

fraction pattern. In electron diffraction such a low-angle maximum cannot be resolved from the primary beam. Therefore Prof. C. H. MacGillivray suggested to use the negative of the electron-micrograph as a mask for the preparation of an optical transform. An optical diffractometer as described by Taylor and Lipson (1964, p. 30), was used. In fact, the pattern in the negative produced a broad optical diffraction maximum around the primary beam, Figure 3. The centre of this maximum corresponds to a distance of 0.3 mm in the mask or to a pseudoperiod of about 50 Å in the heated gibbsite material. Therefore it is concluded that the low-angle X-ray diffraction maximum is caused by the same textural periodicity. This explanation is expected to hold true for the maxima observed after heating at lower temperatures. The periodicity is probably brought about by concentration of mass after expulsion of structural water by heating.

Analogous X-ray diffraction maxima, caused by similar textural ordering might occur in diffraction patterns of heated minerals with structures similar to gibbsite, and also in patterns of heated natural clays, containing such minerals.

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SYNTHESIS OF THE GROSSULARITE-SPESSARTITE SERIES¹

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Although a solubility gap has been thought to exist under natural conditions between the pyralspite and ugrandite groups of garnets, an interpretation stemming from the surveys of garnet analyses by Boeke (1914) and by A. N. and H. Winchell (1951), analyses have recently been sum-

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marized by Frondel and Ito (1965) that indicate a probably complete series extends under some natural conditions between grossularite and spessartite. We have now synthesized the end-compositions and four compositions between $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$ and $\text{Mn}_3\text{Al}_2(\text{SiO}_4)_3$. The solid solubility in this series under the conditions of our experiments appears to be complete.

In our first method, gelatinous $\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot n\text{H}_2\text{O}$ was precipitated by the addition of NH_4OH , to a final pH of 8, to a slightly acid solution containing 2mM of aluminum nitrate and 3mM sodium silicate. A gelatinous precipitate of 3mM of the desired composition $(\text{Ca}_{1-x}\text{Mn}_x)\text{CO}_3$ was immediately added and the mixture stirred mechanically for 1 hour. The preparation was then centrifuged, washed twice with about 300 ml of distilled water, and dried at 120° in a vacuum oven. The dried gel was then powdered and samples were run hydrothermally in a cold-seal rod bomb fitted with a silver liner. Each composition was run at periods of 24 to 48 hours under three different conditions: 450°C and 1000 bars, 550°C and 2000 bars, and 700°C and 3000 bars. Garnets were obtained only in the runs at 550°C and 700°C . Another method of synthesis also was used successfully, but required a chemical analysis to establish the composition of the product. In this method, a solution containing Ca, Mn, Al and Si ions in the desired proportion was precipitated by a mixture of NH_4OH and ammonium carbonate to a final pH of 8. Further treatment of the gel was as described above.

The synthetic products were distinctly crystalline under the microscope and a dodecahedral habit could be discerned in the high-Ca runs. The high-Mn runs were finer grained and contained up to a few per cent of extraneous material. The unit-cell dimension of the synthetic garnets was determined by the diffractometer method, using filtered Cu radiation and Si as internal standard. The values of a were obtained by averaging the individual values from the 400, 420, 422, 521, 611, 640, 642 and 800 reflections. The variation in the unit-cell dimension and in the index of refraction is shown graphically in Figure 1.

Although essentially anhydrous grossularite is stable at 2000 bars at temperatures from 860°C down to at least 550°C according to Roy and Roy (1960), slightly hydrated hydrogrossularite can be obtained metastably in this region in runs of relatively short duration. The unit-cell dimension a 11.87 Å found for our grossularite end-composition is slightly higher than the values a 11.86 Å and a 11.851 Å found by Roy and Roy (1960) and by Skinner (1956) for anhydrous material, and our value n 1.733 for the index of refraction is slightly lower than the values n 1.736 and n 1.734 found by these authors. This indicates the presence of a small amount of tetrahedral (OH) in our material. The unit-cell dimension of our spessartite end-composition is identical with the value a

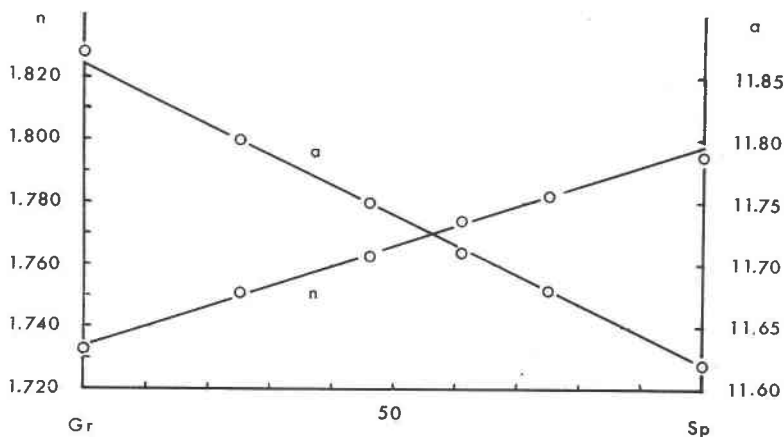


FIG. 1. Variation in unit-cell dimension and refraction index with composition.

11.621 Å found by Skinner (1956) for synthetic anhydrous material; optically, however, the sample ranged from n 1.800, corresponding to his value, down to about n 1.792 with the bulk near n 1.796.

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SOME EXPERIMENTAL DATA ON THE STABILITY OF PUMPELLYITE

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The hydrothermal stability of pumpellyite, $\text{Ca}^4(\text{Mg, Fe}^{+2}, \text{Mn})(\text{Al, Fe}^{+3}, \text{Ti})_5\text{O}(\text{OH})_3[\text{Si}_2\text{O}_7]_2[\text{SiO}_4]_2 \cdot 2\text{H}_2\text{O}$, a common mineral of low grade

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