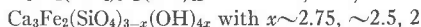
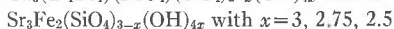
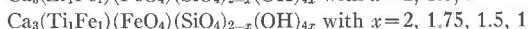
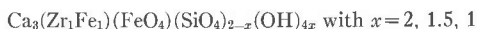


NEW SYNTHETIC HYDROGARNETS

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ABSTRACT

Microcrystalline hydrogarnets in the following series were synthesized by the aging of precipitated gels at 85°–105°C and 1 atm in NaOH solutions of pH 13.5:



We have similarly synthesized the hydrogarnets $\text{Sr}_3\text{Sc}_2(\text{OH})_{12}$, $\text{Sr}_3\text{In}_2(\text{OH})_{12}$, $\text{Sr}_3(\text{Sc}_1\text{Fe}_1)(\text{OH})_{12}$, $\text{Sr}_3(\text{Sc}_1\text{In}_1)(\text{OH})_{12}$, $\text{Sr}_3(\text{In}_1\text{Fe}_1)(\text{OH})_{12}$ and $\text{Sr}_3\text{Sc}_2(\text{SiO}_4)_{0.25}(\text{OH})_{11}$. The unit-cell dimension and, in some instances, the index of refraction is given for the preparations. Efforts to synthesize $\text{Ca}_3\text{Fe}_2(\text{OH})_{12}$ and the Ba_3Fe_2 , Pb_3Fe_2 , Sr_3TiFe and Sr_3ZrFe analogues of the Sr_3Fe_2 hydrogarnets failed.

In connection with the preparation of gels to be used for the synthesis of anhydrous garnets containing Zr or Ti, it was established that precipitates deficient in Si could be obtained from water solutions at temperatures of 85°–105°C that gave the X-ray pattern of hydrogarnet. The present note describes various hydrogarnets containing Ca or Sr in the 8-coordinated position and Zr, Ti, Fe, Sc or In in the 6-coordinated position of the garnet structure. The reagents employed in the syntheses were 0.2M solutions of calcium nitrate, strontium nitrate, ferric chloride, zirconyl chloride, titanyl chloride (dissolved in 4M HCl) and sodium metasilicate, and a 7M solution of NaOH. In the preparation of hydrogarnets containing Sc and In, solutions of the oxides In_2O_3 (99.99 percent pure) and Sc_2O_3 (99.99 percent pure) in dilute HCl were employed. In the syntheses, 1 millimol equivalent of the reagents needed for the garnet composition desired were placed in a 250 ml Pyrex beaker and appropriate amounts of HNO_3 were added if needed to keep the solution clear. The solution was heated to boiling, approximately 105°C, and was then adjusted to pH 13.5 by the addition of NaOH. After boiling for 10 minutes, the contents of the beaker were transferred to a polyethylene beaker of 400 ml capacity, to avoid contamination by Si from the glass, and the precipitate was heated in its solution for 24–72 hours at 85°. The Sr hydrogarnets containing Sc and In were precipitated at pH 14 and were held at 105°C for 20 hours in Teflon beakers. Nucleation of the hydrogarnet generally began within a few minutes during the initial boiling with the formation of a bulky precipitate. The precipitates gradually

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coarsened and settled out. They were then centrifuged, without washing, and were dried in air at 120°.

All of the products gave good X-ray powder diffractometer patterns without significant line broadening. Indexed powder data for the Si-free end-compositions are given in Table 2. The values of a computed by averaging the values obtained from the 400, 420, 422, 521, 611, 640, 642 and 800 reflections are given in Table 1. The variation in a as a function of composition of the Zr and Ti hydrogarnets is shown in Figure 1.

TABLE 1. SYNTHESSES OF HYDROGARNETS

| No. | Composition | $a_0(\text{Å})$ | n |
|-----|---|-----------------------------|--------|
| 1. | $\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_{0.25}(\text{OH})_{11}$ | 12.60 | ~1.69 |
| 2. | $\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_{0.5}(\text{OH})_{10}$ | 12.56 | |
| 3. | $\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_1(\text{OH})_8$ | 12.52 | |
| 4. | $\text{Ca}_3(\text{Zr}_1\text{Fe}_1)(\text{FeO}_4)(\text{OH})_8$ | 12.72 | |
| 5. | $\text{Ca}_3(\text{Zr}_1\text{Fe}_1)(\text{FeO}_4)(\text{SiO}_4)_{0.5}(\text{OH})_6$ | 12.64 | ~1.755 |
| 6. | $\text{Ca}_3(\text{Zr}_1\text{Fe}_1)(\text{FeO}_4)(\text{SiO}_4)(\text{OH})_4$ | 12.58 | |
| 7. | $\text{Ca}_3(\text{Ti}_1\text{Fe}_1)_2(\text{FeO}_4)(\text{OH})_8$ | 12.68 | ~1.75 |
| 8. | $\text{Ca}_3(\text{Ti}_1\text{Fe}_1)(\text{FeO}_4)(\text{SiO}_4)_{0.25}(\text{OH})_7$ | ~12.63 | |
| 9. | $\text{Ca}_3(\text{Ti}_1\text{Fe}_1)(\text{FeO}_4)(\text{SiO}_4)_{0.5}(\text{OH})_6$ | 12.55 | |
| 10. | $\text{Ca}_3(\text{Ti}_1\text{Fe}_1)(\text{FeO}_4)(\text{SiO}_4)(\text{OH})_4$ | 12.45 | |
| 11. | $\text{Ca}_3(\text{Ti}_{.5}\text{Fe}_{1.5})_2(\text{FeO}_4)_{0.5}(\text{OH})_{10}$ | 12.65 | |
| 12. | $\text{Sr}_3\text{Fe}_2(\text{OH})_{12}$ | 13.23 | ~1.68 |
| 13. | $\text{Sr}_3\text{Fe}_2(\text{SiO}_4)_{0.25}(\text{OH})_{11}$ | 13.16 | |
| 14. | $\text{Sr}_3\text{Fe}_2(\text{SiO}_4)_{0.5}(\text{OH})_{10}$ | 13.02 | |
| 15. | $\text{Sr}_3\text{Sc}_2(\text{OH})_{12}$ | 13.39 | |
| 16. | $\text{SrSc}_2(\text{SiO}_4)_{0.25}(\text{OH})_{11}$ | ~13.39 | |
| 17. | $\text{SrSc}_2(\text{SiO}_4)_{0.50}(\text{OH})_{10}$ | 13.39 and 13.28 (two phase) | |
| 18. | $\text{SrSc}_2(\text{SiO}_4)_1(\text{OH})_8$ | 13.38 and 13.26 (two phase) | |
| 19. | $\text{SrSc}_2(\text{SiO}_4)_2(\text{OH})_4$ | — | |
| 20. | $\text{Sr}_3\text{In}_2(\text{OH})_{12}$ | 13.53 | |
| 21. | $\text{Sr}_3\text{InFe}(\text{OH})_{12}$ | 13.39 | |
| 22. | $\text{Sr}_3\text{ScFe}(\text{OH})_{12}$ | 13.31 | |
| 23. | $\text{Sr}_3\text{ScIn}(\text{OH})_{12}$ | 13.46 | |

Under the microscope, runs 5 and 7 were found to consist of distinct crystals although the crystal form could not be clearly made out. Run 7 contained a proportion of skeletonized crystals rather similar to those figured by Flint, McMurdie and Wells (1941, Fig. 3) in $\text{Ca}_3(\text{Fe},\text{Al})_2(\text{OH})_{12}$. The remaining runs were either microcrystalline or submicrocrystalline. The particle size in general decreased with increasing content of Si. In only a few instances could reliable measurements be made of the index of refraction (Table 1). The runs of the Sr_3Fe_2 garnets often

contained very small amounts of hematite and of strontium carbonate (?), the latter probably produced by CO_2 from the atmosphere, and trace amounts of hematite and of unidentified products were present in some of the other runs.

None of the solid products were analyzed chemically, although the residual solutions were tested to ascertain if the precipitation of the cations was quantitative. The compositions attributed to our products are based on the formulated compositions of runs in which solid by-products

TABLE 2. X-RAY POWDER DATA FOR SYNTHETIC HYDROGARNETS.
CU RADIATION, NI FILTER, SI INTERNAL STANDARD,
IN ANGSTROM UNITS. RELATIVE INTENSITIES IN
ARBITRARY CHART UNITS

| <i>hkl</i> | $\text{Ca}_3(\text{Zr}_1\text{Fe}_1)$ $(\text{FeO}_4)(\text{OH})_8$ | | $\text{Ca}_3(\text{Ti}_1\text{Fe}_1)$ $(\text{FeO}_4)(\text{OH})_8$ | | $\text{Ca}_3(\text{Ti}_{1.5}\text{Fe}_{1.5})$ $(\text{FeO}_4)_{0.5}(\text{OH})_{10}$ | | $\text{Sr}_3\text{Li}_{12}(\text{OH})_{10}$ | | $\text{Sr}_3\text{Sc}_2(\text{OH})_{12}$ | | $\text{Sr}_3\text{Fe}_2(\text{OH})_{12}$ | |
|------------|--|----------|--|----------|---|----------|---|----------|--|----------|--|----------|
| | <i>d</i> | <i>I</i> | <i>d</i> | <i>I</i> | <i>d</i> | <i>I</i> | <i>d</i> | <i>I</i> | <i>d</i> | <i>I</i> | <i>d</i> | <i>I</i> |
| 211 | 5.20 | 20 | 5.20 | 40 | 5.17 | 20 | 5.521 | 60 | 5.507 | 100 | 5.39 | 80 |
| 220 | 4.50 | 100 | 4.49 | 100 | 4.48 | 70 | 4.771 | 95 | 4.731 | 5 | 4.67 | 25 |
| 321 | 3.40 | 10 | 3.40 | 10 | 3.38 | 10 | 3.610 | 40 | 3.584 | 75 | 3.53 | 80 |
| 400 | 3.180 | 90 | 3.171 | 80 | 3.162 | 80 | 3.376 | 80 | 3.351 | 60 | 3.300 | 60 |
| 420 | 2.845 | 50 | 2.841 | 60 | 2.831 | 100 | 3.021 | 50 | 2.999 | 100 | 2.955 | 100 |
| 332 | 2.699 | 10 | 2.699 | 10 | 2.699 | 5 | — | — | 2.852 | 5 | 2.812 | 5 |
| 422 | 2.598 | 95 | 2.592 | 50 | 2.584 | 90 | 2.758 | 100 | 2.733 | 50 | 2.695 | 60 |
| 510 | 2.496 | 5 | 2.489 | 10 | 2.481 | 20 | 2.642 | 5 | 2.627 | 20 | 2.591 | 15 |
| 521 | 2.319 | 50 | 2.319 | 40 | 2.309 | 60 | 2.464 | 30 | 2.445 | 70 | 2.413 | 65 |
| 611 | 2.064 | 30 | 2.062 | 30 | 2.054 | 50 | 2.245 | 20 | 2.172 | 60 | 2.144 | 65 |
| 620 | 2.012 | 20 | 2.009 | 10 | 2.003 | 15 | 2.137 | 15 | — | — | 2.083 | 3 |
| 444 | — | — | — | — | — | — | — | — | 1.936 | 10 | 1.908 | 10 |
| 640 | 1.766 | 30 | 1.762 | 15 | 1.755 | 30 | 1.876 | 15 | 1.895 | 40 | 1.882 | 35 |
| 552 | 1.732 | 10 | 1.729 | 10 | 1.722 | 5 | 1.839 | 5 | 1.823 | 30 | 1.798 | 30 |
| 642 | 1.703 | 50 | 1.697 | 50 | 1.691 | 50 | 1.807 | 60 | 1.788 | 50 | 1.766 | 50 |
| 651 | — | — | — | — | 1.608 | 5 | 1.718 | 10 | 1.702 | 20 | 1.678 | 20 |
| 800 | 1.594 | 10 | 1.590 | 10 | 1.583 | 10 | 1.691 | 10 | 1.673 | 15 | 1.652 | 20 |
| 822 | — | — | — | — | — | — | 1.594 | 8 | — | — | — | — |
| 840 | — | — | — | — | — | — | 1.511 | 10 | 1.498 | 10 | 1.478 | 20 |
| 842 | — | — | — | — | — | 7 | 1.475 | 5 | 1.463 | 8 | 1.442 | 15 |
| 921 | — | — | — | — | — | — | 1.458 | 5 | 1.446 | 5 | 1.425 | 10 |
| 664 | — | — | — | — | — | — | 1.441 | 8 | 1.426 | 3 | — | — |

either were not formed or were negligible in amount on the basis of optical and X-ray examination.

Our hydrogarnets containing Zr in general were less well crystallized, judging from the X-ray patterns and optical study, than were the analogous Ti hydrogarnets. The anhydrous garnets $\text{Ca}_3\text{Zr}_2(\text{FeO}_4)_2(\text{SiO}_4)$ and $\text{Ca}_3\text{Ti}_2(\text{FeO}_4)_2(\text{SiO}_4)$ have been synthesized by dry sintering at 1050°C (Ito and Frondel, 1967). Efforts to prepare hydrogarnets extending from these compositions failed. The experimental products were very poorly crystallized, with unit-cell dimensions identical with those of the com-

positions listed in Table 1 containing (Zr_1Fe_1) or (Ti_1Fe_1) instead of Zr_2 or Ti_2 in the 6-coordinated position. We did obtain, however, a hydrogarnet containing $(Ti_{0.5}Fe_{1.50})$ in this position.

The existence of an isometric compound $Sr_3Al_2(OH)_{12}$ with a $13.04 \pm .01$ A was reported by Brandenberger (1933) but without details of the preparation. Flint *et al.* (1941) failed to obtain either $Sr_3Al_2(OH)_{12}$ or the Ba analogue thereof by the slow addition of aluminum chloride solution to a boiling solution of Sr or Ba hydroxide or by the reaction of glasses of the

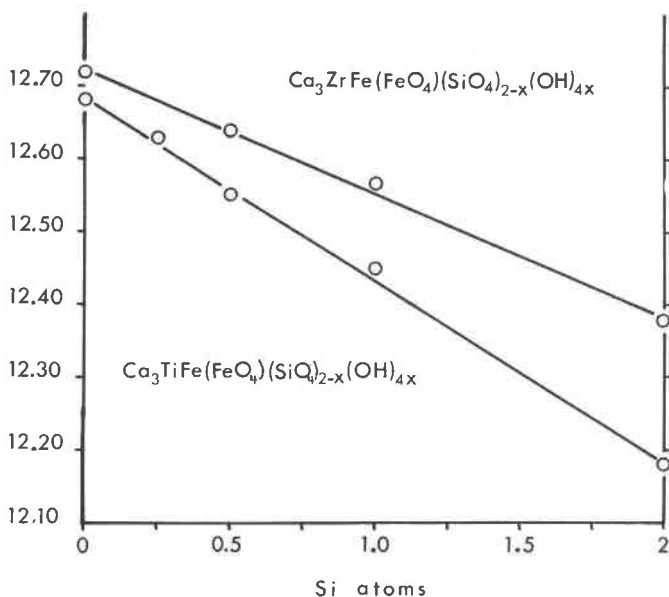


FIG. 1. Variation in a as a function of composition. Values of the end-compositions $Ca_3(Zr_1Fe_1)(Fe_1Si_2O_{12}) = 12.38$ A and $Ca_3(Ti_1Fe_1)(Fe_1Si_2O_{12}) = 12.18$ A from Ito and Frondel (1966).

appropriate composition with H_2O at 500° and 400 atm for periods of 1 to 3 weeks. Efforts to prepare Ba_3Fe_2 , Pb_3Fe_2 , Sr_3TiFe and Sr_3ZrFe hydrogarnets also failed. However, preparations of the composition $Sr_3Fe_2(OH)_{12}$, $Sr_3In_2(OH)_{12}$ and $Sr_3Sc_2(OH)_{12}$ were homogeneous. Complete solid solutions probably exist between these compositions since homogeneous phases with intermediate cell dimensions were obtained in which the 6-coordinated positions were occupied by (In_1Fe_1) , (Sc_1Fe_1) and (Sc_1In_1) . It did not prove possible to obtain homogeneous preparations of the composition $Sr_3Sc_2(SiO_4)_{2-x}(OH)_{4x}$ with $x=0.5, 1$ or 2 ; the latter material was very poorly crystallized.

Flint *et al* (1941) found that it was difficult to prepare $\text{Ca}_3\text{Fe}_2(\text{OH})_{12}$ free from Si, and comment that the phase appears to be unstable when Si is not present. Our method also failed to produce the end-composition $\text{Ca}_3\text{Fe}_2(\text{OH})_{12}$, although phases with $x=2, 2.5$ and 2.75 as indicated by the ratios of the starting gels were obtained. The unit-cell dimensions of the two latter phases are somewhat smaller than those observed by Flint *et al* (1941) for compositions with $x=2.62, 2.58$ and 2.46 and suggest that our preparations may be higher in Si than indicated. Our preparation with $x=2$, however, falls on a straight line connecting the value of a for $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$ and that calculated by Flint *et al* (1941) for hypothetical $\text{Ca}_3\text{Fe}_2(\text{OH})_{12}$. The slope of this graph is virtually identical with that for the series $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{OH})_{4x}$ as given by Yoder (1950).

We observed that precipitates of Ca_3Fe_2 hydrogarnets with x smaller than 2 crystallized very slowly and imperfectly and generally afforded amorphous hydrous silicates. Amorphous $\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3 \cdot n\text{H}_2\text{O}$ obtained by our method converted in a few minutes to crystalline andradite when heated in air at 1050°C . Peters (1965) has described a natural andradite containing (OH), with $x \sim 0.13$. Small amounts of (OH) may be commonly present in natural andradite and other garnets, as has been suggested by Yoder (1950) for grossularite, but has been overlooked because of difficulties attending the recognition and quantitative determination of small amounts of (OH) retained to high temperatures in minerals.

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