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NOTE ON SCHIRMERITE

L. H. BRIXNER, *Pigments Department, Experimental Station,*
E. I. du Pont de Nemours & Co., Inc.,
Wilmington, Delaware.

The principle of using naturally occurring minerals as models for synthetic compositions in materials research has been successfully employed in cases such as the ferromagnetic rare earth iron garnets ($Gd_3Fe_5O_{12}$, for example) which can be derived from the mineral grossularite ($Ca_3Al_2Si_3O_{12}$) by substituting iron for the aluminum and silicon and restoring electroneutrality by introducing the trivalent rare earths for the divalent calcium, or the thermoelectric composition $AgSbSe_2$ which is a selenide analog of the mineral miargyrite $AgSbS_2$. With a similar consideration in mind, we planned to use the mineral schirmerite ($PbAg_4Bi_4S_9$) as a model for a selenide or telluride analog in the hope of finding a useful thermoelectric composition.

According to Donnay *et al.* (1954), schirmerite ($PbAg_4Bi_4S_9$) crystallizes in the b.c.c. space group T_d^3 and has a cell edge of 10.36 Å (ASTM 11-63). We synthesized the composition $PbAg_4Bi_4S_9$ by interacting the constituent high-purity elements in a sealed quartz ampoule. A clear, homogeneous melt was obtained at approximately 750° C. The uniform product which did not react with the quartz was an n-type semiconductor which crystallized in the O_h^5 space group with an a of 5.690 ± 0.001 Å. The corresponding selenide, $PbAg_4Bi_4Se_9$, was also synthesized in the same manner and melted at approximately 650° C. It is a p-type semiconductor, isostructural with the corresponding sulfide, and has a cell edge of 5.874 ± 0.001 Å.

This finding is best explained if one assumes these compositions to be solid solutions of the constituent compositions PbS and $AgBiS_2$ and PbSe and $AgBiSe_2$, respectively, all of which crystallize in the reported cubic structure. The parameters for the four compounds as given in the literature are: PbS, $a = 5.936$ Å (ASTM 5-0592); $AgBiS_2$, $a = 5.646$ Å (2); PbSe, $a = 6.124$ Å (ASTM 6-0354); and $AgBiSe_2$, $a = 5.833$ Å (3). If one plots a as a function of composition for the system $PbS/AgBiS_2$ or the system $PbSe/AgBiSe_2$, the parameters obtained from the graphs are practically identical with the ones we measured for the synthesized compositions.

In summary, we can state that the synthetic composition $PbAg_4Bi_4S_9$ does not crystallize in the T_d^3 structure and it is doubtful whether the naturally occurring mineral does. The "schirmerite" listed by Harcourt (1942) is most likely of different composition. This was already suggested by Wickman (1948) who assumed that Harcourt (1942) really was dealing with a member of the tetrahedrite family.

REFERENCES

DONNAY, J. D. H. AND W. NOWACKI (1954) *Crystal Data*, p. 554.
HARCOURT, G. A. (1942) *Am. Mineral.* **27**, 63–113.
ROSI, F. D. *et al.* (1961) RCA Progress Report #8, Contract No. NOBS 77057, p. 11.
WERNICK, J. H., S. GELLER AND K. E. BENSON (1958) *Jour. Phys. Chem. Solids* **7**, 247.
WICKMAN, F. E. (1948) *Am. Mineral.* **33**, 262.

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SYNTHESIS AND PROPERTIES OF CALCIUM VANADIUM GARNET (GOLDMANITE)

R. G. J. STRENS, *Department of Geology and Geophysics, University of California, Berkeley, California.*

In the course of a study of garnets containing trivalent ions of the first transition series, $Ca_3V_2Si_3O_{12}$ was prepared hydrothermally at 530° and 3.0 kilobars, in a 30-day run at the oxygen partial pressure of the hematite-magnetite buffer. The starting material was glass with a Ca:V ratio of 3:2, but with excess silica to suppress the substitution of $(OH)_4^{4-}$ for SiO_4^{4-}. Garnet was obtained in theoretical yield, as a dark green equigranular powder, with n 1.834 ± 0.003, a 12.070 ± 0.005, and D_{calc} 3.765.

Moench and Meyrowitz (1964) have recently described a natural vanadium garnet, containing 60% of the Ca-V end-member, for which they have proposed the name *goldmanite*. Their analysis gives the formula:

$$(Ca_{2.91}Mg_{0.08}Mn_{0.02})_{3.01}(Al_{0.47}Fe_{0.33}V_{1.20})_{2.00}Si_{2.99}O_{12}$$

with n 1.821 ± 0.001, a 12.011, and D_{calc} 3.737. Applying corrections for the content of Mg, Mn, and Fe with the aid of Skinner's (1956) data for the garnet end-members, the writer calculates n 1.836 and a 12.086 for the Ca-V end-member, in reasonable agreement with the values found above.

REFERENCES

MOENCH, R. H. AND R. MEYROWITZ (1964) Goldmanite, a vanadium garnet from Laguna, New Mexico. *Am. Mineral.* **49**, 644–655.
SKINNER, B. J. (1956) Physical properties of end-members of the garnet group. *Am. Mineral.* **41**, 428–436.