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Estimation of Chlorine Content in Single Crystals of Chromium Chalcogenide Spinels by Atomic Absorption Spectrophotometry

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Synopsis. Analyses using the silver atomic absorption indicated that all the crystals grown by the vapor transport method were contaminated with chlorine. Particularly in crystals containing copper, a large amount of chlorine was incorporated. In crystals with an intended composition $CuCr_2S_3Cl$, the chlorine content was much higher than the expected amount.

Single crystals of chromium chalcogenide spinels such as $CuCr_2S_3Cl$, $CdCr_2S_4$, and $CdCr_2Se_4$, are usually grown by the chemical vapor transport method, using chlorine gas as a transport agent.[1] It is known that the chlorine is incorporated as either a major or minor component in the grown crystals[1,2] and affects the magnetic and electrical properties.[1,3,4] The chlorine content as the major component is commonly determined by Vegard's law comparing the lattice constant of single crystals with that of polycrystals having a known composition.[3] Sleight and Jarrett[4] used a chemical analysis to determine the chlorine content of $CuCr_2S_{4-x}Cl_x(0 \leq x \leq 1)$, where the maximum chlorine expected is 11.85 wt%. However, they did not discuss their method of analysis. Similarly, for a chlorine content of less than 0.02 wt% in $CdCr_2Se_4$ crystals, Harbeke and Pinch[5] did not report the details of their chemical analysis. In both cases one must assume that a large number of samples are necessary for the chlorine analysis since the crystals are, at most, 3 mm on edge and weigh only several mg. In the present paper we describe an indirect method, using 10 mg samples, to estimate the chlorine content in some single crystals by atomic absorption spectrophotometry.

The sample is dissolved in nitric acid containing a known amount of silver ions and the chlorine is simultaneously precipitated as AgCl. After filtration, the chlorine content is determined either from the AgCl precipitate dissolved in the ammoniacal solution[6] or the excess silver ions in the filtrate.[7] For the measurement of silver atomic absorption and the precipitation of AgCl, the effects of the constituent elements in the materials are examined.

Experimental

Reagents. (1) Standard chlorine solution: Sodium chloride dried at 110 °C was accurately weighed and dissolved in deionized water. (2) Standard silver solution: Silver nitrate dried at 110 °C was accurately weighed and dissolved in a minimum amount of deionized water, and then diluted with concentrated nitric acid. (3) Other solutions: Metal nitrates and sodium sulfate were dissolved in deionized water and selenium metals were dissolved in nitric acid and then diluted with deionized water. Reagents used were of analytical reagent grade.

Measurement of Silver Atomic Absorption. The silver atomic absorption was measured at 328.1 nm in an acetylene-air flame using a Hitachi Model 208 atomic absorption spectrophotometer and a hollow cathode lamp HLA-3. For the measurement of silver concentrations up to 2 ppm, the nitric acid concentration was adjusted to 0.05 M, taking into account the stability of the dilute silver solution. For this condition, the silver atomic absorption was not affected by 2 ppm Cu^{2+}, Fe^{3+}, and In^{3+}, 3—400 ppm Cr^{3+}, 200—400 ppm Cd^{2+}, 12—1200 ppm SO_4^{2-} and 1000 ppm SeO_3^{2-}. For the measurement from the ammoniacal solution, it was necessary to use at least a 3% ammonia concentration, since the silver atomic absorption remained nearly constant above this concentration.

Precipitation of Silver Chloride. We successfully precipitated more than 10 μg of chlorine as AgCl using a standard chlorine solution. The nitric acid concentration was adjusted to about 1.5 M for this examination. The results suggested that 5 mg of silver was necessary to capture about 1 mg of chlorine and 1 or 0.5 mg of silver was suitable for less than 100 μg of chlorine. Several diverse ions did not interfere with the precipitation of AgCl. Table 1 shows the recovery of chlorine in the presence of diverse ions. The amount of

TABLE 1. RECOVERY OF CHLORINE IN THE PRESENCE OF DIVERSE IONS

Elements[a] added	Cl added	From precipitate		From filtrate	
		Cl found	error	Cl found	error
Cu 2.0 mg	0.500 mg	0.481 mg	−3.8%	0.503 mg	+0.6%
Cr 3.0	1.000	1.000	0	0.985	−1.5
S 3.5	1.500	1.488	−0.8	1.508	+0.5
Cd 3.0 mg	10 μg	9.5 μg	−5.0%	10.8 μg	+8.0%
Cr 3.0	25	24.1	−3.6	26.9	+7.6
	50	51.6	+3.2	51.8	+3.6
S 4.0	100	99.4	−0.6	103.8	+3.8

a) Cu, Cr, and Cd were added as nitrates, and S as sodium sulfate.

added elements was nearly equivalent to the sample weight of 10 mg. The values given on the same line in Table 1 for the precipitate and filtrate were obtained from the same starting solution. The results obtained from both the precipitate and the filtrate are in agreement each other. This indicates that the chlorine can be determined either from the AgCl precipitate dissolved in the ammoniacal solution or the excess silver ions in the filtrate. Considering the simplicity of the experimental procedure, the latter technique seems to be more practical than the former. However, for analyses of the actual samples, both techniques were usually used to attain a satisfactory result as described below.

Analysis of Single Crystals. Ten mg of the sample (usually 5—6 crystals) was dissolved in nitric acid containing excess silver ions of a known quantity and the chlorine was simultaneously precipitated as AgCl to prevent the escape of chlorine from the system during the dissolution.[8] For a sample containing 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 was then diluted to about 20 ml. The solutions were aged for 30 min over a water bath. After the solution was cooled in ice water, the precipitated AgCl was filtered and washed with six 5 ml portions of cold nitric acid (1 : 50), and dissolved in an aqueous ammonia solution. After the dilution of both the ammoniacal solution and the filtrate to an appropriate silver concentration, chlorine was usually determined indirectly from the silver content in both solutions. The results obtained were corrected by the blank test.

TABLE 2. RESULTS OF SINGLE CRYSTAL ANALYSIS

Sample Intended composition	Cl found, wt% From precipitate	Cl found, wt% From filtrate
$CuCr_2S_3Cl$ (1)	13.2	12.9
$CuCr_2S_3Cl$ (2)	13.8	13.6
$CuCr_2S_3Cl$ (3)	14.1	13.8
$Cu_{0.5}In_{0.5}Cr_2S_4$	2.39—3.56	—
$Fe_{1-x}Cu_xCr_2S_4$ (x=0.4—0.6)	4.52—8.32	—
$FeCr_2S_4$	0.61	—
$CdCr_2S_4$	0.01—0.04	0.01—0.05
$CdCr_2S_4$[a]	0.004—0.07	0.003—0.07
In-doped $CdCr_2S_4$	0.02—0.04	0.03—0.04
Ag-doped $CdCr_2S_4$	0.08—0.14	—
Cu-doped $CdCr_2S_4$	0.22—0.33	0.22—0.34
$CdCr_2Se_4$	0.03	0.04
In-doped $CdCr_2Se_4$	—	0.05
Ag-doped $CdCr_2Se_4$	0.06—0.15	—
Cu-doped $CdCr_2Se_4$	0.13—0.14	0.14

a) Annealed in vacuum at 500—600 °C for 2—15 days.

The results of the analyses are given in Table 2. The chlorine content determined from both the precipitate and the filtrate are in good agreement each other. In the case of crystals with an intended composition $CuCr_2S_3Cl$, the chlorine content was much higher than the 11.85 wt% expected for the intended composition while Sleight and Jarrett obtained crystals containing a nearly stoichiometric amount of chlorine.[4] In a separate experiment, however, it was found that the sulfur content in our crystals was consistently lower than the stoichiometric amount.[9] Such deviations from the stoichiometric composition would strongly affect the magnetic and electric properties of the crystals.[9] For the other crystals, Table 2 also indicates that all the single crystals grown by the vapor transport method using chlorine gas as a transport agent, were always contaminated with chlorine. Particularly in crystals containing copper, a large amount of chlorine was incorporated.

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