

THE HYDROTHERMAL CRYSTALLIZATION OF YTTRIUM IRON GARNET AND YTTRIUM GALLIUM GARNET AND A PART OF THE CRYSTALLIZATION DIAGRAM Y_2O_3 - Fe_2O_3 - H_2O - Na_2CO_3

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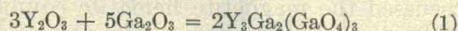
Yttrium iron garnet, $Y_3Fe_2(FeO_4)_3$, and yttrium gallium garnet, $Y_3Ga_2(GaO_4)_3$, have been crystallized under hydrothermal conditions. Yttrium gallium garnet was observed to transport in a temperature gradient and crystallized on a seed in 1 *M* Na_2CO_3 at 1500 atm. and 360°, when the starting materials were Ga_2O_3 and Y_2O_3 . The system Fe_2O_3 - Y_2O_3 - H_2O - Na_2CO_3 was investigated and yttrium iron garnet was found to form in optimum yields in from one to six days between 685 and 765° at 1330 atm. in approximately 3 *M* Na_2CO_3 . Slow decompositions of both garnet and Fe_2O_3 to Fe_3O_4 were observed to decrease the yields at longer times and a mechanism for this effect is proposed. Yttrium iron garnet was found to be congruently saturating and parts of the crystallization diagram were determined. Garnets as large as 2 mm. were prepared.

Introduction

A series of magnetic compounds with a garnet structure has recently been discovered^{1,2} and a method for the growth of single crystals of $R_3Fe_2(FeO_4)_3$ where R is Y, Sm, Er or Gd has been published.³ These crystals were grown from molten PbO and from PbO-PbF₂ mixtures where yttrium iron garnet (Y.I.G.) is incongruently saturating. Parts of the Fe_2O_3 -YFeO₃ phase diagram where yttrium iron garnet has been found to be incongruently melting and the PbO- Y_2O_3 - Fe_2O_3 phase diagram were determined.³ Since crystals free of molten salt inclusions and of Fe⁺⁺ grown at low temperature might present some advantages, hydrothermal crystallization suggested itself as a new means of preparation for these magnetic garnets.

Experimental

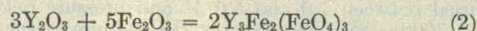
Attempts to form yttrium gallium garnet, $Y_3Ga_2(GaO_4)_3$ (Y.G.G.), according to the reaction



from reagent purity Y_2O_3 and Ga_2O_3 were made directly in steel vessels of the sort described by Walker and Buehler.⁴ Identification of phases was made by means of microscopic examination and X-ray powder pictures. Chromium radiation was used with a camera in which the sample holder was a wedge. This arrangement was found better capable of detecting small quantities of one phase in the presence of

another than the conventional capillary or filamentary sample holder.

Preliminary experiments showed a need for the careful determination of parts of several hydrothermal systems in which yttrium iron garnet could be formed by the reaction



in a hydrothermal vessel which did not present metallic iron or any other reducing agents to the solution. Weighed quantities of the component oxides, ground and mixed as nearly as possible to a uniform particle size in an agate mortar, were placed in gold capsules one end of which had been previously welded on a microarc welder. The capsule dimensions were 2.50 inch length \times 0.160 inch inside diameter \times 0.005 inch wall thickness. The capsule was filled by means of a microburet to a predetermined fraction of its free volume with the appropriate solvent. The per cent. of fill was calculated from Kennedy's⁵ *p-v-t* data for pure water since the pressures in a hydrothermal solution of the sort studied in this work would not be expected to be greatly different. The capsules were placed in individual 0.25 inch internal diameter \times 10 inch internal length cold-seat-cone-closure vessels.⁶ The vessels were connected to Bourdon gauges and an air driven intensifier,⁷ heated by kanthal wound tube furnaces and so arranged that they could be individually brought to any predetermined temperature from 100 to 800° and any pressure up to pressures in excess of 2000 atm. The pressure transmitting fluid outside the capsules was water. Provision was made for rapid quenching by means of an air blast at the conclusion of a run. Reliability in the pressures reported is probably no better than $\pm 2\%$, and in the temperature no better than $\pm 3^\circ$.

Parts of the system Ga_2O_3 - Y_2O_3 - H_2O - Na_2CO_3 were investigated in an effort to form the gallium garnet, Y_3Ga_2 -

(1) F. Bertaut and F. Forrat, *Compt. rend. Acad. Sci. (Paris)*, **242**, 382 (1956).

(2) S. Geller and M. A. Gilleo, *Acta Cryst.*, **10**, 239 (1957).

(3) J. W. Nielsen and E. F. Dearborn, *J. Phys. Chem. Solids*, **5**, [3] 202 (1958).

(4) A. C. Walker and E. Buehler, *Sci. Monthly*, **69**, 148 (1949).

(5) G. C. Kennedy, *Am. J. Sci.*, **248**, 540 (1950).

(6) Obtained from Tempress, Inc., State College, Pa.

(7) Manufactured by Sprague Engineering Corp., P. O. Box 121, Gardena, Calif.

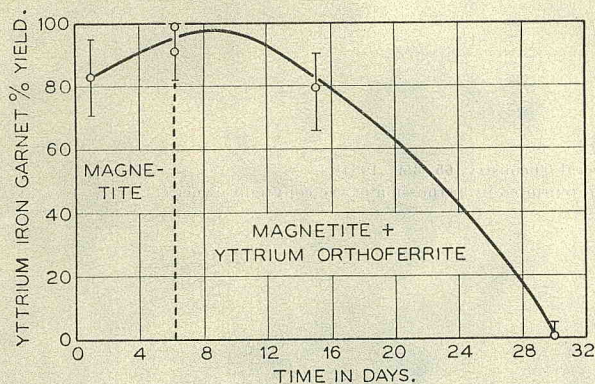


Fig. 1.—Yttrium iron garnet yield vs. time at 725°.

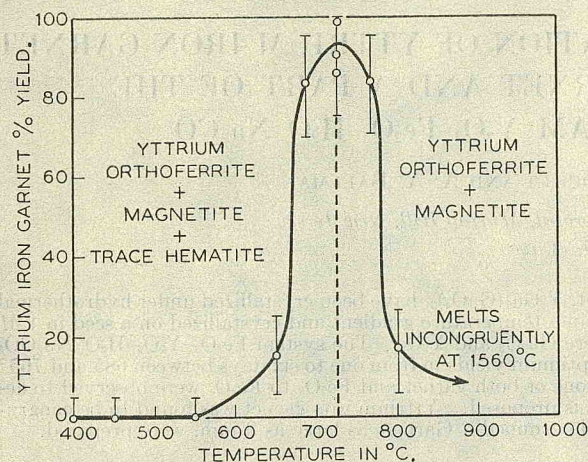


Fig. 2.—Yttrium iron garnet yield vs. temperature one to six days.

(GaO_4). In all cases the ratio $\text{Ga}_2\text{O}_3/\text{Y}_2\text{O}_3$ was 5/3 (the stoichiometry of the garnet). Temperatures from 360 to 500° were investigated; sodium carbonate concentrations varied between 1.0 and 5.0 *M* and pressure between 1000 and 3000 atm. In all cases the gallium garnet was the principal phase formed. Time of runs varied between one day and several weeks. The only contaminating phase formed, which was present in very small quantities in a few runs, was gallium oxyhydroxide, GaOOH .

The gallium garnet was observed to transport in a temperature gradient and deposit on a seed as evidenced by the formation of growth steps on a smoothly polished seed easily visible under 50 \times magnification. Conditions where growth was observed were: crystallization temperature 360°, temperature difference (Δt) between dissolving and growth zone 40°, nutrient $\text{Ga}_2\text{O}_3/\text{Y}_2\text{O}_3$ ratio 5/3, pressure about 1500 atm. and solvent 1 *M* Na_2CO_3 .

In gold capsules, parts of the system $\text{Fe}_2\text{O}_3\text{-Y}_2\text{O}_3\text{-H}_2\text{O-Na}_2\text{CO}_3$ were investigated. More than one hundred runs were made so that only data finally shown to be pertinent to the observed transitions will be mentioned here. Figure 1 summarizes certain runs important to the deduction of equilibrium time at a temperature of 725°. The mole ratio $\text{Fe}_2\text{O}_3/\text{Y}_2\text{O}_3$ was 5/3. Unless otherwise mentioned, the weight fraction of Na_2CO_3 was held constant at 0.228 which in most cases corresponded to a solution about 3.1 *M* in Na_2CO_3 .

The height of the bars on the points of Figs. 1 and 2 gives some indication of the precision in the estimation of the abundance of phases. Phase abundances were estimated visually from the intensity of the X-ray powder diagrams. Standards of varying percentages of magnetite and yttrium iron garnet were used for comparison where appropriate. It was found that as little as 5% magnetite could be detected in the presence of garnet. The runs were made in gold tubes at a pressure of 1330 atm. As can be seen six days or a time slightly greater is sufficient for the complete conversion to garnet and the garnet yield varies little be-

tween one and six days. The only phase detected in addition to garnet up to six days was magnetite. At 30 and 15 days the products were magnetite and yttrium orthoferrite, YFeO_3 . Crystalline flux grown garnet decomposed similarly in 30 days. A precession picture of a representative single crystal of the magnetite confirmed that it was not $\gamma\text{-Fe}_2\text{O}_3$ whose X-ray powder pattern is nearly identical to that of magnetite.

Figure 2 shows the dependence of garnet yield on temperature for reaction times of one to six days. The conditions of the runs of Fig. 2 were generally similar to those of Fig. 1. As can be seen the optimum yield of garnet occurred near 725°. The phases in addition to the garnet which were found below 725° were magnetite, yttrium orthoferrite and hematite. Above 725° magnetite and yttrium orthoferrite were found to be the coexisting phases. In general, the yield of magnetite increased with increasing temperature.

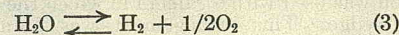
The effect of variation in the $\text{Fe}_2\text{O}_3/\text{Y}_2\text{O}_3$ ratio was studied under the following conditions: temperature, 725°; pressure, 1330 atm.; $N_{\text{Na}_2\text{CO}_3}$ 0.228; time of run, one to six days, and $N_{\text{Fe}_2\text{O}_3} + N_{\text{Y}_2\text{O}_3} = \text{constant} = 0.128$. Under these conditions small quantities of magnetite were observed to form at all $\text{Fe}_2\text{O}_3/\text{Y}_2\text{O}_3$ ratios. The garnet stability region was extremely narrow, when the $\text{Fe}_2\text{O}_3/\text{Y}_2\text{O}_3$ ratio was 5/3 garnet and magnetite formed; however, when the ratio was increased by two mole per cent. hematite, garnet and magnetite formed and when the ratio was decreased by two mole per cent. yttrium orthoferrite, garnet and magnetite formed.

Yttrium iron garnet crystals as large as 1 to 2.5 mm. have been prepared when the ratio was 5/3. The habit is similar to that sometimes observed of molten PbO grown crystals⁸ and in natural garnets, that is dodecahedral showing (110) faces. Lattice constants agreed with those measured on PbO grown and ceramic garnets. The crystals were ordinarily black but became green when ground to a fine powder and were magnetic with a Curie temperature in the neighborhood of 272° in agreement with the properties of PbO grown crystals. No inclusions of other phases were visible upon microscopic examination of ground spheres. Because of their color YFeO_3 and Fe_2O_3 would be especially easy to detect in such an examination but magnetite might escape notice.

Discussion

Yttrium gallium garnet was found to be congruently saturating under all conditions investigated. The small amounts of GaOOH found in several runs probably formed when the vessels were cooled since Hill, Roy and Osborn⁸ have shown that in the system $\text{Ga}_2\text{O}_3\text{-H}_2\text{O}$ GaOOH is stable only below about 300° from 1 to 2000 atm. The pressure-temperature dependence of a similar equilibrium $\text{Al}_2\text{O}_3\text{-AlOOH}$ in the system $\text{Al}_2\text{O}_3\text{-H}_2\text{O}$ has been shown to be little influenced by the presence of low concentrations of Na_2CO_3 .⁹ Yttrium gallium garnet has been shown to dissolve, transport and recrystallize on a seed crystal under conditions where it is congruently saturating.

At 1560°, Y.I.G. melts incongruently into orthoferrite and an Fe_2O_3 rich liquid.³ Eugster¹⁰ has discussed the magnetite-hematite equilibrium and shown that in the absence of water hematite will be stable at ambient pressure over the temperature range of this work. However, in the presence of water under hydrothermal conditions the dissociation



(8) V. G. Hill, R. Roy and E. F. Osborn, *J. Am. Ceram. Soc.*, **35**, [6] 136 (1952).

(9) R. A. Laudise and A. A. Ballman, *J. Am. Chem. Soc.*, **80**, 2655 (1958).

(10) H. P. Eugster, "Researches in Geochemistry," edited by P. H. Abelson, John Wiley and Sons, New York, N. Y., 1959, p. 397.

tion must be considered. Wagman, *et al.*¹¹ have tabulated K_p for reaction 3 at a total pressure of one atmosphere for several temperatures, Eugster¹⁰ has interpolated values from these results, and Baker¹² has calculated the pressure dependence of the dissociation. These data show that in contact with an excess of pure water at the pressure of our experiments hematite would be the stable solid phase at temperature below 1050°.

Yet, as Fig. 1 shows in the system Y_2O_3 - Fe_2O_3 - H_2O - Na_2CO_3 , slow decomposition of both garnet and hematite to magnetite does occur. The data of Fig. 1 were obtained in gold tubes, since the diffusivity of hydrogen in platinum could result in the gradual loss of hydrogen formed in the capsule or the gradual incursion of hydrogen into the capsule from corrosion reactions with the wall of the vessel. The weight fraction of solids was low, so that the system was probably not buffered with respect to solid. Four runs were made at 30 days to decrease the possibility that improper welds in the gold could have allowed hydrogen to enter. Identical results were obtained in all these runs and it was shown that flux grown crystalline garnet decomposed in the same way. Preliminary runs were made in gold tubes in the systems Fe_2O_3 - Fe_3O_4 - H_2O , Fe_2O_3 - Fe_3O_4 - H_2O - Na_2CO_3 and Fe_2O_3 - Fe_3O_4 - H_2O - $NaOH$ at 400° and 1330 atm. The duration of the runs was 30 days and 3 *M* carbonate and hydroxide solutions were used. In all three systems when the starting material was either Fe_2O_3 or Fe_3O_4 , the products were mixtures of Fe_2O_3 and Fe_3O_4 . The yield of hematite was somewhat higher when hematite was the starting material and was perhaps higher in the absence of base.

The preliminary data on the magnetite-hematite equilibrium discussed in the preceding paragraph suggest that both the magnetite-hematite equilibrium and equation 3 may be *pH* dependent or that there may be a measurable diffusivity of H_2 through gold at the conditions of these experiments. It should be pointed out that the equilibrium oxygen pressure over garnet might be markedly different from that over hematite.

On first sight the extremely long times necessary to achieve equilibrium are surprising. However, in the system Mn - O - H_2O at high water pressures, it has been noted that P_{O_2} near a solid phase whose oxidation state is undergoing change may be quite different from P_{O_2} in the remainder of the system.¹³ The mean free path of the oxygen molecules is so reduced that mixing times in such a system may be quite long.¹³ Consequently, one might expect that the decomposition of garnet might proceed slowly and an equilibrium time of the order of 30 days is not inordinately long.

Thus we can see that the ratio Fe^{++}/Fe^{+++} will be important in effecting the formation of garnet and that the time for optimum garnet formation is

(11) D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Spitzer and F. D. Rossini, *J. Res. Natl. Bur. Standards*, **34**, 143 (1945).

(12) D. R. Baker, private communication.

(13) C. Klingsberg and R. Roy, *Am. Mineral.*, **44**, 819 (1959).

probably of the order of a few days. Certainly, exact replication of optimum time for a heterogeneous reaction of this sort will be hard to achieve since it will depend on particle size, tube geometry, slight temperature and pressure changes and other variables which are hard to control. However, in view of the size of the heterogeneously nucleated Y.I.G., true recrystallization and not sintering was responsible for garnet growth.

The formation of $YFeO_3$, magnetite and hematite at temperatures below 725° as shown in Fig. 2 can be explained on the assumption that garnet formation proceeds through orthoferrite and that unreacted hematite decomposes to magnetite.

The formation of magnetite at times below six days as shown in Fig. 1 can be explained by the reduction of unreacted Fe_2O_3 and the fact that the unreacted Y_2O_3 may have a high enough solubility to remain in solution. The formation of magnetite and orthoferrite at temperatures above 725° as shown in Fig. 2 and the formation of magnetite and orthoferrite at 30 days as shown in Fig. 1 is not surprising in view of the fact that garnet melts incongruently into orthoferrite and an Fe_2O_3 rich liquid at 1560°, if we assume that water may lower the liquidus temperature substantially.

Small quantities of white phases found at the higher temperatures and occasionally under other conditions gave powder pictures which were identifiable as $YOOH$ or were phases which could not be indexed. Both the $YOOH$ and the unidentified phases were shown by spectrochemical analysis to contain principally yttrium. $YOOH$ has been recently identified by Shafer and Roy¹⁴ in the system Y_2O_3 - H_2O . $YOOH$ was shown by Shafer and Roy to be stable only below 650° at 1330 atm. and may have formed in the system described here during the cooling of the vessels, especially since Shafer and Roy report that $YOOH$ is best formed from the high temperature side in the system. The unidentified phases are probably also oxyhydroxides or basic carbonates of yttrium which formed during cooling. It is interesting to note that in the system Y_2O_3 - H_2O yttrium oxide was found to be stable only above 650° at 1330 atm. As Fig. 2 shows, no garnet was formed below 650° although in preliminary longer term runs in the presence of metallic iron, garnet was formed at temperatures as low as 400°. Perhaps a change in the yttrium containing species at 650° greatly increases the velocity of garnet formation.

The effect of the variation of the Fe_2O_3/Y_2O_3 ratio is as would be expected even for a slightly soluble but congruently saturating substance where decomposition to magnetite can take place.

Acknowledgments.—The authors would like to thank G. T. Kohman for advice and encouragement throughout the work. Mrs. M. H. Read is especially to be thanked for identification of phases by X-ray diffraction as is J. W. Nielsen for many interesting discussions of the problems of garnet synthesis. S. Geller is especially to be thanked for advice in the precession camera work.

(14) M. W. Shafer and R. Roy, *J. Am. Ceram. Soc.*, **42**, 563 (1959).