

matched¹⁴. These data indicate that melting-points cannot be used as criteria of bond energy in the solid state.

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MINERALOGY

A Green Variety of Yoderite

THE spectacular purple magnesium-iron-aluminosilicate, yoderite^{1,2}, was described from Mautia Hill, Kongwa, Tanganyika (now Tanzania), by McKie in 1959. Since that date, no other occurrence of the mineral has been recorded and unpublished analyses of yoderite from variant associations at Mautia Hill have been found to be not significantly divergent.

During the field season of 1961 a party of geologists engaged on training traverses across Mautia Hill sent a parcel of specimens, including a small specimen of a quartz talc schist containing an emerald-green mineral, to the laboratories of the Geological Survey of Tanganyika, where it was discovered that the optical properties (α , 1.691; β , 1.693; γ , 1.712 (all ± 0.003); $2V\gamma$, 30° ; with pleochroic scheme α , green; β , pale yellow; γ , yellow) and X-ray-powder diffraction pattern of the green mineral were closely similar to those of yoderite. The locality on Mautia Hill from which the specimen came was not recorded at the time of finding and subsequent visits to the hill have failed to rediscover it. In due course, single crystal X-ray studies served to confirm the identification of the green mineral as yoderite.

The green mineral has the same space group, its unit-cell dimensions are identical (within the limits of accuracy quoted by McKie¹), and its diffraction pattern exhibits the same distinctive array of subsidiary (non-Bragg) reflexions as yoderite. The chemical composition of the green yoderite has been determined by Mr. J. H. Scoon as: SiO₂, 36.05; TiO₂, 0.10; Al₂O₃, 43.46; Fe₂O₃, 3.85; FeO, 1.72; MnO, <0.01; MgO, 12.25; CaO, <0.01; H₂O + 3.13 ($\Sigma 100.56$) corresponding to an average unit-cell content of (Fe_{0.16}^{II}Ti_{0.01}Mg_{1.99}Fe_{0.32}^{III}Al_{3.51})^[5,6]Al_{2.00}^[5](Al_{0.07}Si_{3.93})^[4]O_{17.72}(OH)_{2.28}.

The estimation of Fe^{II} in purple yoderite¹ was never regarded as completely satisfactory, and its titanium and calcium contents have been shown by electron-probe analysis, kindly performed by Dr. J. V. P. Long, to have been significantly over-estimated; a new analysis (shortly to be published elsewhere) leads to an average unit-cell content of (Ca_{<0.01}Mn_{0.03}^{II}Ti_{0.01}Mg_{1.98}Mn_{0.06}^{III}Fe_{0.41}^{III}Al_{3.55})^[5,6]Al_{2.00}^[5](Al_{0.08}Si_{3.92})^[4]O_{18.06}(OH)_{1.94}. Fe^{II} in green yoderite and excess oxygen in purple yoderite have been determined by the method of Ingamells⁹ and both values are now thought to be reliable. The new analysis suggests that the colour of purple yoderite is to be attributed to the presence of the chromophore group Mn³⁺—O—Mn²⁺ rather than Fe³⁺—O—Fe²⁺ as was suggested earlier¹; the

green colour of manganese-deficient yoderite bears out this conclusion in that in the absence of the manganese chromophore the mineral exhibits much the same colour as a wide range of aluminosilicates of similar ferrous and ferric iron content.

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CRYSTALLOGRAPHY

Crystallographic Data on New Rare Earth-Germanium and Silicon Compounds

DURING an investigation of samarium-germanium compounds of composition near Sm₅Ge₃, X-ray powder diffraction photographs indicated additional lines which could not be indexed on the basis of the hexagonal unit cell established for Sm₅Ge₃ by Gladyshevskii¹. Investigations of single crystals showed the phase to be orthorhombic and of a new structure-type. An analysis of the crystal structure² showed the stoichiometry to be Sm₅Ge₄.

Five other lanthanide metals in combination with both germanium and silicon have now been examined for the occurrence of this phase. The preparations were made by arc-melting the component metals in an argon atmosphere. Lattice constants were derived from oscillation and Weissenberg photographs with an estimated accuracy of about 0.2–0.3 per cent.

The results are as follows: when germanium was used as the combining element, all the rare earths studied exhibited the orthorhombic 5 : 4 phase. The lattice constants, summarized in Table 1, follow a uniform lanthanide contraction so that the axial ratio, $a : b : c$, remains rather constant. It seems likely that most, if not all, of the rare-earth elements will form a germanide of this type.

Table 1. CRYSTALLOGRAPHIC DATA. SPACE GROUP: $Pn2_1a$ (FROM STRUCTURE DETERMINATION ON Sm₅Ge₄). UNIT CELL CONTAINS FOUR FORMULA UNITS

Compound	a (Å)	b (Å)	c (Å)	Volume (Å ³)
Nd ₅ Ge ₄	7.86	15.06	7.93	939
Sm ₅ Ge ₄	7.75	14.94	7.84	908
Gd ₅ Ge ₄	7.69	14.75	7.76	880
Tb ₅ Ge ₄	7.62	14.60	7.72	862
Er ₅ Ge ₄	7.51	14.41	7.59	821
Y ₅ Ge ₄	7.63	14.63	7.68	860
Tb ₅ Si ₄	7.41	14.58	7.69	831
Er ₅ Si ₄	7.27	14.32	7.58	789
Y ₅ Si ₄	7.39	14.52	7.64	819

For the analogous silicon compounds, the situation is more complex. Three of the lanthanide elements, terbium, erbium and yttrium, formed Sm₅Ge₄-type compounds. It is probable that gadolinium also forms a similar compound. However, this preparation did not yield sufficiently large crystals for investigations to be carried out on individual ones. X-ray powder diffraction patterns, using chromium $K\alpha$ radiation and a 57.3-mm radius camera, indicated that gadolinium monosilicide³ (FeB-type) was the major phase. The remaining lines fit a pattern expected for the orthorhombic 5 : 4 phase. Additional work is necessary to establish the occurrence of Gd₅Si₄ with absolute certainty. The results indicate that the orthorhombic R₅Si₄ compounds will occur most readily for the heavier lanthanides, that is those having smaller atomic radii.

In support of this, the silicide preparation using neodymium yielded crystals with a primitive tetragonal cell in which $a = 7.87$ Å and $c = 14.79$ Å. The unit cell volume corresponds with the orthorhombic 5 : 4 series;