COMPLETE SUBSTITUTION OF ALUMINUM FOR SILICON: THE SYSTEM

$3\text{MnO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 - 3\text{Y}_2\text{O}_5 \cdot 5\text{Al}_2\text{O}_3$

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ABSTRACT

Thermal, optical, and x-ray data indicate that there is a complete solid solution series between spessartite, $\text{Mn}_3\text{Al}_3(\text{SiO}_4)_5$, and yttrogarnet, $\text{Y}_3\text{Al}_3(\text{AlO}_4)_5$. The substitution $\text{Y}^{3+}\text{Al}^{3+} - \text{Mn}^{2+}\text{Si}^{4+}$ may be represented by the formula:

$\text{(Mn}_n\text{Al}_3\text{Y}_x\text{)}\text{Al}_2(\text{Si}_3\text{Al}_x\text{)}\text{O}_{12}$.

Yttrogarnet has a cube edge of 12.01 ± 0.02 Å and the space group O₄. Using the co-ordinates of grossularite as determined by Menzer, good agreement was obtained between calculated and observed intensities. The atomic positions are:

- Al in 16(o) 0 0 0
- Y in 24(c) 4 0 0
- Al in 24(d) 4 3 0
- O in 96(h) x y z

where x, y, and z are 0.04, 0.055, and 0.64, respectively. The yttrium is in eightfold coordination; the aluminum is in both four- and sixfold coordination. Yttrogranet inverts to a high form, yttroalumite, at 1970 ± 50°C.

This is the first case on record of the complete substitution of aluminum for silicon in an orthosilicate. The complete solid solution series contradicts the prevalent idea that the substitution of aluminum for silicon always decreases as the Si/O ratio decreases.

INTRODUCTION

It was pointed out by Jaffe (1950) that some natural spessartite garnets contain as much as 2.6 per cent $\text{Y}_3\text{O}_5$. He suggested that yttrium occupies manganese positions in the garnet structure, and that the substitution should occur as $\text{Y}^{3+}\text{Al}^{3+} - \text{Mn}^{2+}\text{Si}^{4+}$. Jaffe expressed the opinion that proof of the proposed substitution might be obtained by synthesizing yttrian spessartites. The above substitution may be represented by the following formula:

$\text{(Mn}_3-x\text{Y}_x\text{)}\text{Al}_2(\text{Si}_3-x\text{Al}_x\text{)}\text{O}_{12}$.

When $x=3$, the end member becomes $\text{Y}_3\text{Al}_2\text{Al}_3\text{O}_{12}$. Therefore, the system $3\text{MnO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 - 3\text{Y}_2\text{O}_5 \cdot 5\text{Al}_2\text{O}_3$ was explored experimentally.
Preparation of Mixtures

Mixtures were made from SiO₂, Al₂O₃, Y₂O₃, and MnCO₃. The silica and alumina were obtained from the prepared stock of J. F. Schairer of this Laboratory; the yttria was secured by H. W. Jaffe from A. D. Mackay and was analyzed spectrographically by M. J. Peterson of the U. S. Bureau of Mines;¹ the MnCO₃ was C. P. Grade material from J. T. Baker Chemical Company. The powders were weighed to 0.1 mg. into a platinum crucible in the requisite proportions to make from 2 to 5 grams of the desired product. After stirring to incorporate the silica, the powder was transferred to an agate mortar and ground for a minimum of 15 minutes to insure thorough mixing. Several different methods were required to prepare further the mixtures for use in the thermal investigation. For six lower-melting mixtures, those which melted completely below 1550°, a portion of the powder was heated in a platinum crucible suspended in a nitrogen atmosphere, in a vertical platinum-wound resistance furnace similar to that described by Bowen and Schairer (1932, p. 183). The charge was lowered to the furnace hot spot in stages to prevent loss of material due to possible violent escape of CO₂. The preparations were held for about 15 hours at the required temperature in the nitrogen atmosphere and then quenched by dropping into mercury. For two higher-melting mixtures, the powders were pressed under several tons per square inch into the form of thin disks. Each disk was placed in a platinum crucible, heated at 1700° to 1730° for several hours in a Meker gas furnace, and the charge was then quickly cooled by placing the crucible in water. The glasses and sintered products prepared in this way were then used in the thermal investigation.

¹ The analysis gave:

<table>
<thead>
<tr>
<th>Per cent</th>
<th>Component</th>
</tr>
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<tr>
<td>&gt;10</td>
<td>Y₂O₃</td>
</tr>
<tr>
<td>0.3 to 3</td>
<td>K₂O</td>
</tr>
<tr>
<td>0.2 to 2</td>
<td>SmO₂</td>
</tr>
<tr>
<td>0.02 to 0.2</td>
<td>Dy₂O₃, Ce₂O₃, Gd₂O₃, Pr₂O₃</td>
</tr>
<tr>
<td>0.01 to 0.1</td>
<td>ZrO₂, La₂O₃, Nd₂O₃, HfO₂, Na₂O</td>
</tr>
<tr>
<td>0.005 to 0.05</td>
<td>Sc₂O₃</td>
</tr>
<tr>
<td>&lt;0.01</td>
<td>Al₂O₃, Fe₂O₃, SiO₂, MgO, MnO, CaO</td>
</tr>
<tr>
<td>not detected</td>
<td>Li₂O, Cs₂O, Rb₂O</td>
</tr>
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</table>

The x-ray powder pattern agrees with that given in the original set of Diffraction Data Cards published by the American Society for Testing Materials. The index of refraction is 1.910 ± 0.002. Since yttria is very hygroscopic, the material was fired at 1400° for fifteen minutes before the measurement was made. The crystals are isometric and occur as rectilinear plates.
THE SYSTEM 3MnO·Al₂O₃·3SiO₂·3Y₂O₃·5Al₂O₃

METHODS OF THERMAL INVESTIGATION

Because of the large range of temperature required and the necessity of maintaining the manganese in the manganous state, several different techniques were used to determine the equilibrium relationships. The method of suspending small portions of the prepared glass in a platinum packet or crucible in a nitrogen-atmosphere quenching furnace was employed for most of the charges with liquidus temperatures below 1500°. A few longer runs were made by sealing platinum packets containing the charges in evacuated silica glass tubes which could then be suspended in the resistance furnace without the otherwise necessary atmosphere of purified nitrogen. Temperatures were measured with a platinum vs. platinum-10 rhodium thermocouple calibrated at the melting points of gold and diopside, 1062.6° and 1391.5°, respectively, in accordance with the temperature scale used at the Geophysical Laboratory. In order to avoid contamination of the thermocouple, temperature readings were made only before and after a run, according to a fixed time schedule, the furnace temperature being held constant with a regulator of the Wheatstone bridge type (Roberts, 1941). Runs at temperatures between 1500° and 1730° were made in a Meker gas furnace in which a reducing atmosphere was maintained by adjustment of the gas to air ratio. Gas furnace temperatures were measured with an optical pyrometer. A fourth method, used for charges near the high-yttria end of the system, consists of placing a sintered disk of the charge in a molybdenum or iridium boat and heating for 1 to 5 minutes in a graphite-resistor vacuum furnace (Urry and Piggot, 1941). The temperature was determined approximately from a chart (power input vs. temperature) based on optical pyrometer measurements and on a calibration at the melting point of Al₂O₃ (2050° ± 10°).

It is to be emphasized that the thermal investigation is of an exploratory nature. The temperatures of the runs, particularly the higher temperatures reported, are not precisely known and the composition of the mixtures is subject to several sources of error. For example, other oxides of manganese than manganous oxide are present in the glasses and sintered products even though the best available techniques were employed. In addition, some of the manganese is lost to the platinum container through alloying. This effect is reduced somewhat by using the same crucible for succeeding runs. Snow (1943) demonstrated that neither of those two sources of error is serious, although the index of refraction of the glasses is raised with increasing length of run. For example, the following changes of index of refraction were noted for the glass of spessartite composition:
In general the loss of manganese lowers the index and an increase in MnO raises the index. The color of the glass changes from colorless to brown with increasing length of run.

**RESULTS OF THERMAL INVESTIGATION**

Results of the determination of the phases at the various temperatures are given in Table 1. A preliminary temperature-composition diagram for the system 3MnO·Al₂O₃·3SiO₂—3Y₂O₃·5Al₂O₃, based on the data in Table 1, is given in Fig. 1. It was found that there is continuous solid solution between spessartite and yttrogarnet.² the liquidus near the end member 3Y₂O₃·5Al₂O₃ is complicated by the existence of two crystalline forms having that composition. The liquidus temperature was obtained in the usual way by observing the presence or absence of crystals in quenched charges and the solidus was estimated from the proportion of glass to crystals in quenched charges from runs in the liquid + crystals region. Corroborative evidence for the position of the solidus was obtained from a plot of the change in unit-cell size of the crystals; the method of obtaining such evidence is described in a following section. The usual method of determining the solidus by observing the temperature at which crystallization is complete is not precise for the present study because films of glass about the crystals are easily overlooked. For this reason no great effort was made to fix the solidus precisely by thermal runs in this preliminary investigation. The dashed portions of the curves represent estimates of the equilibrium relations thought to exist in that region.

Equipment was not available to determine precisely either the transition from yttrogarnet to yttroalumite or the melting point of yttroalumite. The best estimate of the transition is 1970°±50° and of the melting point of yttroalumite, 2110°±70°. The reversible transformation between yttrogarnet and yttroalumite takes place in the solid state. The compound 3Y₂O₃·5Al₂O₃ has not been synthesized previously. The synthesis of Y₂O₃·Al₂O₃ and 3Y₂O₃·Al₂O₃ have been reported (Goldschmidt, Barth, and Lunde, 1925, p. 33), but the system Y₂O₃—Al₂O₃ has not been studied completely.

² The name yttrogarnet is proposed for the low form of 3Y₂O₃·5Al₂O₃. Yttrium-bearing garnets have been called yttrium garnet, yttriferous garnet, emildine, erinadine, yttrogarnet, yttrogarnet, and yttrogarnet. The last name is in accord with the present system of nomenclature and adequately describes the compound Y₃Al₈(AlO₁₈). The members of the series may be referred to as yttrian spessartites after Jaffe. The name yttroalumite is proposed for the high form of 3Y₂O₃·5Al₂O₃.
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<th>MnO</th>
<th>Y₂O₃</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>Composition</th>
<th>Initial condition</th>
<th>$^\circ$ C.</th>
<th>Time</th>
<th>Phases present (per cent)</th>
<th>$n$</th>
<th>$n$</th>
<th>$d_{45}$</th>
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<td>1080</td>
<td>18 hrs</td>
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<td>15 hrs</td>
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<td>garnet + glass</td>
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<td>glass</td>
<td>1600</td>
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<td>1.680</td>
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<td>1720</td>
<td>1 hr</td>
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<td>1.694</td>
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<td>pellet</td>
<td>1650</td>
<td>2 hrs</td>
<td>garnet</td>
<td>-</td>
<td>1.823</td>
<td>1.605</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>yttroalumite</td>
<td>1970</td>
<td>2 min</td>
<td>garnet + residual yttroalumite (few)</td>
<td>-</td>
<td>1.823</td>
<td>1.608</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>garnet</td>
<td>1970</td>
<td>5 min</td>
<td>garnet</td>
<td>-</td>
<td>1.824</td>
<td>1.608</td>
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<td>yttroalumite</td>
<td>2020</td>
<td>5 min</td>
<td>residual yttroalumite (90)+garnet</td>
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<td>1.823</td>
<td>1.608</td>
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<td>pellet</td>
<td>2040</td>
<td>5 min</td>
<td>garnet (probably poor quench)</td>
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<td>1.823</td>
<td>1.608</td>
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<td></td>
<td></td>
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<td>garnet</td>
<td>2160</td>
<td>2 min</td>
<td>melted: yttroalumite (99)+residual garnet</td>
<td>-</td>
<td>see text</td>
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<td>2170</td>
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<td>1.608</td>
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<td>-</td>
<td>see text</td>
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<td>5 min</td>
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<td>-</td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

*Composition slightly off join.*

$d_{45}$ = spacing of plane 642 in Å

$n$ = index of refraction

n. d. = not determined
The melting point of spessartite crystallized from a glass having an index of refraction of 1.655 was found to be $1195\pm2^\circ$. Spessartite has been synthesized by Gorgeu (1883), Menzer (1929), and Snow (1943). Snow determined the melting point of spessartite to be $1200\pm5^\circ$; however, his analysis indicates that the mix was slightly off composition. (The theoretical composition for spessartite is also given incorrectly.) In view of the experimental difficulties the agreement is considered to be good.

**Optical Data**

The index of refraction of the glasses in some of the quenched charges in the system $3\text{MnO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 - 3\text{Y}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$ is given in Table 1 and plotted in Fig. 2. The index of refraction of the glasses from the shortest runs which quenched to glass only is represented by circles and used to construct the curve. The dots represent the index of refraction of glasses obtained from runs in the liquid + crystals region. By using
the curve in Fig. 2, the composition of the liquid phase for each experiment may be approximated and compared with the composition determined by the temperature method of fixing the liquidus (see Bowen, 1913, p. 585). The poor agreement obtained was to be expected because of the fact that the index of refraction of the glasses changes with increasing length of run.

![Graph showing index of refraction vs. weight percentage of components.](image)

**Fig. 2.** Index of refraction of glasses in the system $3\text{MnO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 - 3\text{Y}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$.

It was not possible to quench $3\text{Y}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$ to a glass with the equipment at hand; therefore, the index of refraction of that glass is obtained by extrapolation of the curve in Fig. 2. The index of refraction of the $3\text{Y}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$ glass is estimated to be 1.719. From the Gladstone and Dale relation (Larsen and Berman, 1934, p. 30) and using $k_{\text{Y}_2\text{O}_3} = 0.176$, determined in the present investigation, and $k_{\text{Al}_2\text{O}_3} = 0.193$, the density of the glass is calculated to be 3.92 as compared with a calculated density of 4.12 for its high temperature crystalline equivalent yttroalumite. If Larsen and Berman’s value of $k_{\text{Y}_2\text{O}_3} = 0.144$ is used, the density of the glass is calculated to be higher than that of yttroalumite.

The index of refraction of the garnet crystals obtained is given in Table 1 and presented in Fig. 3. Reference liquids having high indices of refraction were obtained from Dr. Esper S. Larsen, Jr. and Miss Sarah C. Johnson of the U. S. Geological Survey, and from Mr. Howard W. Jaffe of the U. S. Bureau of Mines. The liquids obtained through the courtesy of Dr. Larsen are almost colorless ($n = 1.801-1.998$); they were calibrated by the minimum deviation method. The index of refraction of some of the reference liquids was measured by H. W. Jaffe on a Leitz-Jelley Microrefractometer at the same time as the measurement.
of the index of refraction of the crystal was being made. Within the error of measurement (±0.003) the index of refraction of the garnet crystals indicates that there is continuous solid solution between spessartite and yttrogarnet. The deviations are probably due largely to errors in the determination of the composition of the crystals, and it is assumed, therefore, that the change of index of refraction from spessartite to yttrogarnet is essentially linear.

![Graph showing index of refraction of garnets in the system spessartite-yttrogarnet.]

**Spessartite.** Spessartite crystallizes into irregular, light green grains up to 10 microns in diameter. Rare well-formed crystals were developed and these appeared as dodecahedrons. The crystals are isotropic and have an index of refraction of 1.800±0.003. This agrees exactly with the index of refraction of 1.800 predicted for the pure compound by Ford (1915, p. 37). Snow gave a value of 1.810±0.005 for a synthetic spessartite which may not have been of the proper composition.

**Yttrogarnet.** These crystals were observed as rounded, light green, isotropic grains approximately one to five microns in diameter. Only a few dodecahedral crystals were observed. The index of refraction was found to be 1.823±0.003.

**Yttrialumite.** The high form of 3Y₂O₃·5Al₂O₃ was observed as rounded, tabular crystals up to five microns in size. Most grains were observed to have biaxial negative figures, extinction inclined to the elongation, and n_{max} = 1.942, n_{min} = 1.927. One grain gave a uniaxial negative figure. The x-ray data indicate that yttrialumite is tetragonal, and therefore the biaxial figures are anomalous. It is noteworthy that the high-temperature form of 3Y₂O₃·5Al₂O₃ has lower symmetry than the low-temperature form and has indices of refraction greater than those of its component oxides.
Two values of the specific refractivity of $Y_2O_3$ were obtained from the Gladstone and Dale relation, using the following data:

<table>
<thead>
<tr>
<th>Material</th>
<th>$n$ (measured)</th>
<th>$\rho$ (calculated from x-ray data)</th>
<th>$k$ (calculated specific refractivity for $Y_2O_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ytrogarnet</td>
<td>1.823</td>
<td>4.55</td>
<td>0.172</td>
</tr>
<tr>
<td>Yttria</td>
<td>1.910</td>
<td>5.04</td>
<td>0.180</td>
</tr>
<tr>
<td>mean</td>
<td></td>
<td></td>
<td>0.176</td>
</tr>
</tbody>
</table>

where $n =$ index of refraction, $\rho =$ density, and $k_{Al_2O_3} = 0.193$ (Larsen and Berman, 1934, p. 31). The calculated mean refractive index of yttragarnet, using $\rho = 4.12$, $k_{Y_2O_3} = 0.176$, and $k_{Al_2O_3} = 0.193$, was found to be 1.755, which is considerably below the observed mean refractive index (1.934). Either the Gladstone and Dale relation does not hold in this case or the measured indices of refraction are anomalous.

![Fig. 4. Change of spacing, $d$, of the plane 642 in garnet crystals in the system spessartite-yttragarnet with temperature of formation.](image-url)

**X-RAY DIFFRACTION DATA**

Powder patterns were obtained for the products of all runs below the liquidus (see Table 1). A plot of $d_{642}$ as a function of the temperature of formation of crystals in equilibrium with liquid is given in Fig. 4. The curve is essentially a reproduction of the solidus. Because there were not in all cases sufficient crystals present in the glass to give a good pattern, it was necessary to choose arbitrarily a prominent peak to indicate the change of unit-cell dimension. (In the isometric system the spacing of all planes is proportional to $a_0$.) The continuous nature of the change in unit-cell size with change in composition (see Fig. 5), in addition to the regular change in intensities, indicates that spessartite and yttragarnet are isostructural. Regular positive deviations from Vegard’s Law (Vegard, 1921) are not uncommon and in the present case may be due in part to the manner in which the composition of the crystals was
fixed by the location of the solidus. If Vegard's Law were assumed to be exactly satisfied, that is, if the unit-cell parameter varied linearly with composition expressed in atomic per cent, the solidus would be more convex toward the yttrogarnet composition. That being the case, estimated compositions of crystals would be higher in the yttrogarnet end member. Had other methods been lacking, the solidus could have been fixed approximately by applying Vegard's Law.

![Figure 5](image.png)

**Fig. 5.** Change of spacing, \(d\), of the plane 642 in garnet crystals in the system spessartite-yttrogarnet with composition.

The cell edge for spessartite, space group \(O_h^{10}-Ia3d\), is \(11.63 \pm 0.02 \text{ Å}\), and for yttrogarnet it is \(12.01 \pm 0.02 \text{ Å}\). The intensities of the recorded reflections are given in Table 2. The observed intensities were taken to be proportional to the heights of the peaks on the graph from the Norelco x-ray spectrometer, and the height of the peak from the 420 plane was assigned the value 10. The increase in cell edge from spessartite to yttrogarnet was expected from the change of ionic radii; \(\text{Mn}^{2+} = 0.82 \text{ Å}\) is replaced by \(\text{Y}^{3+} = 0.96 \text{ Å}\), and \(\text{Si}^{4+} = 0.39 \text{ Å}\) is replaced by \(\text{Al}^{3+} = 0.47 \text{ Å}\) (radii from Pauling, 1945). The cell edge of grossularite, \(\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3\), whose structure was determined by Menzer (1929), is \(11.864 \text{ Å}\). Here \(\text{Ca}^{2+} = 1.02 \text{ Å}\) is replaced by \(\text{Y}^{3+} = 0.96 \text{ Å}\); the change in spacing apparently is more than counteracted by the difference in Si and Al radii.

To test the isostructural character of grossularite, spessartite, and yttrogarnet, the intensities were calculated using as a first approximation the coordinates given by Menzer for grossularite (Table 3).

\(^{3}\) The superscripts indicate the valence; the subscripts, the coordination number.
### Table 2

<table>
<thead>
<tr>
<th>Grossularite</th>
<th>Spessartite (synthetic)</th>
<th>Yttrogarnet (synthetic)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Og</strong></td>
<td><strong>d</strong></td>
<td><strong>d</strong></td>
</tr>
<tr>
<td><strong>hkl</strong></td>
<td><strong>Calc.</strong></td>
<td><strong>Obs.</strong></td>
</tr>
<tr>
<td>211</td>
<td>4.84</td>
<td>N.O.</td>
</tr>
<tr>
<td>212</td>
<td>4.19</td>
<td>N.O.</td>
</tr>
<tr>
<td>321</td>
<td>3.37</td>
<td>N.O.</td>
</tr>
<tr>
<td>400</td>
<td>2.96</td>
<td>2.96</td>
</tr>
<tr>
<td>420</td>
<td>2.65</td>
<td>2.65</td>
</tr>
<tr>
<td>332</td>
<td>2.53</td>
<td>2.53</td>
</tr>
<tr>
<td>442</td>
<td>2.42</td>
<td>2.42</td>
</tr>
<tr>
<td>431</td>
<td>2.32</td>
<td>2.33</td>
</tr>
<tr>
<td>521</td>
<td>2.16</td>
<td>2.16</td>
</tr>
<tr>
<td>440</td>
<td>2.09</td>
<td>2.10</td>
</tr>
<tr>
<td>631</td>
<td>1.922</td>
<td>1.920</td>
</tr>
<tr>
<td>532</td>
<td>1.874</td>
<td>1.879</td>
</tr>
<tr>
<td>451</td>
<td>1.828</td>
<td>N.O.</td>
</tr>
<tr>
<td>631</td>
<td>1.747</td>
<td>N.O.</td>
</tr>
<tr>
<td>444</td>
<td>1.710</td>
<td>1.713</td>
</tr>
<tr>
<td>543</td>
<td>1.676</td>
<td>1.678</td>
</tr>
<tr>
<td>640</td>
<td>1.643</td>
<td>1.647</td>
</tr>
<tr>
<td>721</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>633</td>
<td>1.613</td>
<td>1.616</td>
</tr>
<tr>
<td>552</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>642</td>
<td>1.583</td>
<td>1.586</td>
</tr>
<tr>
<td>732</td>
<td>1.505</td>
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<tr>
<td>651</td>
<td>1.481</td>
<td>1.485</td>
</tr>
<tr>
<td>800</td>
<td>1.376</td>
<td>0.001</td>
</tr>
<tr>
<td><strong>r</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*I* = Intensity; **I** = 10

<table>
<thead>
<tr>
<th>CuKα</th>
<th>= 1.5418 Å</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>n(No</th>
<th>Number of formula weights per unit cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>d</td>
<td>spacing of planes in Å</td>
</tr>
<tr>
<td>N.O.</td>
<td>Not Observed</td>
</tr>
<tr>
<td>Nickel Filter</td>
<td></td>
</tr>
<tr>
<td>Norelco X-ray Spectrometer</td>
<td></td>
</tr>
<tr>
<td>n = Index of Refraction</td>
<td></td>
</tr>
</tbody>
</table>

Intensities were calculated for 25 reflections by means of the formula:

\[
I \propto |F|^2 m \frac{1 + \cos^2 \theta}{\sin^2 \theta \cos \theta}
\]

where \( F \) is the structure factor, \( m \) the multiplicity factor, and \( \theta \) the glancing angle. The calculations were made using James and Brindley's values.
for the scattering powers of the ions as given in the Internationale Tabellen. Scattering factors for Y\(^{3+}\) and Mn\(^{2+}\) were obtained by graphical approximation; the following values were used:

\[
\begin{align*}
10^{-8}x \sin \theta / \lambda & : 0.0 \quad 0.1 \quad 0.2 \quad 0.3 \quad 0.4 \quad 0.5 \quad 0.6 \\
f_0 - Y^{3+} & : 36.0 \quad 33.8 \quad 30.1 \quad 26.1 \quad 22.7 \quad 20.0 \quad 17.8 \\
f_0 - Mn^{2+} & : 23.0 \quad 21.3 \quad 18.2 \quad 14.6 \quad 12.3 \quad 10.8 \quad 9.7
\end{align*}
\]

Results of the calculations are given in Table 2.\(^4\) It can be seen on inspection that the agreement of the observed intensities to the calculated intensities is very good.\(^5\) It is concluded that the assumed structures are essentially correct.

Pauling’s electrostatic bond rule is completely satisfied in each case. In intermediate compositions, the positions 24(c) and 24(d) comprise variate atom equipoints (Barth and Posnjak, 1931).

A study of a solid model of Menzer’s grossularite structure shows that Ca is surrounded by eight nearly equidistant oxygens. Within the stated limits of error, the Ca-O distances are indistinguishable. Menzer gives Ca-O: 2.46±0.20 Å for four distances and Ca-O: 2.36±0.13 Å for the other four. The oxygens about the calcium form a hexahedron which in this case is a greatly distorted cube. Eight-fold coordination is common for Ca\(^{2+}\), but it is unusual for Mg\(^{2+}\), Fe\(^{2+}\), and Mn\(^{2+}\) which replace Ca\(^{2+}\). More precise data are needed to ascertain the bond lengths in these structures.

\(^4\) The calculations for grossularite have been made previously by Pabst (1937, p. 863; 1942, p. 790). The agreement is good when account is taken of the differences in radiation and the discrepancies resulting from differences in interpolation of the scattering, Lorentz and polarization factors. Dr. Pabst kindly located several errors in the preliminary calculations.

\(^5\) The discrepancy factor \(\sum |F_{\text{obs}}| - |F_{\text{calc}}| / \sum |F_{\text{obs}}| = 0.14\) compares favorably with previous factors reported in the literature. It has been suggested that regression analysis (see for example Snedecor, 1946, pp. 103–137) of the data would provide a more meaningful test. Perfect agreement between \(I_{\text{obs}}\) and \(I_{\text{calc}}\) would generate regression and correlation coefficients equal to unity. For the yttrogarnet data the regression coefficient is 1.19, with an error of 0.086, and the correlation coefficient is 0.959. According to the conventional statistical interpretation, the assumed structure thus accounts satisfactorily for the observations.
Within the knowledge of the writers, yttrogarnet and γ-Al₂O₃ are the only examples on record of structures in which silicon is absent, possessing aluminum in two coordinations. Yttrogarnet is also an example of a rare combination involving metal atoms each of which has three positive charges.

The powder diffraction data for yttroalumite are given in Table 4. A preliminary study by Dr. Gabrielle Donnay indicates a tetragonal cell with \( a = 7.51 \text{ Å}, c = 4.24 \text{ Å} \), and one formula weight per cell giving \( \rho_{\text{calc}} = 4.12 \). The lattice is primitive; no systematic absences are found.

<table>
<thead>
<tr>
<th>( d ) in Å</th>
<th>( I/I_{10} \times 10 )</th>
<th>( d ) in Å</th>
<th>( I/I_{10} \times 10 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.24</td>
<td>0.5</td>
<td>1.694</td>
<td>0.2</td>
</tr>
<tr>
<td>3.70</td>
<td>4.5</td>
<td>1.655</td>
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</tr>
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<td>3.68</td>
<td>4.0</td>
<td>1.640</td>
<td>2.5</td>
</tr>
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<td>3.36</td>
<td>2.5</td>
<td>1.605</td>
<td>1.0</td>
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<tr>
<td>3.32</td>
<td>2.0</td>
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<td>1.5</td>
</tr>
<tr>
<td>2.89</td>
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<td>1.5</td>
</tr>
<tr>
<td>2.67</td>
<td>4.0</td>
<td>1.503</td>
<td>4.5</td>
</tr>
<tr>
<td>2.62</td>
<td>10.0</td>
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<td>0.5</td>
</tr>
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<td>2.59</td>
<td>3.0</td>
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</tr>
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<td>2.51</td>
<td>2.5</td>
<td>1.312</td>
<td>2.0</td>
</tr>
<tr>
<td>2.26</td>
<td>0.3</td>
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<td>2.22</td>
<td>1.5</td>
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<td>0.5</td>
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<td>2.5</td>
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<td>0.5</td>
</tr>
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<td>1.224</td>
<td>1.0</td>
</tr>
<tr>
<td>2.05</td>
<td>1.5</td>
<td>1.194</td>
<td>0.1</td>
</tr>
<tr>
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<td>0.3</td>
</tr>
<tr>
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<td>0.3</td>
<td>1.173</td>
<td>3.0</td>
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<tr>
<td>1.859</td>
<td>4.0</td>
<td>1.170</td>
<td>3.0</td>
</tr>
<tr>
<td>1.845</td>
<td>3.0</td>
<td>1.159</td>
<td>0.5</td>
</tr>
<tr>
<td>1.806</td>
<td>2.0</td>
<td>1.154</td>
<td>1.0</td>
</tr>
</tbody>
</table>

* CuKα radiation, Nickel filter, Norelco X-ray Spectrometer.

**Discussion**

The importance of the synthesis and structural identification of the yttrogarnet is twofold. It demonstrates one of the ways in which yttrium may enter the garnet structure. It should be clear that this is not the only way in which yttrium might go into the garnet structure. Jaffe (1950), in his discussion of the yttrian garnet from Iisaka (Iizaka), Japan, suggests that \( Na^{+1}Y^{3+} \rightarrow 2Mn^{2+} \). In this case the sodium and yttrium atoms would be distributed randomly over the 24(c) position.
and would cause little distortion of the structure. Rankama and Sahama
(1950, p. 526) suggest that yttrium goes into garnet in another manner
which the present writers interpret as follows: $Y^{+3}Mg^{+2} \rightarrow Mn^{+2}Al^{+3}$.
Magnesium is about the only atom with a valence of two which has the
requisite radius that could substitute in the $16(a)$ position. The limiting
end member in this substitution would be a compound of the composition
$(MnY)_{2}Mg_{2}(SiO_{4})_{3}$. In the past magnesium has been thought to enter
the garnet structure only in the $24(c)$ position, as in pyrope.

The series spessartite-yttrogarnet is, in addition, the first example of
an orthosilicate in which the substitution of aluminum for silicon can
be carried to completion. It contradicts the prevalent idea that the
substitution of aluminum for silicon always decreases as the Si/O ratio
decreases. That concept has been presented by Machatschki (1928),
Warren (1930), Bragg (1930), and more specifically by de Jong (1935).
The limits to which aluminum may substitute for silicon in the various
linkages of tetrahedra are given by de Jong as follows:

\[
\begin{array}{ccc}
\text{SiO}_4 & \text{Orthosilicate group} & \text{none or little} \\
\text{Si}_2\text{O}_7 & \text{Complex group} & \text{none or little} \\
\text{SiO}_2 & \text{Chain} & \frac{1}{4} \\
\text{Si}_2\text{O}_7 & \text{Double chain} & \frac{1}{4} \\
\text{SiO}_6 & \text{Sheet} & \frac{1}{2} \text{ to } \frac{3}{2} \\
\text{SiO}_3 & \text{Network} & \frac{1}{2} \\
\end{array}
\]

Although the complete substitution which has been experimentally
demonstrated for an orthosilicate may be an exception, further study
should be given to the general concept of the limits of aluminum substitu-
tion for silicon.

Acknowledgments

Drs. Gabrielle Donnay and J. D. H. Donnay gave many helpful sug-
gestions as well as instruction in the structure factor calculations. The
continuing interest and stimulative discussions of Howard W. Jaffe are
gratefully acknowledged.

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33–49.
THE SYSTEM $3\text{MnO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 - 3\text{Y}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$


Jaffe, H. W., The role of yttrium and other minor elements in the garnet group: Am. Mineral., 36, 133-155 (1951)


Manuscript received Oct. 13, 1950