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COMPLETE SUBSTITUTION OF ALUMINUM FOR SILICON: THE SYSTEM

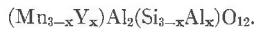


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ABSTRACT

Thermal, optical, and x -ray data indicate that there is a complete solid solution series between spessartite, $\text{Mn}_3\text{Al}_2(\text{SiO}_4)_3$, and yttr garnet, $\text{Y}_3\text{Al}_2(\text{AlO}_4)_3$. The substitution $\text{Y}^{+3}\text{Al}^{+3} \rightarrow \text{Mn}^{+2}\text{Si}^{+4}$ may be represented by the formula:



Yttr garnet has a cube edge of $12.01 \pm 0.02 \text{ \AA}$ and the space group O_h^{10} . Using the coordinates of grossularite as determined by Menzer, good agreement was obtained between calculated and observed intensities. The atomic positions are:

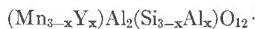
Al in 16(<i>a</i>)	0	0	0
Y in 24(<i>c</i>)	$\frac{1}{4}$	$\frac{1}{8}$	0
Al in 24(<i>d</i>)	$\frac{1}{4}$	$\frac{3}{8}$	0
O in 96(<i>h</i>)	<i>x</i>	<i>y</i>	<i>z</i>

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. Yttr garnet inverts to a high form, yttrioalumite, at $1970 \pm 50^\circ \text{C}$.

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 Y_2O_3 . He suggested that yttrium occupies manganese positions in the garnet structure, and that the substitution should occur as $\text{Y}^{+3}\text{Al}^{+3} \rightarrow \text{Mn}^{+2}\text{Si}^{+4}$. 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:



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

PREPARATION OF MIXTURES

Mixtures were made from SiO_2 , Al_2O_3 , Y_2O_3 , and MnCO_3 . 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 MnCO_3 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 CO_2 . 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:

Per cent	
>10	Y_2O_3
0.3 to 3	K_2O
0.2 to 2	SmO_2
0.02 to 0.2	Dy_2O_3 , Ce_2O_3 , Gd_2O_3 , PrO_2
0.01 to 0.1	ZrO_2 , La_2O_3 , Nd_2O_3 , HfO_2 , Na_2O
0.005 to 0.05	Sc_2O_3
<0.01	Al_2O_3 , Fe_2O_3 , SiO_2 , MgO , MnO , CaO
not detected	Li_2O , Cs_2O , Rb_2O .

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 rectangular plates.

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 Al_2O_3 ($2050^\circ \pm 10^\circ$).

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:

<i>Present Work</i>	<i>Snow</i>
1 hr. $n=1.655$	1 hr. $n=1.666$
15 hrs. $n=1.662$	5 hrs. $n=1.671$

In general the loss of manganese lowers the index and an increase in Mn_2O_3 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 $3MnO \cdot Al_2O_3 \cdot 3SiO_2 - 3Y_2O_3 \cdot 5Al_2O_3$, based on the data in Table 1, is given in Fig. 1. It was found that there is continuous solid solution between spessartite and yttrigarnet;² the liquidus near the end member $3Y_2O_3 \cdot 5Al_2O_3$ 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 yttrigarnet to yttrioalumite or the melting point of yttrioalumite. The best estimate of the transition is $1970^\circ \pm 50^\circ$ and of the melting point of yttrioalumite, $2110^\circ \pm 70^\circ$. The reversible transformation between yttrigarnet and yttrioalumite takes place in the solid state. The compound $3Y_2O_3 \cdot 5Al_2O_3$ has not been synthesized previously. The synthesis of $Y_2O_3 \cdot Al_2O_3$ and $3Y_2O_3 \cdot Al_2O_3$ have been reported (Goldschmidt, Barth, and Lunde, 1925, p. 33), but the system $Y_2O_3 - Al_2O_3$ has not been studied completely.

² The name yttrigarnet is proposed for the low form of $3Y_2O_3 \cdot 5Al_2O_3$. Yttrium-bearing garnets have been called yttrium garnet, yttriferous garnet, emildine, erinadine, yttergarnet, yttriogarnet, and yttrigarnet. The last name is in accord with the present system of nomenclature and adequately describes the compound $Y_3Al_2(AlO_4)_3$. The members of the series may be referred to as yttrian spessartites after Jaffe. The name yttrioalumite is proposed for the high form of $3Y_2O_3 \cdot 5Al_2O_3$.

TABLE 1

Composition				Initial condition	$t^{\circ} \text{C.}$	Time	Phases present (per cent)	n glass	n crystal	d_{612} crystal
MnO	Y ₂ O ₃	Al ₂ O ₃	SiO ₂							
43.00	—	20.60	36.40	glass	1080	18 hrs	garnet	—	1.800	1.557
				glass	1180	15 hrs	garnet (95)+glass	n. d.	1.800	1.557
				glass	1193	30 min	garnet (rare)+glass	1.653	n. d.	n. d.
				glass	1196	30 min	glass	1.653	—	—
				glass	1200	30 min	glass	1.655	—	—
				powder	1216	1 hr	glass	1.655	—	—
				powder	1218	15 hrs	glass	1.662	—	—
				powder	1256	15 hrs	glass	1.668	—	—
*40.63	3.00	21.78	34.59	glass	1177	17 hrs	garnet+glass (rare)	n. d.	1.801	1.560
				powder	1306	15 hrs	glass	1.663	—	—
*38.70	5.88	22.66	32.76	glass	1202	15 hrs	garnet	—	1.801	1.564
				powder	1269	22 hrs	garnet (10)+glass	1.663	1.805	1.575
				powder	1317	2 hrs	glass	1.660	—	—
36.30	8.89	24.08	30.73	glass	1247	1 hr	garnet (50)+glass	1.660	1.805	1.571
				glass	1250	15 hrs	garnet (50)+glass	1.661	1.803	1.571
				glass	1290	30 min	garnet (10)+glass	1.665	n. d.	1.576
				powder	1329	19 hrs	garnet (rare)+glass	1.662	n. d.	n. d.
				glass	1335	1 hr	glass	1.665	—	—
				garnet+glass	1340	3 hrs	glass	1.669	—	—
				glass	1439	5 min	glass	1.666	—	—
32.25	14.27	26.18	27.30	glass	1273	1 hr	garnet (90)+glass	1.667	1.807	1.577
				glass	1364	1 hr	garnet (10)+glass	1.671	1.810	1.589
				powder	1446	16 hrs	glass	1.670	—	—
25.80	22.83	29.53	21.84	pellet	1334	10 hrs	garnet (80)+glass	1.658	1.812	1.587
				powder	1499	5 hrs	garnet (5)+glass	1.683	1.816	1.598
				powder	1550	5 min	glass	1.682	—	—
17.20	34.24	34.00	14.56	garnet+glass	1451	1 hr	garnet (95)+glass	1.667	1.818	1.597
				glass	1498	1 hr	garnet (95)+glass	1.672	1.816	1.598
				glass	1600	15 min	garnet (90)+glass	1.680	1.821	1.600
				glass	1640	30 min	garnet (80)+glass	1.682	n. d.	n. d.
				pellet	1720	1 hr	glass	n. d.	—	—
				pellet	1730	10 min	glass	1.694	—	—
—	57.07	42.93	—	pellet	1650	2 hrs	garnet	—	1.823	1.605
					1730	1 hr				
				yttrioalumite	1970	2 min	garnet+residual yttrioalumite (few)	—	1.823	1.608
				garnet	1970	5 min	garnet	—	1.824	1.608
				pellet	1970	5 min	garnet	—	1.823	1.608
				yttrioalumite	2020	5 min	residual yttrioalumite (90)+garnet	—	see text	
				pellet	2040	5 min	garnet (probably poor quench)	—	1.823	1.608
				garnet	2160	2 min	melted: yttrioalumite (99)+residual garnet	—	see text	
				pellet	2170	2 min	melted: garnet+yttrioalumite (rare)	—	1.823	1.608
				pellet	2180	2 min	melted: yttrioalumite (99)+garnet	—	see text	
				garnet	2180	1 min	melted: yttrioalumite (99)+garnet	—	see text	
				pellet	2180	5 min	melted: yttrioalumite (95)+garnet	—	see text	

* Composition slightly off join.

 d_{612} =spacing of plane 642 in Å n =index of refraction

n. d.=not determined

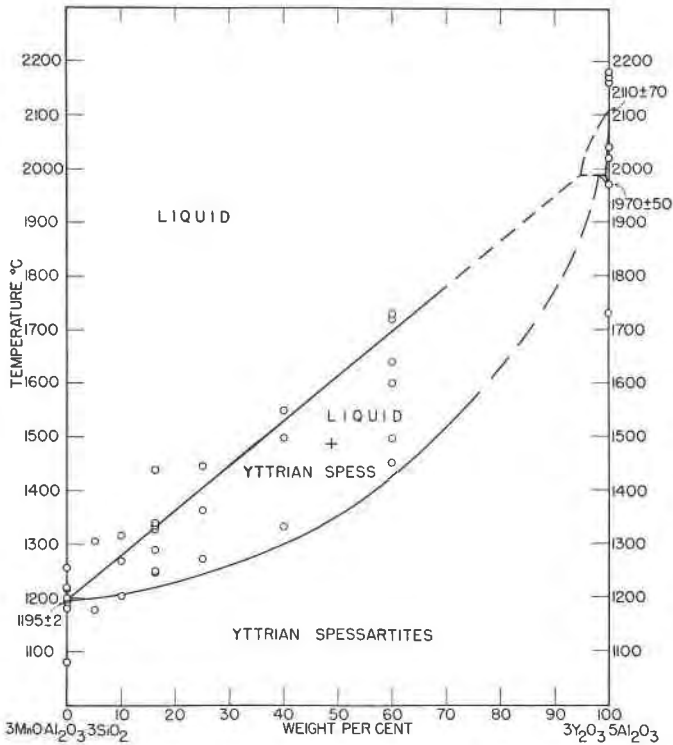


FIG. 1. Preliminary temperature-composition diagram for the system $3\text{MnO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 - 3\text{Y}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$.

The melting point of spessartite crystallized from a glass having an index of refraction of 1.655 was found to be $1195^\circ \pm 2^\circ$. Spessartite has been synthesized by Gorgeu (1883), Menzer (1929), and Snow (1943). Snow determined the melting point of spessartite to be $1200^\circ \pm 5^\circ$; 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.

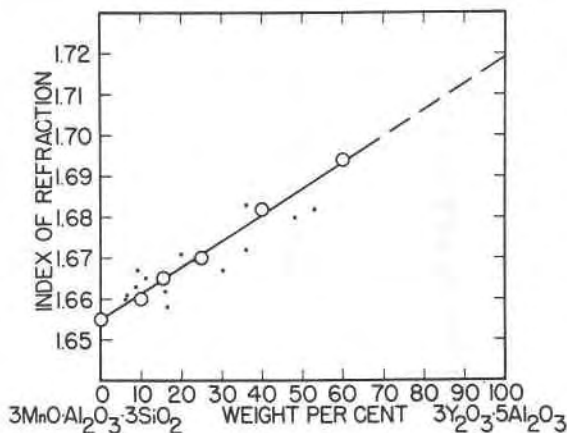


FIG. 2. Index of refraction of glasses in the system $3MnO \cdot Al_2O_3 \cdot 3SiO_2 - 3Y_2O_3 \cdot 5Al_2O_3$.

It was not possible to quench $3Y_2O_3 \cdot 5Al_2O_3$ 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 $3Y_2O_3 \cdot 5Al_2O_3$ glass is estimated to be 1.719. From the Gladstone and Dale relation (Larsen and Berman, 1934, p. 30) and using $k_{Y_2O_3} = 0.176$, determined in the present investigation, and $k_{Al_2O_3} = 0.193$, 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 yttralumite. If Larsen and Berman's value of $k_{Y_2O_3} = 0.144$ is used, the density of the glass is calculated to be higher than that of yttralumite.

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 yttrigarnet. 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 yttrigarnet is essentially linear.

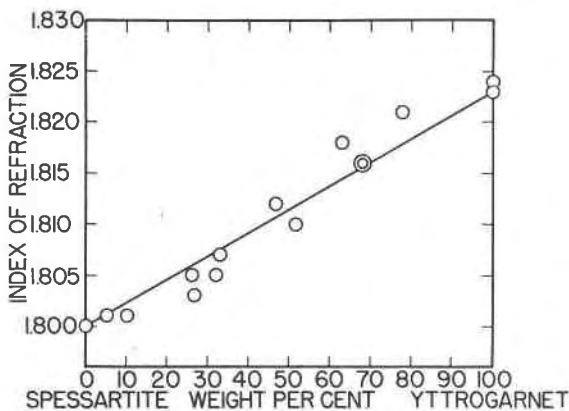


FIG. 3. Index of refraction of garnets in the system spessartite-yttrigarnet.

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.

Yttrigarnet. 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 .

Yttrioalumite. The high form of $3Y_2O_3 \cdot 5Al_2O_3$ 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 yttrioalumite is tetragonal, and therefore the biaxial figures are anomalous. It is noteworthy that the high-temperature form of $3Y_2O_3 \cdot 5Al_2O_3$ 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:

	n	ρ	k
	(measured)	(calculated from x -ray data)	(calculated specific refractivity for Y_2O_3)
Yttrogarnet	1.823	4.55	0.172
Yttria	1.910	5.04	0.180
			mean 0.176

where n = index of refraction, ρ = density, and $k_{Al_2O_3} = 0.193$ (Larsen and Berman, 1934, p. 31). The calculated mean refractive index of yttroalumite, 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.

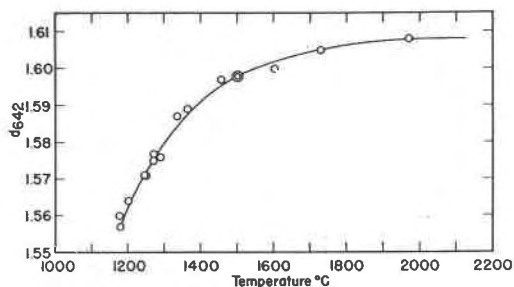


FIG. 4. Change of spacing, d , of the plane 642 in garnet crystals in the system spessartite-yttrogarnet with temperature of formation.

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 yttrogarnet 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.

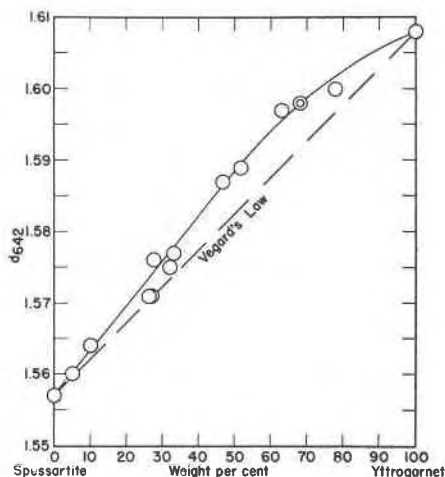


FIG. 5. Change of spacing, d , of the plane 642 in garnet crystals in the system spessartite-yttrogarnet with composition.

The cell edge for spessartite, space group $O_h^{10} - Ia3d$, is $11.63 \pm 0.02 \text{ \AA}$, and for yttrogarnet it is $12.01 \pm 0.02 \text{ \AA}$. 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; $Mn_{VIII}^{+2} = 0.82 \text{ \AA}$ is replaced by $Y_{VIII}^{+3} = 0.96 \text{ \AA}$, and $Si_{IV}^{+4} = 0.39 \text{ \AA}$ is replaced by $Al_{IV}^{+3} = 0.47 \text{ \AA}$ (radii from Pauling, 1945).³ The cell edge of grossularite, $Ca_3Al_2(SiO_4)_3$, whose structure was determined by Menzer (1929), is 11.864 \AA . Here $Ca_{VIII}^{+2} = 1.02 \text{ \AA}$ is replaced by $Y_{VIII}^{+3} = 0.96 \text{ \AA}$; 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

C_h^{10} hkl	Grossularite Georgetown, California				Spessartite (synthetic)				Yttrogarnet (synthetic)						
	d Calc.	d Obs.	I^* Calc.	I Obs.	d Calc.	d Obs.	I^* Calc.	I Obs.	d Calc.	d Obs.	I^* Calc.	I Obs.			
211	4.84	N.O.	0.16	—	4.75	4.76	0.74	0.5	4.90	4.89	2.49	3.5			
220	4.19	N.O.	0.11	—	4.11	N.O.	0.00	—	4.25	4.24	0.38	1			
321	3.17	N.O.	0.25	—	3.11	3.10	0.80	0.7	3.21	3.21	2.19	2			
400	2.96	2.96	3.59	4.5	2.91	2.91	3.06	2.5	3.00	3.00	2.37	3			
420	2.65	2.65	10.00	10	2.60	2.60	10.00	10	2.69	2.69	10.00	10			
332	2.53	2.53	0.95	1	2.48	2.48	0.32	1	2.56	N.O.	0.00	—			
422	2.42	2.42	2.50	2.5	2.37	2.37	2.40	1.5	2.45	2.45	2.24	2.5			
431	2.32	2.33	1.57	3	2.28	2.28	1.09	1	2.36	2.36	0.55	0.5			
521	2.16	2.16	1.61	2	2.12	2.13	1.71	1.5	2.19	2.19	2.18	3			
440	2.09	2.10	0.36	0.5	2.06	2.06	0.41	0.5	2.12	2.13	0.47	0.5			
611	1.922	1.920	1.40	4	1.887	1.886	1.26	2	1.948	1.952	1.30	3			
532			1.14				2.38						1.58		
620	1.874	1.879	0.00	0.5	1.839	1.836	0.01	0.2	1.899	N.O.	0.15	—			
541	1.828	N.O.	0.03	—	1.794	1.797	0.02	0.2	1.853	N.O.	0.01	—			
631	1.747	N.O.	0.13	—	1.715	1.710	0.02	0.2	1.771	1.772	0.11	0.2			
444	1.710	1.713	1.40	2	1.679	1.681	1.41	2	1.734	1.734	1.70	2.5			
543	1.676	1.678	0.27	0.5	1.645	1.650	0.18	0.5	1.698	N.O.	0.09	—			
640	1.643	1.647	3.49	4	1.613	1.614	3.11	3	1.666	1.666	3.11	4			
721			0.01	0.5			0.04	0.5			0.28	1			
633	1.613	1.616	0.00			1.583	1.586		0.01		1.634		1.635	0.11	
552			0.14						0.16					0.31	
642	1.583	1.586	4.56	5	1.554	1.557	3.71	4	1.605	1.608	2.84	3.5			
732			0.01	—			0.00	0.2			0.15	0.5			
651	1.505	N.O.	0.00			1.477	1.482		0.03		1.525		1.528	0.33	
800	1.481	1.485	1.18	1	1.454	1.456	1.09	1.5	1.501	1.503	1.12	1.5			
a_0	$11.85 \pm 0.01 \text{ \AA}$				$11.63 \pm 0.02 \text{ \AA}$				$12.01 \pm 0.02 \text{ \AA}$						
ρ calc.	3.595				4.179				4.552						
ρ obs.	3.53				>4.0				>4.0						
n	1.736 ± 0.001				1.800 ± 0.003				1.823 ± 0.003						
z	8				8				8						

* I = Intensity; $I_{120} = 10$
 $\lambda(\text{CuK}\alpha) = 1.5418 \text{ \AA}$
 z = Number of formula weights per unit cell
 d = spacing of planes in \AA
 N.O. = Not Observed
 Nickel Filter
 ρ = density
 Norelco X-ray Spectrometer
 n = Index of Refraction

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

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

where F is the structure factor, m the multiplicity factor, and θ the glancing angle. The calculations were made using James and Brindley's values

TABLE 3

Grossularite	Spessartite	Yttrogarnet	Atomic positions			
Ca ⁺²	Mn ⁺²	Y ⁺³	24(c)	$\frac{1}{4}$	$\frac{1}{8}$	0
Al ⁺³	Al ⁺³	Al ⁺³	16(a)	0	0	0
Si ⁺⁴	Si ⁺⁴	Al ⁺³	24(d)	$\frac{1}{4}$	$\frac{3}{8}$	0
O ⁻²	O ⁻²	O ⁻²	96(h)	$x=0.04$ $y=0.055$ $z=0.64$		

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:

$10^{-8}x \sin \theta/\lambda$	0.0	0.1	0.2	0.3	0.4	0.5	0.6
$f_0 - Y^{+3}$	36.0	33.8	30.1	26.1	22.7	20.0	17.8
$f_0 - Mn^{+2}$	23.0	21.3	18.2	14.6	12.3	10.8	9.7

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 $\sum ||F_{obs.}| - |F_{calc.}|| / \sum |F_{obs.}| = 0.14$ 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_{obs} and I_{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, yttrigarnet and γ - Al_2O_3 are the only examples on record of structures in which silicon is absent, possessing aluminum in two coordinations. Yttrigarnet is also an example of a rare combination involving metal atoms each of which has three positive charges.

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

TABLE 4. POWDER X-RAY DIFFRACTION DATA FOR SYNTHETIC YTTRIOALUMITE*

d in \AA	$I/I_{10} \times 10$	d in \AA	$I/I_{10} \times 10$
4.24	0.5	1.694	0.2
3.70	4.5	1.655	1.0
3.68	4.0	1.640	2.5
3.36	2.5	1.605	1.0
3.32	2.0	1.531	1.5
2.89	0.3	1.519	1.5
2.67	4.0	1.503	4.5
2.62	10.0	1.485	0.5
2.59	3.0	1.389	1.0
2.51	2.5	1.312	2.0
2.26	0.3	1.296	0.5
2.22	1.5	1.243	0.5
2.16	2.5	1.229	0.5
2.12	2.0	1.224	1.0
2.05	1.5	1.194	0.1
1.996	0.3	1.187	0.3
1.972	0.3	1.173	3.0
1.859	4.0	1.170	3.0
1.845	3.0	1.159	0.5
1.806	2.0	1.154	1.0

* CuK_{α} radiation, Nickel filter, Norelco X-ray Spectrometer.

DISCUSSION

The importance of the synthesis and structural identification of the yttrigarnet 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:

SiO ₄	Orthosilicate group	none or little
Si ₂ O ₇	Complex group	none or little
SiO ₃	Chain	$\frac{1}{4}$
Si ₄ O ₁₁	Double chain	$\frac{1}{4}$
Si ₂ O ₆	Sheet	$\frac{1}{4}$ to $\frac{1}{2}$
SiO ₂	Network	$\frac{1}{2}$

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 substitution for silicon.

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