Atomic Absorption Spectrophotometric Determination of Rare Earths (Y, Eu, Gd, Dy, Ho, and Er) in Single Crystals of Magnetic Garnets and Sulfides

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(Received June 13, 1974)

Atomic absorption spectrophotometric studies were carried out on single-crystal rare-earth magnetic garnets, $(R_1,R_2)_3(Fe,Ga)_5O_{12}$, where R_1 and R_2 are Y, Eu, Gd, and Er, and sulfides RCr_3S_6, where R is Y, Gd, Dy, Ho, and Er. A method using lanthanum chloride to suppress the interference effects of other elements was demonstrated for the atomic-absorption determination of rare earths. Lanthanum chloride is much better than alkaline metal chlorides (NaCl, KCl, and CsCl) and chelating agents ($EDTA\cdot 2Na$ and $EDTA\cdot 2NH_4$) for removing the interference effects of foreign elements from the yttrium measurement. Similar results with lanthanum chloride are observed with other rare earths. Experimental results for various samples are also presented. The present method has been utilized for several years in our laboratories to analyse rare earths in newly prepared materials.

Atomic absorption spectrophotometry (AAS), as an important analytical tool, can be used to determine more than 60 elements which are major and minor constituents of cements, metals, alloys, glass, agricultural materials, and minerals, *etc.* In the case of rare earths, however, several workers[1-6] have studied the atomic absorption behavior, but very little in the way of applications has been published, presumably because sensitivity is poor in the air-acetylene flame which is routinely used. The rare earths are not totally dissociated in this flame. In a higher temperature flame, such as nitrous oxide-acetylene, the rare earths are generally dissociated but in many cases they are easily ionized and affected by other elements of the compound. Therefore, the determination of rare earths by AAS technique has usually been performed in the presence of easily ionized elements such as alkaline metals[6-8] and lanthanum,[9] so that the sensitivity of rare earths is increased and the interference of associated elements is overcome. In the present work, to establish a condition for the determination of rare earths in single crystals of magnetic garnets $(R_1,R_2)_3(Fe,Ga)_5O_{12}$, ($R_1$ and R_2=Y, Eu, Gd, and Er), and sulfides RCr_3S_6 (R=Y, Gd, Dy, Ho, and Er), we first studied the yttrium absorption in the presence of the following agents; compounds of easily ionized elements (NaCl, KCl, CsCl, and $LaCl_3$) and chelating agents ($EDTA\cdot 2Na$ and $EDTA\cdot 2NH_4$). Among these agents, it was found that lanthanum chloride is most effective in removing the interference effects of other elements from the yttrium measurement. The usefulness of lanthanum chloride, in contrast with other agents, is demonstrated in the results given in Table 1 for a measurement of 50 ppm yttrium in the presence of foreign elements. Similar results are obtained for other rare earths with lanthanum chloride. Therefore, a method using lanthanum chloride is proposed for the atomic-absorption determination of rare earths which are a major component in crystals of the above-mentioned garnets and sulfides and the results for various samples are presented.

The garnets are dissolved in hydrochloric acid and the sulfides are dissolved in nitric acid. Hydrochloric acid is then used to acidify the sample solution because the atomic absorption of rare earths is reduced in the presence of nitric acid[5,6] and nitrate anions.[5] This acidification for the sulfide analyses is performed after the removal of nitric acid by evaporation with hydrochloric acid. In the case of zirconium and calcium rare-earth silicates,[9] however, rare earths were determined in a nitric acid and lanthanum nitrate medium. In order to demonstrate the applicability of this method for the analyses of individual single crystals a maximum sample weight of 20 mg was used.

Experimental

Apparatus. The atomic absorptions were measured in a nitrous oxide-acetylene flame using a Hitachi Model 208 atomic absorption spectrophotometer and Westinghouse hollow-cathode lamps. The following analytical lines were used; Y, 410.2 nm; Eu, 459.4 nm; Gd, 368.4 nm; Dy, 421.2 nm; Ho, 410.4 nm; Er, 400.8 nm.

Reagents. (1) Standard rare earth solutions: Rare-earth chloride hexahydrates were dissolved in deionized water and standardized by chelatometry using EDTA (1 mg rare earth/ml). These solutions were stocked as 0.1 M hydrochloric acid solution and working solutions were prepared by diluting the stock solutions. (2) Other solutions: Chlorides, except for gallium, as well as sodium and ammonium salts of EDTA were dissolved in deionized water to make the required concentration. Gallium solutions were prepared by dissolving high-purity gallium (99.99%) in nitric acid, removing the excess nitric acid by evaporation with hydrochloric acid, and then dissolving the residue in deionized water. Reagents used were of analytical reagent grade.

Results

Measurements of Yttrium Atomic Absorption in Several Matrices. The effects of several agents on the yttrium atomic absorption are shown in Fig. 1. Agents which increase the yttrium absorption are sodium chloride, potassium chloride, and lanthanum chloride, while the chelating agents decrease the yttrium absorption. In the case of cesium chloride, yttrium absorption was enhanced at lower concentrations of cesium chloride but gradually decreased with increasing cesium chloride concentration.

The effect of these agents in removing the interference of foreign elements from the yttrium absorption

Table 1. Measurement of 50 ppm yttrium in different matrices

Foreign[a)] element (ppm)	No Agent (0.1 M HCl)		Agents added[b)] NaCl		LaCl$_3$		EDTA·2Na	
	found (ppm)	error (%)	found (ppm)	error (%)	found (ppm)	error (%)	found (ppm)	error (%)
Fe 50	52.3	+ 4.6	55.0	+10.0	49.2	−1.6	50.1	+ 0.2
Ga 500	57.7	+15.4	51.4	+ 2.8	50.0	0	50.3	+ 0.6
Gd 500	38.3	−23.4	42.4	−15.2	53.2	+6.4	16.5	−67.0
Fe 50 Ga 500 Gd 500	37.2	−25.6	43.5	−13.0	51.3	+2.6	25.8	−48.4

a) Elements were added as chloride. b) Solutions were adjusted to 0.1 M hydrochloric acid and the concentration of agents added was 2,000 ppm for both standards and samples.

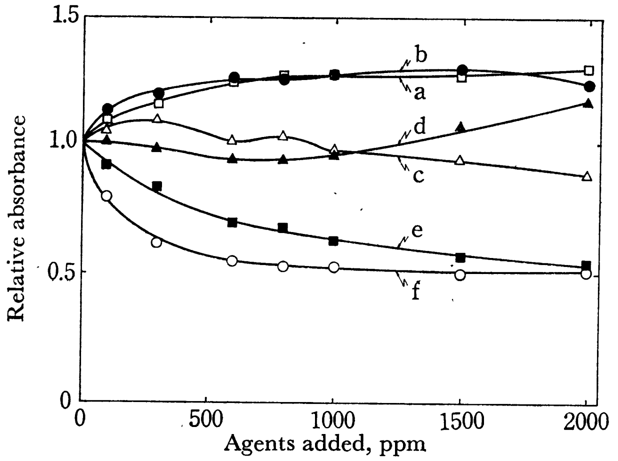

Fig. 1. Effect of several agents on yttrium atomic absorption in 0.1 M hydrochloric acid solution.
(a) NaCl, (b) KCl, (c) CsCl, (d) LaCl$_3$, (e) EDTA·2Na, (f) EDTA·2NH$_4$. Y: 50 ppm.

measurement was examined by adding 2000 ppm of agents to both of the yttrium-standard and the sample solutions. Foreign elements, such as iron, gallium, and gadolinium, were added as chlorides to the sample solutions. Typical results are summarized in Table 1, where sodium chloride and lanthanum chloride are chosen as the enhancement agent for yttrium absorption and EDTA disodium salt for the reducing agent. For comparison, measurements of the solution without the agents are also shown. In the solutions without agents all the foreign elements interfered with the yttrium measurement. Sodium chloride significantly reduced the interference effect of gallium but was not effective for iron and gadolinium. EDTA was useful in the presence of iron and gallium, but the yttrium absorption was greatly reduced by the coexistence of gadolinium. In the lanthanum chloride matrix, the yttrium measurements were generally satisfactory although a small enhancement by gadolinium remained. In comparison with the above-mentioned agents, lanthanum chloride seemed to be the most effective agent for removing the interference effects by foreign elements from the yttrium measurement. Furthermore, lanthanum chloride did not reduce the yttrium absorption as shown in Fig. 1. Therefore, in the work which follows, the measurement of rare earths is performed in the presence of lanthanum chloride with concentrations as high as 10000 ppm.

Effect of Lanthanum Chloride on Rare Earth Atomic Absorptions. As shown in Fig. 2, the absorption of rare earths was enhanced with an increase of lanthanum chloride concentration. For example, comparing the absorption for a solution containing 5000 ppm of lanthanum chloride to one without this agent, the following increased ratios of absorption are observed: Y 1.32, Eu 2.22, Gd 1.51, Dy 1.58, Ho 1.42, and Er 1.22.

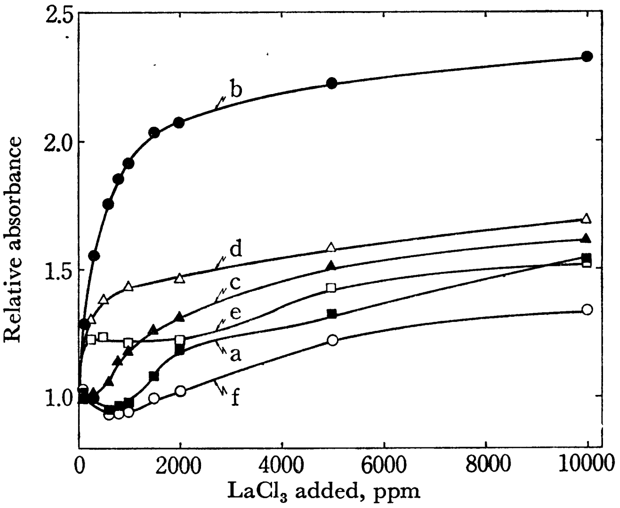

Fig. 2. Effect of lathanum chloride on atomic absorptions of rare earths in 0.1 M hydrochloric acid solution.
(a) Y 50 ppm, (b) Eu 50 ppm, (c) Gd 500 ppm,
(d) Dy 50 ppm, (e) Ho 50 ppm, (f) Er 50 ppm.

As a demonstration of the usefulness of lanthanum chloride in removing the interference effects of foreign elements from the rare earth measurements, the results of yttrium and europium are tabulated by comparing with the results obtained without lanthanum chloride in Table 2. The matrix matching is the same between standard and sample solutions with respect to the concentrations of lanthanum chloride and hydrochloric acid. As seen from Table 2, the results with lanthanum chloride are much better than without. For the measurement of yttrium, the interference effect of gadolinium is overcome by the use of 5000 ppm of lanthanum chloride, although a small effect of gadolinium does remain if only 2000 ppm is used, as shown previously in Table 1. It was observed that lanthanum chloride,

TABLE 2. COMPARISON OF MEASUREMENTS FOR YTTRIUM AND EUROPIUM WITH AND WITHOUT LANTHANUM CHLORIDE ADDED.

Analyte	Foreign[a)] element (ppm)	Sample Solution: No $LaCl_3$ (0.1 M HCl) found (ppm)	No $LaCl_3$ (0.1 M HCl) error (%)	5,000 ppm $LaCl_3$[b)] found (ppm)	5,000 ppm $LaCl_3$[b)] error (%)
Y 50 ppm	Cr 50	64.5	+29.0	49.0	−2.0
	Fe 50	52.3	+ 4.6	49.9	−0.2
	Ga 500	57.7	+15.4	49.3	−1.4
	Ba 50	51.7	+ 3.4	50.1	+0.2
	Gd 500	38.3	+23.4	51.0	+2.0
	Cr 50 Ba 50	68.6	+37.2	49.5	−1.0
	Fe 50 Ga 500 Gd 500	37.2	−25.6	49.6	−0.8
Eu 50 ppm	Fe 100	50.6	+ 1.2	49.8	−0.4
	Ga 2500	90.4	+80.8	49.8	−0.4
	Gd 2500	77.0	+50.4	49.6	−0.8
	Er 100	55.0	+10.0	50.0	0
	Fe 100 Ga 500 Gd 500 Er 100	73.6	+47.2	49.9	−0.2
	Ga 2500 Gd 2500	91.4	+82.8	49.2	−1.6

a) Elements were added as chloride. b) The concentration added the was same between standards and samples, and solutions were adjusted to 0.1 M hydrochloric acid.

for concentrations between 5000 and 10000 ppm, suppresses the interference effects of foreign elements. It was also confirmed that the concentration of gallium and gadolinium can be increased up to 1000 ppm for the measurement of yttrium in the lanthanum chloride matrix. At concentrations higher than 1000 ppm of gallium and gadolinium, the interference effects of these elements were not suppressed by the addition of lanthanum chloride.

In the case of europium, the usefulness of lanthanum chloride is more striking than for yttrium. The error in the europium measurement is about 50 to 80% in the presence of gadolinium or gallium for solutions without lanthanum chloride, but is only 1 to 2% with its addition. Similar effects with lanthanum chloride were observed in measuring other rare earths such as gadolinium, dysprosium, holmium, and erbium. The error in the measurement of the rare earths due to the effects of all the foreign elements examined for the garnet and sulfide analyses was reduced to within 1 to 2% in the 5000 ppm of lanthanum chloride matrix, while the interference effects in solutions without this agent remained. Therefore, it is concluded that the present method using lanthanum chloride is useful for the measurement of rare earths in the presence of several foreign elements.

Analysis of Samples. Analyses were performed for a mixture of oxides with a known composition prior to the analysis of the actual samples. Results are given in Table 3 for yttrium, gadolinium, europium, and erbium determinations, where oxides of rare earths are mixed with iron and gallium oxides. All the oxides have a purity of at least 99.9%. Twenty mg of the mixtures were dissolved in concentrated hydrochloric acid and the sample solutions were diluted to an appropriate concentration of analytes. The final sample solutions were adjusted to 0.1 M hydrochloric acid and 5000 ppm of lanthanum chloride. The same adjustment was carried out for the standards and the atomic absorptions were then measured. Each value shown in Table 3 is an average of at least three atomic absorption measurements of the same sample solution. The difference between the maximum and minimum observed values is shown in the "*R*" column. In all cases the tabulated results in Table 3 agree, within 1 to 2%, with the calculated values, and this technique is applicable to the analysis of rare earths.

TABLE 3. RESULTS OF MIXED OXIDES ANALYSIS

Sample[a)]	Analyte	wt% calcd	wt% obsd	*R*[b)]
1	Y	35.34	35.2	1.2
2	Y	30.98	30.7	0.3
	Eu	5.88	5.9	0.1
3	Y	26.91	26.6	0.9
	Gd	11.90	11.7	0.3
4	Eu	15.71	15.4	0.1
	Er	34.58	34.8	0.3
5	Gd	46.60	47.1	0.6

a) Oxides were mixed with the following mole ratio;
1, 3.0 Y_2O_3: 3.8 Fe_2O_3: 1.2 Ga_2O_3
2, 2.7 Y_2O_3: 0.3 Eu_2O_3: 3.7 Fe_2O_3: 1.3 Ga_2O_3
3, 2.4 Y_2O_3: 0.6 Gd_2O_3: 4.0 Fe_2O_3: 1.0 Ga_2O_3
4, 1.0 Eu_2O_3: 2.0 Er_2O_3 : 4.3 Fe_2O_3: 0.7 Ga_2O_3
5, 3.0 Gd_2O_3: 5.0 Ga_2O_3
b) Difference between the maximum and minimum observed values.

The results for single crystal magnetic-garnet and sulfide samples are shown in Table 4, where sample weights from 10 to 20 mg were used. The garnets, except for $Gd_3Ga_5O_{12}$, were flux grown by Wada and Harada of these Laboratories while the sulfides were grown by Takahashi and Yamada,[10)] also of these Laboratories, using chemical vapor transport. The $Gd_3Ga_5O_{12}$ sample was obtained from Lambda/Airtron. The garnets were dissolved in concentrated hydrochloric acid and the solutions were diluted to an appropriate concentration of analytes. Sulfides were dissolved in concentrated nitric acid containing bromine and the excess nitric acid was removed by evaporation with hydrochloric acid, and the solutions were then diluted. The final solutions in both cases were adjusted to 0.1 M hydrochloric acid and 5000 ppm of lanthanum chloride. The standard solutions were adjusted to similar hydrochloric acid and lanthanum chloride concentrations. Each value shown in Table 4 is the average of three atomic absorption measurements for the same sample solution. As shown in Table 4, the results are generally in good agreement with the calculated values. The measurement of other components in the garnets, such as iron and gallium, was performed

TABLE 4. RESULTS OF SINGLE CRYSTALS ANALYSIS

Sample intended composition	Analyte	wt%		
		calcd	obsd	*R*a)
$Y_3Fe_{3.8}Ga_{1.2}O_{12}$	Y	35.34	35.2	1.0
$Y_{2.7}Eu_{0.3}Fe_{3.7}Ga_{1.3}O_{12}$	Y	30.98	30.6	0.2
	Eu	5.88	5.7	0.1
$Y_{2.5}Eu_{0.5}Fe_{3.7}Ga_{1.3}O_{12}$	Y	28.22	27.9	0.2
	Eu	9.65	9.6	0.0
$Y_{2.4}Gd_{0.6}Fe_{3.7}Ga_{1.3}O_{12}$	Y	26.77	26.2	0.2
	Gd	11.84	12.3	0.3
$Eu_3Fe_4GaO_{12}$	Eu	48.45	48.4	0.1
$Eu_2ErFe_{4.3}Ga_{0.7}O_{12}$	Eu	31.92	31.1	0.4
	Er	17.57	17.9	0.1
$EuEr_2Fe_{4.3}Ga_{0.7}O_{12}$	Eu	15.71	15.4	0.2
	Er	34.58	34.7	0.3
$Gd_3Ga_5O_{12}$	Gd	46.60	46.9	1.4
YCr_3S_6	Y	20.33	20.0	2.2
$GdCr_3S_6$	Gd	31.10	30.9	3.8
$DyCr_3S_6$	Dy	31.81	31.6	0.4
$HoCr_3S_6$	Ho	32.13	29.0	0.4
$ErCr_3S_6$	Er	32.44	31.9	0.3

a) Difference between the maximum and minimum observed values.

in a separate experiment, and the resultant data supported these results. For the sulfide analyses, the observed wt% values were sometimes lower than the calculated values, because of white insoluble materials (mostly silica) in the dissolution of samples.10) In the case of $HoCr_3S_6$ a remarkably large amount of such insoluble residues were found. The values presented in Table 4 are not corrected for the insoluble residues. In another experiment, a chromium and sulfur analysis indicated that the rare earth content observed in this work was in agreement with the stoichiometric amount expected for the intended composition.10)

The results of Table 2 to 4 substantiate the usefulness of this measurement method for the determination of rare earths in magnetic garnets $(R_1,R_2)_3(Fe,Ga)_5O_{12}$ (R_1 and R_2=Y, Eu, Gd, and Er), and sulfides RCr_3S_6 (R=Y, Gd, Dy, Ho, and Er). This method, therefore, has been utilized in our laboratories for the analysis of rare earths in newly prepared materials, using, at times, only 2 mg of a sample.

The author would like to express his sincere appreciation to Drs. Bernard Hershenov and Fumio Okamoto of these Laboratories for critical reading of the manuscript and helpful suggestions. He is also indebted to Drs. Yasuo Wada and Tatsuo Takahashi, and Messrs. Shigeo Harada and Osamu Yamada of these Laboratories for providing samples.

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