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Synthesis of germanate garnets. By ARTHUR TAUBER, *U.S. Army Signal Engineering Laboratories, Fort Monmouth, N. J.*, EPHRAIM BANKS, *Polytechnic Institute of Brooklyn, Brooklyn, New York* and HORST KEDESDY, *U.S. Army Signal Engineering Laboratories, Fort Monmouth, N. J., U.S.A.*

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Recently, there has been a renewed interest in compounds, isostructural with the mineral garnet, of general formula $A_3^{+2}B_2^{+3}Si_3^{+4}O_{12}$, where A is Ca^{+2} , Mn^{+2} , Mg^{+2} or Fe^{+2} and B is Al^{+3} , Cr^{+3} , Mn^{+3} or Fe^{+3} . Not all of the A - B combinations, however, exist in nature. In this structure the oxygen surrounds the A -ion in eight-fold coordination (irregular dodecahedron), the B -ion in six-fold coordination (octahedron) and the Si -ion in four-fold coordination (tetrahedron). The unit cell is body centred cubic containing eight molecules.

Yoder & Keith (1951) discovered that trivalent Al can substitute for tetravalent Si in synthetic spessartite, $Mn_3Al_2Si_3O_{12}$, if trivalent yttrium is substituted for divalent manganese. Keith & Roy (1954), Bertaut & Forrat (1956*a*, 1956*b*, 1957) and Geller & Gilleo (1957*a*, 1957*b*) demonstrated that trivalent Ga or Fe can also be substituted in four-fold coordination forming compounds which may be represented by a general formula $A_3^{+3}B_2^{+3}C_3^{+3}O_{12}$, i.e., all cations are in the trivalent state. The B and C cations may be the same element, such as Fe, Ga, Al, Sc, In or Cr. Gilleo & Geller (1957*b*, 1957*c*) have demonstrated the preferential substitution of Sc, In and Cr in octahedral coordination and of Al and Ga in tetrahedral coordination. The A -cation is a rare-earth element. These compounds are strictly isostructural with silicate garnet.

Little is known about the crystal chemistry of germanate garnets, $A_3^{+2}B_2^{+3}Ge_3^{+4}O_{12}$. Goldschmidt & Peters (1933) and Oftedal (1939) indicate that germanium has never been found in concentrations greater than 0.01% in natural silicate garnets. Probably the non-availability of germanium rather than the structural incompatibility is here the cause for the low germanium concentration. The known crystal chemistry of germanium compounds shows certain similarities with corresponding silicon compounds, for example the quartz form of GeO_2 , the germanium tetrahalides, and germanium sulfide where tetrahedral coordination of Ge has been found. In addition, the recent work of Mullers & Brasseur (1956) on synthetic germanium micas demonstrates the specific replacement of Ge for silicon in tetrahedrally coordinated silicates. Such evidence suggests that a germanate garnet could exist. The ionic radius of Ge^{+4} (0.55 Å)* is somewhat larger than the ionic radius of Si^{+4} (0.40 Å)*; however, the fact that even larger cations, such as Fe^{+3} (0.67 Å)*, have been completely substituted for silicon in 4-fold positions in synthetic garnet, also suggests that a complete Ge substitution is possible.

In this study an attempt has been made to synthesize germanate garnets in order to elucidate their crystal chemistry, to relate it to that of the garnet family, and to lay the ground for the synthesis of new magnetic garnet compounds. The majority of samples were prepared by solid state reaction of oxide mixture (see Table 1) according to: $3AO + B_2O_3 + 3GeO_2 \rightarrow A_3B_2Ge_3O_{12}$ where

$AO = CaO, MgO, NiO, SnO, CdO, CoO$ and $B_2O_3 = Cr_2O_3, Fe_2O_3, Al_2O_3$.

All samples were prepared from oxides (C.P. or better) by carefully weighing to 0.1 mg. and mixing in an agate mortar with ethyl acetate for $\frac{1}{2}$ hour. The mixtures were pressed into $\frac{1}{4}$ " discs at 25,000 lbs.in.⁻². Alternatively, the oxide mixtures were dissolved in nitric acid, evaporated to dryness and decomposed after the admixing of GeO_2 . A third method employed coprecipitated hydroxides which were dried, then mixed with GeO_2 . The oxide, or nitrate and hydroxide composites after preliminary calcining, were fired between 1050 and 1250 °C. from 2 to 25 hours after which they were removed from the furnace and permitted to cool to room temperature. Debye-Scherrer X-ray patterns were made from portions of the center of each disc for phase identification. Mn-filtered Fe K radiation was used throughout. Seventeen compositions were prepared. Reaction products are tabulated in Table 1.

Samples containing manganese were prepared with both MnO and Mn_3O_4 . Except for possible purity considerations, the initial state of the oxidation of the manganese should not influence the final product, since enough time was available for equilibrium with the oxygen in the atmosphere to be attained (Verwey & van Bruggen, 1935; Kedesdy & Tauber, 1956). Preliminary results indicate no differences in the final products after sufficient heat treatment. However, the use of Mn_3O_4 may have contributed to the reactivity of the mixture by undergoing decomposition during the reaction (Hedvall effect).

Nine preparations (No. 1-9, Table 1) resulted in the formation of compounds isostructural with silicate garnet. The germanium analogues of uvarovite ($Ca_3Cr_2Si_3O_{12}$), andradite ($Ca_3Fe_2Si_3O_{12}$), grossularite ($Ca_3Al_2Si_3O_{12}$), spessartite ($Mn_3Al_2Si_3O_{12}$), and calderite ($Mn_3Fe_2Si_3O_{12}$) (Vermaas, 1950) were successfully synthesized. The $Mn_3Cr_2Ge_3O_{12}$ synthetic garnet (composition 4) has no reported silicate analog in natural garnets, although this is probably a matter of geological environment rather than of lattice structural tolerance. Cadmium garnet analogs of our synthetics (compositions 7, 8, 9) have not been found in natural minerals.

The possibility of spinel formation, especially in manganese compounds containing Cr^{+3} , Al^{+3} , or Fe^{+3} has been called to the authors' attention. Therefore, a careful examination was made of X-ray powder diagrams, both film and diffractometer traces, for several samples prepared under different conditions. In no sample could the presence of spinel be detected, even in highly overexposed diffraction patterns. In several samples of the manganese-iron-germanate prepared by solid state reaction in air, however, three diffraction lines could not be indexed according to $Ia3d$, nor could they be attributed to a spinel phase.

A ponderometer magnetic balance described by Rathe-
nau & Snoek (1946) was used to make magnetization

* Radii according to Goldschmidt.

Table 1. *Reaction products and data*

| No. | Batch composition | Reaction products detected in X-ray powder patterns | Lattice constant | Color | Magnetic properties |
|-----|--|--|------------------|---------------|-----------------------|
| 1 | 3 CaO + Cr ₂ O ₃ + 3 GeO ₂ | Garnet structure | 12.275 Å | Green | |
| 2 | 3 CaO + Fe ₂ O ₃ + 3 GeO ₂ | Garnet structure | 12.312 | Tan-gray | |
| 3 | 3 CaO + Al ₂ O ₃ + 3 GeO ₂ | Garnet structure | | White | |
| 4 | Mn ₃ O ₄ + Cr ₂ O ₃ + 3 GeO ₂ | Garnet structure | 12.027 | Green | Strongly paramagnetic |
| 5 | Mn ₃ O ₄ + Fe ₂ O ₃ + GeO ₂ | Garnet structure | 12.087 | Light-brown | Ferromagnetic |
| 6 | Mn ₃ O ₄ + Al ₂ O ₃ + GeO ₂ | Garnet structure | 11.895 | Beige | |
| 7 | 3 CdO + Cr ₂ O ₃ + 3 GeO ₂ | Garnet structure | 12.213 | Green | |
| 8 | 3 CdO + Fe ₂ O ₃ + 3 GeO ₂ | Garnet structure | | Light-brown | |
| 9 | 3 CdO + Al ₂ O ₃ + 3 GeO ₂ | Garnet structure | | White | |
| 10 | 3 MgO + Al ₂ O ₃ + 3 GeO ₂ | Unidentified | | White | |
| 11 | 3 MgO + Cr ₂ O ₃ + 3 GeO ₂ | Spinel structure + GeO ₂ | | Green | |
| 12 | 3 SnO + Cr ₂ O ₃ + 3 GeO ₂ | Unidentified | | | |
| 13 | 3 Fe ₂ O ₃ + 2 Al ₂ O ₃ + 6 GeO ₂ | Unidentified phase (fired at 1200 °C.) | | Black | |
| | | Spinel structure (fired at 1500 °C.) | | Black | |
| 14 | 3 NiO + Cr ₂ O ₃ + 3 GeO ₂ | Spinel structure + GeO ₂ + Cr ₂ O ₃ | | Green | Ferromagnetic |
| 15 | 3 NiO + Fe ₂ O ₃ + 3 GeO ₂ | Spinel structure | | Black | Ferromagnetic |
| 16 | 3 CoO + Fe ₂ O ₃ + 3 GeO ₂ | Spinel + unidentified phase | | Reddish-brown | Ferromagnetic |
| 17 | 3 CoO + Cr ₂ O ₃ + 3 GeO ₂ | Spinel + unidentified phase | | Light-blue | Ferromagnetic |

experiments. Magnetization experiments conducted to detect ferromagnetic phases in non-ferromagnetic matrices have revealed such phases, when present in far smaller concentrations than can be detected by X-ray diffraction techniques.

The results of preliminary measurements for a single phase garnet (by X-ray diffraction) sample, Mn₃Cr₂Ge₃O₁₂ (Tauber, Kedesdy & Banks, 1957), reveals paramagnetic behavior in fields up to 10,000 Oersteds from room temperature to liquid nitrogen temperatures. Since the low-temperature range was limited to liquid nitrogen in the present study, the magnetic data are inconclusive for the detection of possible ferrimagnetic phase, such as Mn-Cr-spinel. The onset of ferrimagnetism occurs below 77 °K. for this spinel (Schindler, McGuire, Howard & Smart, 1952). A sample of Mn₃Fe₂Ge₃O₁₂, which was determined to be a single garnet phase by X-ray diffraction, exhibited a spontaneous magnetization from liquid nitrogen temperatures to 585 °K., the Curie temperature. At first this seems to indicate the presence of Mn-Fe-spinel, which has a Curie temperature of 603 °K. (Gorter, 1954). Yet, the concentration of the magnetic phase, assuming it is Mn-Fe spinel, would have to be 8% by weight as determined from the magnetization data at room temperature. If the spinel phase were present to such a concentration, as a second phase, it seems reasonable to expect visible indications in X-ray diffraction diagrams. Another possibility is that the observed magnetization could originate from structure defects, variations of cation distribution or impurities in the garnet phase. Several samples of Mn-Fe-germanate containing the second phase described previously, were also measured. These were all paramagnetic from room temperature to liquid nitrogen temperature.

We intend to extend the study of the formation of germanate garnets to include other cations and different methods of preparation. Partial substitution of rare earth cations such as Gd⁺³ at the A sites and transitions metal

cations such as Fe⁺³ on C-sites should lead to magnetic compounds, the properties of which will be studied in detail.

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