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Reprinted from The Journal of Chemical Physics, Vol. 45, No. 5, pp. 1821-1824, 1 September 1966

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Printed in U. S. A.

High-Pressure Decomposition of Synthetic Garnets

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(Received 31 January 1966)

The stability of synthetic garnets $\{Y_3\}[Fe_2](Fe_3)O_{12}$, $\{Y_3\}[Al_2](Al_3)O_{12}$, and $\{Y_3\}[Ga_2](Ga_3)O_{12}$ has been investigated at high pressures and high temperatures. Decomposition to the YXO_3 compound ($X=Fe$ or Al) with the perovskitelike structure and to the sesquioxide with the corundum structure has been found to occur in the former two garnets: $\{Y_3\}[X_2](X_3)O_{12}\rightarrow 3\ YXO_3+X_2O_3$, while in the case of yttrium–gallium garnet no breakdown was detected at pressures up to 44 kbar and 1000°C. The three garnets seem to behave differently at high pressure and high temperature. This appears to be related to the differences in the preference of the three cations for the tetrahedral site.

Results of preliminary studies of the effect of high pressure and high temperature on $Li_{0.5}Fe_{2.5}O_4$ are presented.

The geophysical implications of the decomposition under high pressure and high temperature of the garnet structure are discussed.

INTRODUCTION

SINCE the discovery of the synthetic ferrimagnetic garnets there has been a considerable interest in the crystal chemistry of the garnets. The garnet structure was first established for a large family of naturally occurring silicates with the general formula $A_3B_2(SiO_4)_3$, where A is Ca^{2+}, Mg^{2+}, or Fe^{2+} and B is Al^{3+}, Cr^{3+}, or Fe^{3+} as cubic, space group $Ia3d$, with eight molecules per unit cell.[1] The arrangement can be described as a three-dimensional array of oxygen polyhedra having edges and vertices in common. The centers of these polyhedra are occupied by the cations A^{2+}, B^{3+} and Si^{4+}; A at the center of a dodecahedron and having an eightfold coordination, B at the center of an octahedron and having a sixfold coordination, and Si^{4+} at the center of a tetrahedron and having a fourfold coordination. Each oxygen is shared among four cations, two A, one B, and one Si^{4+}. Since each oxygen is at the corner of only one tetrahedron, the SiO_4 tetrahedra are not linked directly to each other, which makes the garnets a unique family among the silicates.

Geller *et al.*[2] have shown that a large number of ions can enter the garnet structure. Following Geller's notation the general formula of these oxide compounds is written $\{A_3\}[B_2](C_3)O_{12}$ where $A=Ca^{2+}$, Y^{3+}, Sm^{3+} or any heavier rare earth, $B=Fe^{3+}$, Al^{3+}, Ga^{3+}, and $C=Fe^{3+}$, Al^{3+}, Ga^{3+}, Sn^{4+}, Ge^{4+}. The sum of the valence of A and C must be 6. The braces and the brackets and the parentheses, signify that the three cations are in different sites, namely dodecahedral, octahedral, and tetrahedral sites, respectively. A complete list of the synthetic garnets up to 1963 is given by Wyckoff in Ref. 3. Due to the extensive work that has been done on it $\{Y_3\}[Fe_2](Fe_3)O_{12}$, more commonly known as YIG, can be considered the prototype of this family of compounds.

Geller and Gilleo[4] refined the structure of $\{Y_3\}[Fe_2](Fe_3)O_{12}$ and pointed out that the structure of this compound represents inefficient packing. The x-ray density of yttrium–iron garnet is 5.17 g/cm³. If one iron per formula unit could be replaced by an yttrium ion with no structure change, the density of the resulting compound, $4YFeO_3$, would be 5.40 g/cm³. Since the density of $YFeO_3$ with the perovskitelike structure is 5.67 g/cm³ and no cation–oxygen distance in the garnet structure appears to be unduly long, the packing of the oxygen ions in the garnet structure appears to be inefficient.

Because of this circumstance we thought that it would be of interest to study the effect of high pressure and high temperature on yttrium–iron garnet. We have extended the investigation to two other garnets, namely $\{Y_3\}[Al_2](Al_3)O_{12}$ and $\{Y_3\}[Ga_2](Ga_3)O_{12}$. This paper reports the results of these studies and discusses some consequences arising therefrom.

EXPERIMENTAL

All the samples used were made by crushing and grinding single crystals of the garnet in a steel mortar. The resulting powder was thoroughly washed in a hot dilute solution of HNO_3 in water. The garnet crystals were grown from a flux consisting of PbO and B_2O_3. In every case the chemicals used were ultrapure materials which were prepared by the Whittier Research Laboratory of the American Potash and Chemical Corporation.

Pressure was generated in a piston–cylinder apparatus. The pressures are believed to be true within ±2 kbar. The furnace assembly used was the same as

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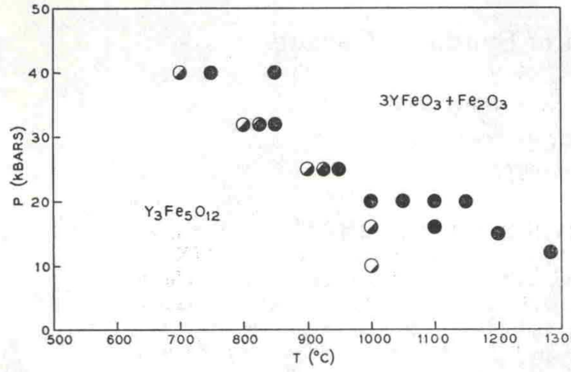

FIG. 1. The decomposition of yttrium–iron garnet at different pressures and temperatures.

the one described by Kennedy et al.[5] The powder was encapsulated in a cylindrical container of dimensions 2.6-mm i.d. by 5.5 mm high, made of tantalum. Pressure was applied to the sample first, then the temperature was brought to the desired value and held for a predetermined interval of time. A Pt/Pt–10% Rh thermocouple in intimate contact with the tantalum container monitored the sample temperature. The furnace power was then turned off quickly and the assembly allowed to cool to the ambient temperature before pressure was released. X-ray powder photographs of the quenched samples were taken using a Norelco camera of 114.6-mm diam and filtered Cr *Kα* radiation.

RESULTS AND DISCUSSION

In the first experiment $\{Y_3\}[Fe_2](Fe_3)O_{12}$ was subjected to a pressure of 40 kbar and 850°C. X-ray photographs of the quenched material revealed that yttrium–iron garnet had decomposed to $YFeO_3$ with the perovskitelike structure and Fe_2O_3 with the corundum structure. The decomposition is according to the formula

$$\{Y_3\}[Fe_2](Fe_3)O_{12}\rightarrow 3YFeO_3+Fe_2O_3.$$

Several runs at different pressures and temperatures were made and the results are shown in Fig. 1. The filled circles represent complete decomposition, while the partially filled circles represent the relative extent of decomposition. The degree of decomposition was visually estimated from the intensity ratio of the two strong lines, one of $\{Y_3\}[Fe_2](Fe_2)O_{12}$ and the other of $YFeO_3$, in the x-ray powder photograph. The effect of time on the decomposition was also investigated. For instance, at 20 kbar and 1000°C, samples were held for 15-min, $2\frac{1}{2}$-h, 5-h, and $16\frac{1}{2}$-h duration, with no appreciable difference in the relative proportions as judged from the x-ray photographs of the last three runs. In the experiments where decomposition occurred the temperature, as indicated by the thermocouple, tended to decrease, whereas in the experiments in which there was no decomposition the temperature remained steady. We interpret this as an indication that the breakdown reaction is endothermic. By subjecting a mixture of $YFeO_3$ and Fe_2O_3 in the molecular ratio of 3:1 to 40 kbar and 600°C for 5 h a small amount of garnet was found in the quenched material, proving that the reaction can be carried out from both sides and implying that one could establish the thermodynamic equilibrium curves in the (P, T) plane between the garnet structure and the perovskite and corundum structures. The average x-ray density of the products of decomposition is 5.57 g/cm^3 ($d_{YFeO_3}=5.67$ and $d_{Fe_2O_3}=5.28$ g/cm^3), as compared with the value of 5.17 g/cm^3 for yttrium–iron garnet. The perovskitelike structure of $YFeO_3$ and the corundum one of Fe_2O_3 are considered close-packed structures.

In the study of the effect of high pressure and high temperature on the $LiMO_2$ compounds (M = B, Al, Ga, In, Tl) a common trend was found, namely, an increase in the coordination number of the cations in going from the normal phase to the high-pressure one.[6] This trend is also observed for yttrium–iron garnet. The tendency of the cations to assume a higher coordination seems to be responsible for the breakdown of the garnet structure. In the latter structure three iron ions per molecule have a fourfold coordination, while the other two have a sixfold coordination, but in the decomposition products the coordination number of the iron ions is 6 in each compound, $YFeO_3$ and Fe_2O_3. The coordination number of the yttrium ions, however, remains the same at 8, both in the yttrium–iron garnet and in the perovskitelike compound. Consequently, the iron ions are those which attain the higher coordination and are therefore unstable under pressure in the tetrahedral sites.

Yttrium–aluminum garnet, as shown by the x-ray photographs of the quenched materials, undergoes a partial decomposition into $YAlO_3$ with the perovskitelike structure and Al_2O_3 with the corundum structure when subjected to 44 kbar and 1000°C for 16 h. Under similar treatment yttrium–gallium garnet does not break down.

These results have led us to conjecture that, while the inefficient packing of the oxygen ions is the cause of the breakdown of the garnet structure under pressure, the difference in the relative behavior among the three garnets under pressure is due to the difference in the preference of the Fe^{3+}, Ga^{3+}, and Al^{3+} ions for the tetrahedral site. To get some qualitative information about this relative preference of the three ions mentioned, we have determined the lowest pressure at which these garnets begin to decompose at a given temperature when held for a given time. These experi-

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ments are meaningful since the breakdown reaction is endothermic and proceeds at a favorable rate, although the possibility that the differences in behavior of the three garnets under pressure could be due to a kinetic effect cannot be ruled out completely.

In the case of yttrium–iron garnet a slight decomposition was observed when a sample was subjected to a pressure of 10 kbar at 1000°C for 5 h, as judged from the appearance of the strongest line of $YFeO_3$ ($d=2.69$ Å), but no detectable decomposition was observed at 8 kbar. The strongest line of $YAlO_3$ ($d=2.61$ Å) begins to appear when yttrium–aluminum garnet is subjected to 38 kbar at 1000°C for 5 h, but the film corresponding to 35 kbar did not show any detectable decomposition. In the case of yttrium–gallium garnet there was no detectable decomposition up to the highest pressure attainable in our apparatus, namely 44 kbar. This garnet may be expected to break down at higher pressures to $YGaO_3$ with the perovskitelike structure and Ga_2O_3 with the corundum structure, in analogy to the iron and aluminum counterparts. The values of the decomposition pressure indicate that gallium is the most stable ion in the tetrahedral sites of the garnet structure, iron the least stable, with aluminum intermediate. This order of stability cannot be explained in terms of a size effect. In Table I three different sets of ionic radii are listed. The values by Geller[7] were obtained from the perovskitelike compounds. It is clear from the table that Al^{3+} is always the smallest of the three ions, with Ga^{3+} and Fe^{3+} almost equal, no matter which set of ionic radii are considered. This unique behavior of the gallium ion is probably due to its electronic configuration.

It can be deduced from magnetic studies[2,8–10] on the gallium- or aluminum-substituted rare-earth–iron garnets that the Fe^{3+}, Al^{3+}, and Ga^{3+} ions have a different site preference for the tetrahedral site in the garnet structure. It increases on going from Fe^{3+} to Al^{3+} to Ga^{3+}. Thus, high-pressure and magnetic studies seem to indicate the same order of site preference.

In order to find out whether this behavior of the gallium ion is characteristic only of the garnet structure more data and studies of other systems are needed. For instance, we intend studying the effect of high pressure and high temperature on spinels such as $Li_{0.5}Fe_{2.5}O_4$, $Li_{0.5}Al_{2.5}O_4$, and $Li_{0.5}Ga_{2.5}O_4$. These compounds are known to have the inverse spinel structure, which consists of a cubic close-packed arrangement of the oxygen ions with the cations distributed over the tetrahedral and octahedral holes. In the ordered structure the trivalent ions occupy the tetrahedral and three quarters of the octahedral sites, while the lithium ions occupy the rest of the octahedral sites. Therefore, from the point of view of the cation coordination the spinel series is very similar to the garnet series.

TABLE I. Ionic radii (Å).

Ion	Pauling	Ahrens	Geller
Fe^{3+}	0.60	0.64	0.63
Al^{3+}	0.50	0.51	0.56
Ga^{3+}	0.62	0.62	0.61

Our preliminary studies on $Li_{0.5}Fe_{2.5}O_4$, subjected to 35 kbar at 1000°C have revealed that this compound breaks down into Fe_2O_3 with the corundum structure and $LiFeO_2$ with the disordered NaCl structure. Since $Li_{0.5}Fe_{2.5}O_4$ has a nearly close-packed structure, its decomposition is due only to the instability of the iron ions in the tetrahedral sites.

The decomposition of the garnet structure might be used to synthesize new compounds with the perovskitelike structure. For instance, $YGaO_3$ has never been prepared, even though the sizes of the yttrium and gallium ions are very favorable for this compound to crystallize with the perovskitelike structure. The tolerance factor for the perovskite structure ABO_3 is

$$t=(R_O+R_A)/\sqrt{2}(R_O+R_B)$$

(where R_O, R_A, and R_B are the ionic radii of the oxygen ion, of the cation A, and of the cation B, respectively). For $YGaO_3$ it falls between those of $YFeO_3$ and $YAlO_3$. One could make $YGaO_3$ and those $(RE)GaO_3$ which have not yet been prepared through the usual techniques, by decomposing the related garnets under pressure.

Transformations in silicate systems are of geophysical interest for they provide some clue to the understanding of the density anomalies in the earth's interior[11,12] and to test the various hypotheses. The naturally occurring garnets $(Mg, Fe, Ca)_3(Al, Fe)_2Si_3O_{12}$ are constituents of the upper mantle and what could happen to them under the combined action of high pressure and temperature is relevant to the density increase in the so-called transition zone. We believe that the mode of breakdown demonstrated for synthetic garnets under moderately high pressures and temperatures would serve as a model for the breakdown of natural garnets such as pyrope $\{Mg_3\}[Al_2](Si_3)O_{12}$ and almandite $\{Ca_3\}[Al_2](Si_3)O_{12}$, namely,

$$\{Fe, Mg, Ca,_3\}[Al_2](Si_3)O_{12} \rightarrow 3(Ca, Mg, Fe)SiO_3+Al_2O_3.$$

Since the silicon ions are very stable in the tetrahedral

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site, much higher pressure and temperature conditions than realizable in the laboratory at present are indicated for the decomposition of the natural garnets. However, the pressure and temperature conditions in the transition zone are very likely to be high enough for the breakdown of these garnets. Also, the presence of other mineral phases is likely to influence not only the breakdown pressure but also introduce other side reactions.

ACKNOWLEDGMENTS

It is a pleasure to thank E. M. Kelly and R. G. Maines for their technical assistance, and D. B. McWhan for helpful discussions.

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