YTTRIAN SPESSARTINE FROM SUISHOYAMA, FUKUSHIMA
PREFECTURE, JAPAN

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Abstract
The chemical analysis gave SiO$_2$ 37.76, Al$_2$O$_3$ 19.47, Fe$_2$O$_3$ 2.74, FeO 12.46, Rare earths
3.20, MnO 21.74, CaO 1.78, remainder (K$_2$O, Na$_2$O, H$_2$O, CO$_2$) 1.51; total 100.66% Cell
constant $a$ = 11.64 Å. 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, ytttrialite, gadolinite, allanite, thalenite (Nagashima and
Kato, 1966), thorogummite, zircon, tengerite, yttrofluorite (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, yttrofluorite 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 yttrofluorite. The X-ray chemi-
cal analysis of rare earth elements disclosed that the yttrofluorite is poor
in cerium group lanthanide, rich in yttrium group with maxima at dys-
prosium and erbium. (Uetani et al., 1968) In hand specimens yttro-
fluorite looks very similar to tengerite. Both yttrofluorite and tengerite
occur as aggregates of small crystals in yttrium-bearing spessartine
garnets of dark reddish brown color. T. Imori (1938) studied the spes-
sartine garnet enclosing tengerite and gave the following results: spe-
cific 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 pegma-
titic 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 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), $(\text{R.E.})_2\text{Al}_2\text{Si}_3\text{O}_8$. (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 $a=11.63 \, \text{Å}$. 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 Tengerite

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Percent 1</th>
<th>Percent 2</th>
<th>Atomic ratio 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>34.95</td>
<td>37.76</td>
<td>3.099</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>14.80</td>
<td>19.47</td>
<td>1.885</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>16.60</td>
<td>12.46</td>
<td>0.854</td>
</tr>
<tr>
<td>FeO</td>
<td>2.45</td>
<td>3.20</td>
<td>0.109</td>
</tr>
<tr>
<td>Rare earths</td>
<td>22.28</td>
<td>21.74</td>
<td>1.510</td>
</tr>
<tr>
<td>MnO</td>
<td>4.52</td>
<td>1.78</td>
<td>0.158</td>
</tr>
<tr>
<td>CaO</td>
<td>1.67</td>
<td>0.30</td>
<td>0.049</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.16</td>
<td>0.27</td>
<td>0.030</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.45</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>H$_2$O(+)</td>
<td>0.45</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>H$_2$O(−)</td>
<td>0.41</td>
<td>0.36</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>98.83</td>
<td>100.66</td>
<td></td>
</tr>
</tbody>
</table>

1. Yttrian spessartine enclosing tengerite analyzed by Imori (1938).
2. Yttrian spessartine enclosing yttrofluorite. Mg, P, Ti were not detected.
*a* Including Br$_2$O$_2$(0.15%) and BeO(0.39%).

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 yttrofluorite with an 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:

$$(\text{Mn, Fe, Ca, RE, Na, K})_{2.710} (\text{Al, Fe})_{2.632} \text{Si}_{3.098} \text{O}_{12}.$$  

(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 RE₂O₅, analyzed by Vorma (1966), the highest for natural spessartine.

**The Distribution Pattern of Rare Earth Elements**

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 Y₂O₃) 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 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 yttrofluorite 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 yttrofluorite.

**Specific Gravity**

The density of the yttrian spessartine measured with a pycnometer was 4.16 g/cm³ (25°C). The value agreed well with the calculated value (4.14 g/cm³) adopting the results of the chemical analysis and the unit cell parameter a.
Fig. 2. Distribution of rare earth elements—yttrian garnet, —yttriofluorite
(Uetani, 1968) Total lanthanoids = 100 atoms.

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References


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