

## YTTRIAN SPESSARTINE FROM SUISHOYAMA, FUKUSHIMA PREFECTURE, JAPAN

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### ABSTRACT

The chemical analysis gave SiO<sub>2</sub> 37.76, Al<sub>2</sub>O<sub>3</sub> 19.47, Fe<sub>2</sub>O<sub>3</sub> 2.74, FeO 12.46, Rare earths 3.20, MnO 21.74, CaO 1.78, remainder (K<sub>2</sub>O, Na<sub>2</sub>O, H<sub>2</sub>O, CO<sub>2</sub>) 1.51; total 100.66%. Cell constant  $a = 11.64 \text{ \AA}$ . Density: 4.16 (meas), 4.14 (calc). Refractive index:  $n = 1.820 \pm 0.002$ . The distribution of lanthanide elements: poor in cerium group; rich in yttrium group with maximum at ytterbium.

### INTRODUCTION

The yttrian spessartine herein described is usually embedded in potash feldspar in Suishoyama pegmatite, Suishoyama, Kawamata-machi, Fukushima Prefecture. The pegmatite is found in a Mesozoic biotite granite body, has a zonal arrangement of felsic minerals, and has been worked for quartz and feldspar for many years. The pegmatite is also well-known for the production of many rare element minerals such as abukumalite, yttrialite, gadolinite, allanite, thalenite (Nagashima and Kato, 1966), thorogummite, zircon, tengerite, yttrifluorite (Uetani *et al.*, 1968), fergusonite, uraninite and some other secondary uranium minerals.

The mineral was collected from a waste outside the quarry, so the mode of occurrence or the paragenesis of minerals is not certain. The mineral usually occurs as a dark reddish brown mass of irregular shape in potash feldspars and encloses the white powdery mineral, yttrifluorite with the composition of Ca 35.50, rare earths 18.84, Mg 0.42, Fe 0.34, Al 0.15, Mn 0.08, F(remainder) 44.67 (Uetani *et al.*, 1968). Figure 1 shows a hand specimen of yttrian spessartine and yttrifluorite. The X-ray chemical analysis of rare earth elements disclosed that the yttrifluorite is poor in cerium group lanthanide, rich in yttrium group with maxima at dysprosium and erbium. (Uetani *et al.*, 1968) In hand specimens yttrifluorite looks very similar to tengerite. Both yttrifluorite and tengerite occur as aggregates of small crystals in yttrium-bearing spessartine garnets of dark reddish brown color. T. Iimori (1938) studied the spessartine garnet enclosing tengerite and gave the following results: specific gravity: 4.21, optically isotropic, the refractive index:  $n_D = 1.830$ , chemical analysis see Table 1.

Jaffe (1951) studied 78 garnets from various localities, and concluded that most of garnets containing higher amount of yttrium are pegmatitic and have spessartine-almandine composition. He also suggested the

replacements of  $\text{Mn}^{2+}\text{Si}^{4+}$  by  $\text{Y}^{3+}\text{Al}^{3+}$  and  $2\text{Mn}^{2+}$  by  $\text{Na}^+\text{Y}^{3+}$ . Concerning the relationship between the composition and other physical characteristics such as unit cell parameter and refractive index of garnets, Sriramadas (1957) made a detailed study and presented many diagrams.

#### OPTICAL AND X-RAY POWDER STUDIES

The refractive index was determined with the immersion method. Under microscope the material is optically isotropic and the measured



FIG. 1. Yttrian garnet and yttriofluorite. Yg: yttrian garnet, Yf: yttriofluorite, F: potash feldspar.

refractive index is  $1.820 \pm 0.002$ . The value is in excellent accordance with the garnet of similar composition reported by other investigators. From the results of the chemical analysis, the composition of the yttrian spessartine is calculated to be 57(60) spessartine, 32(34) almandine, 6(6) andradite, and 4(0) percent yttrogarnet (Yoder and Keith, 1951),  $(\text{R.E.})_2\text{Al}_2\text{Si}_3\text{O}_{12}$ . (The values in parentheses are those when yttrogarnet molecule is neglected.) According to the diagram presented by Sriramadas (1957) a garnet 60 spessartine, 32 almandite, 6 percent andradite, should have the refractive index of  $n_D = 1.816$  and the unit cell edge  $a = 11.63 \text{ \AA}$ . A small difference in the refractive index is probably due to the presence of  $\text{Y}^{3+}$ , etc. proxying for  $\text{Mn}^{2+}$  ions (Yoder and Keith, 1951).

X-ray powder diffraction measurements were made on Geiger-flex

TABLE 1. ANALYSES OF THE YTTRIAN SPESSARTINE ENCLOSING YTTROFLUORITE AND THE YTTRIAN SPESSARTINE ENCLOSING TENERGITE

Constituents	1		2	
	Percent	Percent	Percent	Atomic ratio <sup>b</sup>
SiO <sub>2</sub>	34.95	37.76		3.099
Al <sub>2</sub> O <sub>3</sub>	14.80	19.47		1.885
Fe <sub>2</sub> O <sub>3</sub>	}16.60	2.74		0.168
FeO		12.46		0.854
Rare earths	2.45	3.20		0.109
MnO	22.28	21.74		1.510
CaO	4.52	1.78		0.158
Na <sub>2</sub> O	1.67	0.30		0.049
K <sub>2</sub> O	0.16	0.27		0.030
H <sub>2</sub> O(+)	0.45	0.31		
H <sub>2</sub> O(-)		0.27		
CO <sub>2</sub>	0.41	0.36		
Total	98.83 <sup>a</sup>	100.66		

1. Yttrian spessartine enclosing tenergite analyzed by Iimori (1938).

2. Yttrian spessartine enclosing yttriofluorite. Mg, P, Ti were not detected.

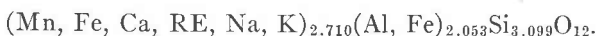
<sup>a</sup> Including B<sub>2</sub>O<sub>3</sub>(0.15%) and BeO(0.39%).

<sup>b</sup> Number of oxygen atom=12.

X-ray Diffractometer. The diffraction data coincide well with those of a spessartine in XRDF card 2-0992; *a* was calculated to be  $11.64 \pm 0.01$  Å.

#### CHEMICAL COMPOSITION

The chemical analysis of the yttrian spessartine was made on the material separated from feldspar and yttriofluorite with a isodynamic separator. The chemical analysis was performed according to the conventional method of silicate analysis. The oxalate precipitate of rare earths was investigated quantitatively by X-ray fluorescence methods. The results of the chemical analysis are given in Table 1. The experimental formula of the yttrian spessartine from Suishoyama calculated on the bases of  $\Sigma$  oxygen = 12.00 is:



(The average atomic weight of the rare earth elements determined by the X-ray fluorescent analysis is 122.7) The rare earths content reaches to 3.20 in weight percent. The value is close to the rare earth content in natural spessartine of the sample from Pyörönmaa, Finland, 3.35 weight

percent  $\text{RE}_2\text{O}_3$ , analyzed by Vorma (1966), the highest for natural spessartine.

#### THE DISTRIBUTION PATTERN OF RARE EARTH ELEMENT

The distribution of lanthanum group elements was determined by the X-ray fluorescence method applying the dilution parameter technique (Wakita and Nagashima, 1968). All the lanthanum series elements except Pm which is not found in nature were detected. Yb showed the maximum content. The results (including  $\text{Y}_2\text{O}_3$ ) in weight percent are listed in Table 2. The quantitative estimation obtained as atomic percentages including a relative error of less than 10 percent is plotted versus atomic numbers in Figure 2 together with the distribution of rare earth elements

TABLE 2. ANALYSIS OF RARE EARTH ELEMENTS IN YTTRIAN GARNET

Constituent	Percent	Constituent	Percent
$\text{Y}_2\text{O}_3$	44.26	$\text{Tb}_2\text{O}_3$	0.71
$\text{La}_2\text{O}_3$	0.06	$\text{Dy}_2\text{O}_3$	5.59
$\text{CeO}_2$	0.32	$\text{Ho}_2\text{O}_3$	2.96
$\text{Pr}_2\text{O}_3$	0.15	$\text{Er}_2\text{O}_3$	11.98
$\text{Nd}_2\text{O}_3$	0.66	$\text{Tm}_2\text{O}_3$	3.62
$\text{Pm}_2\text{O}_3$	—	$\text{Yb}_2\text{O}_3$	22.12
$\text{Sm}_2\text{O}_3$	0.66	$\text{Lu}_2\text{O}_3$	5.65
$\text{Eu}_2\text{O}_3$	0.09		
$\text{Gd}_2\text{O}_3$	1.16	Total	99.99

in fluorite of the Suishoyama pegmatite (Uetani *et al.*, 1968). The figure shows a fundamental coincidence among the distribution pattern of the present spessartine and that of the spessartine from Pyörönmaa, Finland studied by Vorma (1966), as well as with the classical law of abundances set forth by Oddo and Harkins in 1916. The small difference in distribution patterns of rare earths in this spessartine and yttrifluorite from Suishoyama may be attributed to the difference in ionic sizes of the substituted cations, manganese (0.80 Å) in spessartine and calcium (0.99 Å) in yttrifluorite.

#### SPECIFIC GRAVITY

The density of the yttrian spessartine measured with a pycnometer was  $4.16 \text{ g/cm}^3$  ( $25^\circ\text{C}$ ). The value agreed well with the calculated value ( $4.14 \text{ g/cm}^3$ ) adopting the results of the chemical analysis and the unit cell parameter  $a$ .

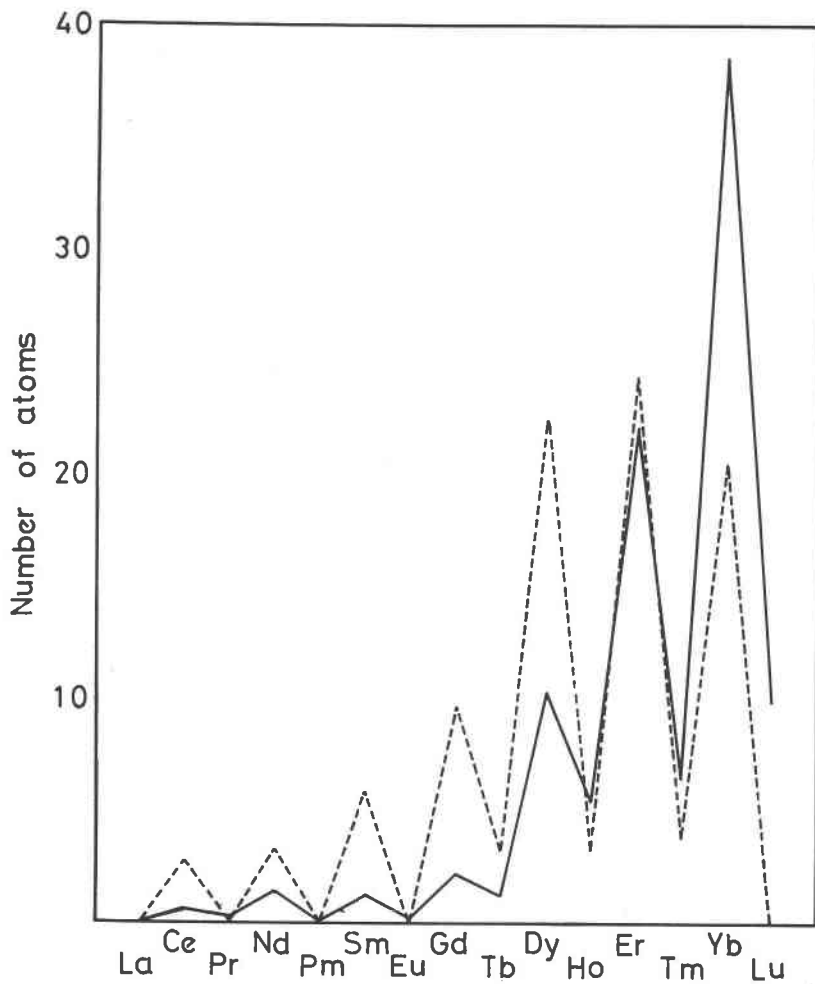


FIG. 2. Distribution of rare earth elements —yttrian garnet, —yttrifluorite (Uetani, 1968) Total lanthanoids=100 atoms.

#### ACKNOWLEDGEMENTS

The authors wish to express their thanks to Dr. Y. Kuroda, Geological and mineralogical Institute, Tokyo University of Education, Mr. K. Harada, Chichibu Museum of National History, for their assistance in the measurements of optical characteristics.

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*Manuscript received, July 6, 1969; accepted for publication September 8, 1969.*