Silicate garnets

The silicate garnets are listed in Table 3. These have been made mostly by hydrothermal techniques. (Even the higher pressure syntheses of COES[18] and our own[31] of $Ca_3V_2Si_3O_{12}$ may be so considered.) Spessartite ($Mn_3Al_2Si_3O_{12}$) is synthesized[40] 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 ($Ca_3Cr_2Si_3O_{12}$) may be obtained by solid-state reaction, but the conditions for attaining a good yield are given in a note published by GELLER and MILLER[32]. The synthesis of uvarovite is usually credited to HUMMEL[41]. 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 $Ca_3Fe_2Si_3O_{12}$. 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 $\{Ca_3\}[B_2^{3+}](Si_3)O_{12}$ have been derived from the rare-earth perovskite-like compounds[42] 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 $3MnO \cdot Al_2O_3 \cdot 3SiO_2$—$3Y_2O_3 \cdot 5Al_2O_3$. 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
Sc^{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 $Ca_3V_2Si_3O_{12}$ to be slightly smaller than that of $Ca_3Fe_2Si_3O_{12}$. 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],
	Sc	12.504[44]			11.895[46]
	V	12.35[29], 12.320[45]		V	12.125[29], 12.099[45]
	Cr	12.265[44], 12.275[46]		Cr	12.027[43,44]
	Mn	12.325[47]		Fe	12.087[43,44]
	Fe	12.320[43], 12.312[44]		Ga	12.043[46]
	Ga	12.251[43]	Cd	Al	12.077[46]
	In	12.62[47], 12.59[49]		Sc	12.447[46]
	Rh	12.35[47]		V	12.29[29]
	Y	12.805[49]		Cr	12.213[46]
	Dy	12.83[49]		Mn	12.27[47]
	Ho	12.81[49]		Fe	12.261[46]
	Er	12.785[49]		Ga	12.191[46]
	Tm	12.765[49]		In	12.515[29]
	Yb	12.74[49]		Rh	12.285[47]
	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. KEDESDY, 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.