

Silicate garnets

The silicate garnets are listed in Table 3. These have been made mostly by hydrothermal techniques. (Even the higher pressure syntheses of COES¹⁵ and our own³¹ of $\text{Ca}_3\text{V}_2\text{Si}_3\text{O}_{12}$ may be so considered.) Spessartite ($\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) is synthesized⁴⁰ by melting a mixture of the appropriate amounts of reactant oxides at a temperature of 1200–1250°C. When cooled, a glass is obtained which is then annealed at 1080° for 18 hours. Synthetic uvarovite ($\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$) may be obtained by solid-state reaction, but the conditions for attaining a good yield are given in a note published by GELLER and MILLER³². The synthesis of uvarovite is usually credited to HUMMEL⁴¹. However, according to the evidence he gives, he did not succeed in synthesizing a garnet. The spacings from his x-ray powder pattern are not indexable on a cubic cell, and it is inconceivable that this can be accounted for by measurement error. Because it is really mainly of importance that this garnet can be synthesized by solid-state reaction, I shall not carry the discussion to the point of comparing HUMMEL's data with ours here. However, SWANSON *et al.*³³ have prepared uvarovite and carefully measured the powder pattern with a diffractometer. As is their custom, they list all previous data by other authors. I therefore refer the reader to this more recent work for confirmation.

In Table 3, there are three values listed for the lattice constant of $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$. The first two were obtained for specimens synthesized hydrothermally, the third specimen was grown from a lithium molybdate flux. It now appears that the 12.048 Å value may be low; no analysis was given for this specimen. The second specimen was said to contain 0.01% Al and the third was not analyzed. It is probable that the lattice constant for a specimen with ideal composition lies between 12.059 and 12.067 Å.

The relative ionic sizes of the B^{3+} ions which fill the octahedral sites in $\{\text{Ca}_3\}[\text{B}_2^{3+}](\text{Si}_3)\text{O}_{12}$ have been derived from the rare-earth perovskite-like compounds⁴² and these have been appropriate to the garnets. The actual values obtained are:

⁴⁰ H. S. YODER and M. L. KEITH, Complete substitution of aluminum for silicon: The system $3\text{MnO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 - 3\text{Y}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$. *Amer. Mineral.* **36** (1951) 519–533.

⁴¹ F. A. HUMMEL, Synthesis of uvarovite. *Amer. Mineral.* **35** (1950) 324–327.

⁴² S. GELLER, Crystallographic studies of perovskite-like compounds. V. Relative ionic sizes. *Acta Crystallogr.* **10** (1957) 248–251. See also *Structure Reports* **21** (1957) p. 315.

In^{3+}	0.714	Fe^{3+}	0.628	Ga^{3+}	0.613
Nb^{3+}	0.686	Mn^{3+}	0.625	Cr^{3+}	0.608
Ti^{3+}	0.633	V^{3+}	0.625	Al^{3+}	0.558

I would thus expect the lattice constant of $\text{Ca}_3\text{V}_2\text{Si}_3\text{O}_{12}$ to be slightly smaller than that of $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$. MILL's value of 12.09 Å is too large,

Table 4. End-member germanate garnets

A^{2+}	B^{3+}	a [Å]	A^{2+}	B^{3+}	a [Å]	
Ca	Al	12.12 ⁴³ , 12.120 ⁴⁴	Mn	Al	11.902 ⁴³ , 11.901 ⁴⁴ , 11.895 ⁴⁶	
	Sc	12.504 ⁴⁴		V	12.125 ²⁹ , 12.099 ⁴⁵	
	V	12.35 ²⁹ , 12.320 ⁴⁵		Cr	12.027 ^{43,44}	
	Cr	12.265 ⁴⁴ , 12.275 ⁴⁶		Fe	12.087 ^{43,44}	
	Mn	12.325 ⁴⁷		Ga	12.043 ⁴⁶	
	Fe	12.320 ⁴³ , 12.312 ⁴⁴		Cd	Al	12.077 ⁴⁶
	Ga	12.251 ⁴³			Se	12.447 ⁴⁶
	In	12.62 ⁴⁷ , 12.59 ⁴⁹			V	12.29 ²⁹
	Rh	12.35 ⁴⁷			Cr	12.213 ⁴⁶
	Y	12.805 ⁴⁹			Mn	12.27 ⁴⁷
	Dy	12.83 ⁴⁹			Fe	12.261 ⁴⁶
	Ho	12.81 ⁴⁹			Ga	12.191 ⁴⁶
	Er	12.785 ⁴⁹			In	12.515 ²⁹
	Tm	12.765 ⁴⁹			Rh	12.285 ⁴⁷
	Yb	12.74 ⁴⁹				
	Lu	12.73 ⁴⁹				
	Sr	Sc		12.785 ⁴⁹		
In		12.87 ⁴⁹ , 12.88 ⁴⁹				
Y		13.085 ⁴⁹ , 13.091 ⁴⁵				
Ho		13.09 ⁴⁹				
Er		13.065 ⁴⁹				
Tm		13.04 ⁴⁹				
Yb		13.03 ⁴⁹				
Lu		13.01 ⁴⁹				

⁴³ S. GELLER, C. E. MILLER and R. G. TREUTING, New synthetic garnets. *Acta Crystallogr.* **13** (1960) 179–186.

⁴⁴ A. TAUBER, C. G. WHINFREY and E. BANKS, The crystal chemistry of some germanium garnets. *J. Physics Chem. Solids* **21** (1961) 25–32.

⁴⁵ S. GELLER and G. P. ESPINOSA, data not previously published.

⁴⁶ A. TAUBER, E. BANKS and H. KEDESZY, Synthesis of germanate garnets. *Acta Crystallogr.* **11** (1958) 893–894.

⁴⁷ B. V. MILL', Synthesis of garnets containing Mn^{3+} and Rh^{3+} . *Zhur. Strukt. Khim.* **6** (1965) 471–473.

⁴⁸ H. E. SWANSON, M. I. COOK, E. H. EVANS and J. H. DE GROOT, Standard x-ray diffraction powder patterns. NBS Circular 539, Vol. 9 (1960) pp. 15–20.

⁴⁹ B. V. MILL', Synthesis of garnets with large cations. *Dokl. Akad. Nauk [USSR]* **165** (1965) 555–558.