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SILICATE GARNET—YTTRIUM-IRON GARNET SOLID SOLUTIONS

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ABSTRACT

In the system $Ca_3Al_2(SiO_4)_3$—$Y_3Fe_2(FeO_4)_3$, a series of solid solutions exists over the range 10–100% $Y_3Fe_2(FeO_4)_3$. Similar to the system spessartite—yttrium-aluminum garnet, this system does not follow a linear composition vs. lattice constant law. Under the conditions of the experiments, a complete series of solid solutions does not exist in the system $Mn_3Al_2(SiO_4)_3$—$Y_3Fe_2(FeO_4)_3$ although there is some solution at the ends. The system $Ca_3Al_2(SiO_4)_3$—$Gd_3Fe_2(FeO_4)_3$ is similar to that of the $Ca_3Al_2(SiO_4)_3$—$Y_3Fe_2(FeO_4)_3$ system but under similar experimental conditions does not appear to have as wide a range.

INTRODUCTION

In a continuing program designed to learn more about the crystal chemistry of and interactions among magnetic ions in the garnets (1–4), we have studied in some detail the systems $Ca_3Al_2(SiO_4)_3$—$Y_3Fe_2(FeO_4)_3$ and $Mn_3Al_2(SiO_4)_3$—$Y_3Fe_2(FeO_4)_3$. We have also examined solid solutions in the system $Ca_3Al_2(SiO_4)_3$—$Gd_3Fe_2(FeO_4)_3$.

GROSSULARITE—YTTRIUM-IRON GARNET SYSTEM

In the preparation of specimens, the appropriate amounts of oxides were thoroughly mixed. The mixture of reactants was compressed into a pellet. Firing was carried out at 1350–1400° C. Samples containing more than 50 mole % of the silicate reactants melted to form glasses; on annealing these glasses at about 1150° C. for two hours, single garnet phases were obtained. Samples with 50 mole % or less of silicate reactants did not melt; these were usually fired for about 2 hrs, cooled, reground, compacted and refired. The procedure was repeated (2–3 times) until the powder photograph indicated a single phase.

In the $Ca_3Al_2(SiO_4)_3$—$Y_3Fe_2(FeO_4)_3$ system, solid solutions containing between 0 and 90 mole % $Ca_3Al_2(SiO_4)_3$ were obtained. The lattice constants of the solid solutions (Table 1 and Fig. 1) do not follow a linear law. The behavior is similar to that of the spessartite—yttrium-aluminum garnet system; (5) that is, the values of a_0 lie above the line joining the lattice constants of the end-members.

Grossularite itself has been studied in great detail (6) and synthesized by Yoder (7) and by Coes (8). Apparently, it has not been found possible to synthesize grossularite at atmospheric pressure or thus far from the dry components, although Yoder (6) has shown that it should be possible for it to form in this way.

TABLE 1. LATTICE CONSTANTS, $Ca_3Al_2(SiO_4)_3-Y_3Fe_2(FeO_4)_3$ SYSTEM

Mole % $Y_3Fe_2(FeO_4)_3$	Lattice constant, Å
0	11.851 (Ref. 7)
10	12.005
30	12.11
50	12.225
80	12.35
90	12.365
100	12.376

Attempts were made to crystallize the garnet phase out of 99, 98 and 95 mole % silicate (reactants) melts under the conditions described above; these were unsuccessful. Nevertheless, it is interesting that the presence of only 10 mole % of the yttrium-iron garnet constituents leads to the nucleation of the garnet phase.

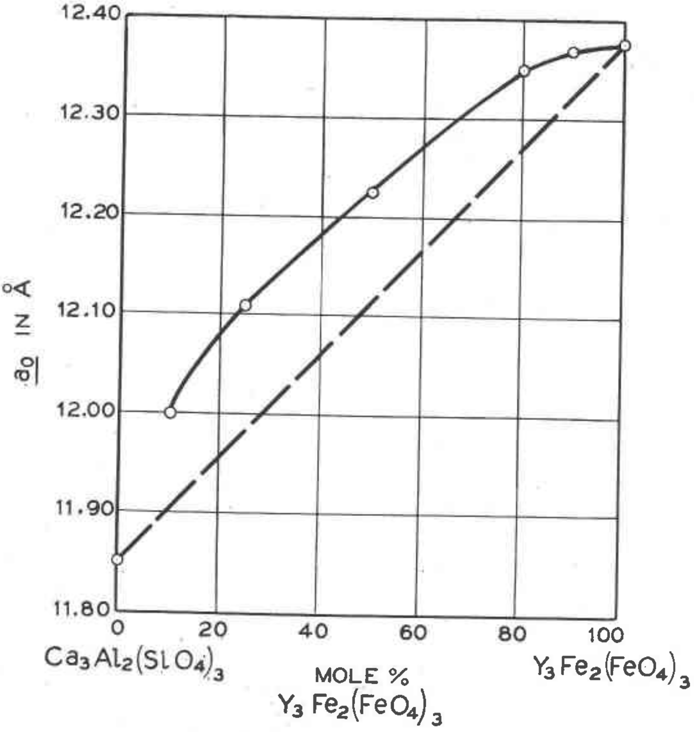

FIG. 1. Grossularite—yttrium-iron garnet system.

SPESSARTITE—YTTRIUM-IRON GARNET SYSTEM

The experiments in this system indicate that the two garnets, spessartite and yttrium-iron garnet, are not completely miscible.* There is indication that perhaps somewhat more than 20 mole % $Mn_3Al_2(SiO_4)_3$ will dissolve in $Y_3Fe_2(FeO_4)_3$. Samples containing 50 mole % (reactants) of each gave two or more phases. In all cases garnet phases appeared. Also present was a spinel-type phase, probably $Mn_xSi_yFe_{3-x-y}O_4$.

The samples containing 5, 10 and 90 mole % *yttrium-iron garnet* did not contain extraneous phases. However, a solution range was indicated in the photograph of the 10 mole % specimen. The sample containing 80 mole % $Y_3Fe_2(FeO_4)_3$ was mostly a garnet phase but the powder photograph indicated the presence of an extraneous phase. Thus the lattice constant, 12.229±0.003 Å, of the garnet phase is probably not representative of the 80 mole % solution.

TABLE 2. LATTICE CONSTANTS, $Mn_3Al_2(SiO_4)_3-Y_3Fe_2(FeO_4)_3$ SYSTEM

Mole % $Y_3Fe_2(FeO_4)_3$	Lattice constant, Å
0	11.621±0.004
5	11.68 ±0.01
10	11.73 ±0.01
90	12.34 ±0.01
100	12.376±0.004

The 20 mole % yttrium-iron garnet specimen contained a wide solid-solution range of garnet phases with lattice constant range of approximately 11.71–11.90 Å, indicating that the high end represents an approximately 20 mole % yttrium-iron garnet solid solution. The 50 mole % specimens gave various results; the largest lattice constant observed for a garnet phase in these was 12.02 Å, probably indicating a 30–40 mole % yttrium-iron garnet solid solution.

The lattice constants (Table 2) of the pure garnet phases are plotted in Fig. 2. In this system also, a linear composition vs. lattice constant law is not followed.

GROSSULARITE—GADOLINIUM-IRON GARNET SYSTEM

Because the sizes of the Y^{3+} and Gd^{3+} ions do not differ very much, it should be possible to form a series of solid solutions in the $Ca_3Al_2(SiO_4)_3$—$Gd_3Fe_2(FeO_4)_3$ system, at least as extensive as that of the $Ca_3Al_2(SiO_4)_3$—$Y_3Fe_2(FeO_4)_3$ system. We have actually studied only

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* That is, under the *conditions* of the experiments.

the ends of the system. A very good specimen of the solid solution containing 80 mole % $Gd_3Fe_2(FeO_4)_3$ has been made yielding a lattice constant of 12.402±0.003 Å. As expected, this result gives a point on the lattice constant vs. composition diagram (Fig. 3) lying significantly above the straight line joining the end-member lattice constants.

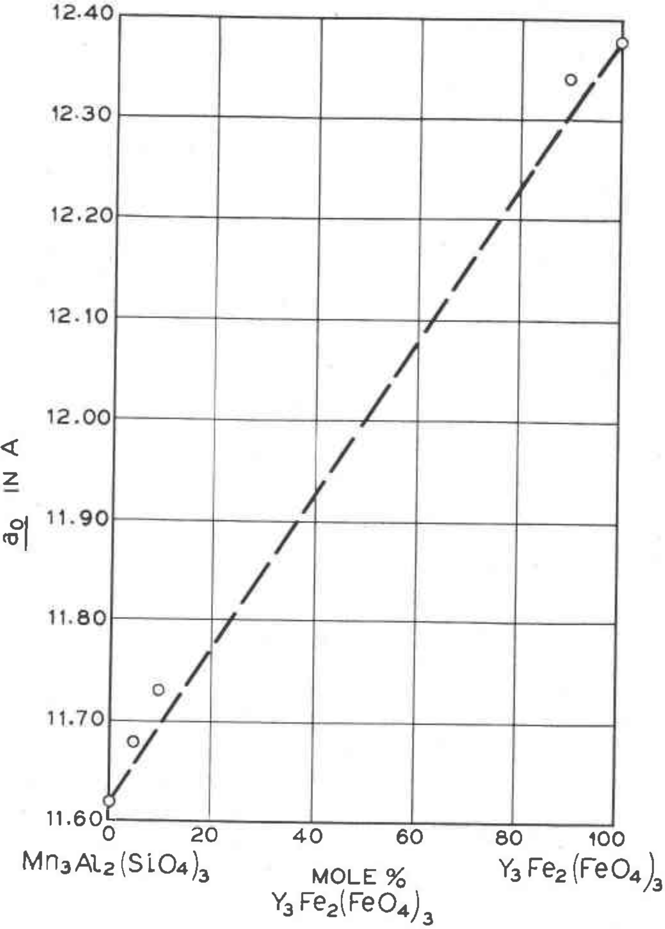

FIG. 2. Spessartite—yttrium-iron garnet system.

Attempts to prepare solid solutions containing 10 and 20 mole % $Gd_3Fe_2(FeO_4)_3$ in the same way as in the preparation of like solutions with $Y_3Fe_2(FeO_4)_3$ did not yield garnets. Thus, under these conditions, the series of solid solutions in the $Ca_3Al_2(SiO_4)_3$—$Gd_3Fe_2(FeO_4)_3$ system does not extend as far as in the $Ca_3Al_2(SiO_4)_3$—$Y_3Fe_2(FeO_4)_3$ system.

ADDITIONAL COMMENTS

The deviation of solid solutions of mixed valency garnets from a linear lattice constant law may be a consequence of ion distribution and of the disorder which is caused by the differences in ionic size and electrostatic effects arising from valency differences. A report is in preparation on the ionic distribution in some of these solid solutions as determined by means of magnetic susceptibility vs. temperature measurements (9).

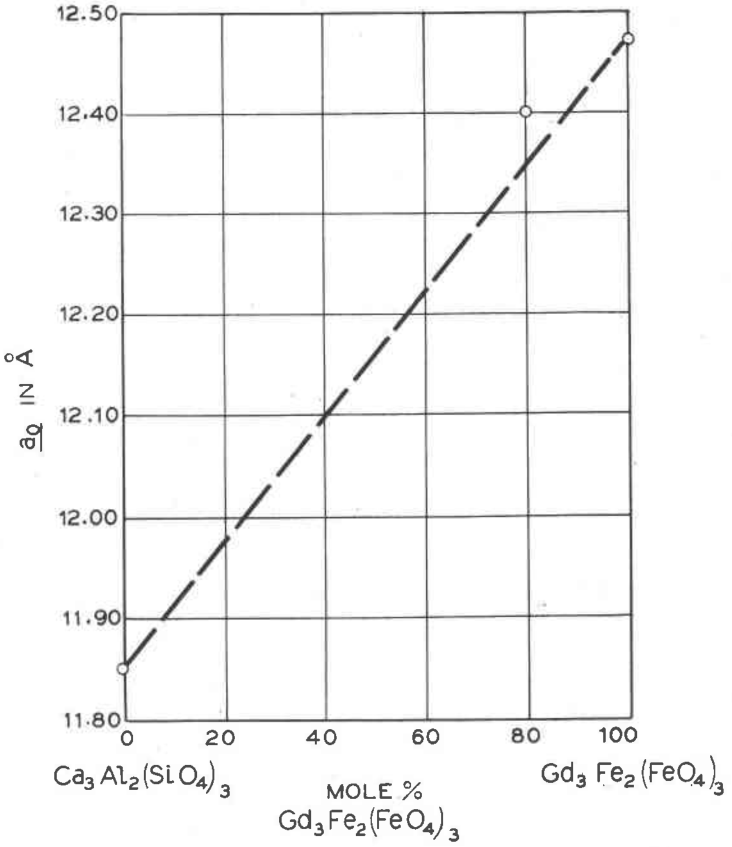

FIG. 3. Grossularite—gadolinium-iron garnet system (in part).

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