using procedure (A) so that the observed Ag value was the sum of the Ag content in both the filtrate and precipitates.

anionic sites did not give the copper deficiency, but the chlorine content was much less than the stoichiometric content. The halochalocogenides, contrary to the general understanding, seem to contain a considerable amount of bivalent copper ions. For other crystals of the copper-based spinels, it was often observed that the total amount of metals was lower than that expected for the nominal composition and the amount of chlorine was high. The lower amounts of metals are mainly due to an insufficient amount of tetrahedral-site elements. The composition of single crystals of cadmium-based spinels, compared to that of the copper-based spinels, more closely approximated the nominal formula ($CdCr_2X_4$) but all the crystals were contaminated with a small amount of chlorine. The chlorine content was much less than that of the copper-based spinels and increased in the order of indium-doped, undoped, silver-doped, and copper-doped crystals. The content of dopants was usually less than the nominal content. From the present results, it can be concluded that Vegard's law is not useful to determine the intermediate composition of the vapor-phase-grown single-crystals of multicomponent systems such as $Cu_{1-x}Fe_x$-Cr_2S_4 and $CuCr_2X_{4-x}Y_x$, and that a complete analysis, including the determination of both major and minor constituents or impurities, is necessary to interpret the physical properties of crystals; a partial analysis fails to notice a compositional variation of components other than elements of interest. The present work also indicates that individual crystals in a growth batch can be characterized by AAS techniques if somewhat large crystals are grown.

The author would like to express his sincere appreciation to Drs. Bernard Hershenov and Fumio Okamoto for critical reading of the manuscript, and to Mr. Katsuhiro Kato for measurements of the lattice constants and discussions during the course of this work. He is also indebted to Drs. Fumio Okamoto and Yasuo Wada, and Messrs. Katsuhiro Kato and Takao Oka for providing samples. All the above-mentioned personnel are with RCA Research Laboratories, Inc., Tokyo.

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26) Analyses were performed for one crystal in the individual growth batches. Pulverized crystals weighing 1 mg were dissolved in concentrated nitric acid. The sample solution was evaporated nearly to dryness. After removal of the nitric acid by evaporation with hydrochloric acid, the residue was dissolved in deionized water. Copper was determined by colorimetry using cupferazone as a color-producing reagent, where the absorbance was measured at 600 nm. Iron was determined by the absorbance at 470 nm using the colorimetric thiocyanate method.

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29) Two hundred mg of the sample was dissolved in concentrated nitric acid in a distillation flask and steam-distillation simultaneously performed until the sample completely dissolved, whereupon the distillate containing bromine was absorbed by a solution mixed with sodium hydroxide and hydrogen peroxide. Bromine in the distillate was determined by iodometry after removal of the excess hydrogen peroxide. The nitric acid solution remaining in the distillation flask was converted to hydrochloric acid solution and elemental selenium was precipitated by adding sulfurous acid. The precipitated selenium was filtered and determined by gravimetry. From the filtrate, copper and chromium were determined by chelatometry with EDTA using PAN and Zincon, respectively, as indicators. The procedure was confirmed using polycrystalline samples with the composition of $CuCr_2Se_{3.2}Br_{0.8}$ or $CuCr_2Se_3Br$, and satisfactory results were obtained.

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