

MILL' has succeeded in making the garnets  $\text{Ca}_3\text{Mn}_2^{3+}\text{Ge}_3\text{O}_{12}$  and  $\text{Cd}_3\text{Mn}_2^{3+}\text{Ge}_3\text{O}_{12}$ <sup>47</sup>. MILL' has also succeeded in making two germanate garnets with  $\text{Rh}^{3+}$  ions in the *a* sites<sup>47</sup>, namely those of  $\text{Ca}^{2+}$  and  $\text{Cd}^{2+}$ .

It should be mentioned here that KEITH and ROY<sup>56</sup> and SCHNEIDER, ROTH and WARING<sup>57</sup> have also had indication that rare earths or yttrium replaced  $\text{Ga}^{3+}$  or  $\text{Al}^{3+}$  in the gallium and aluminum garnets. I shall leave this, however, for later discussion.

The lattice constant, 12.251 Å, for  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  given by SWANSON *et al.*<sup>48</sup> seems small relative to either one given for the Cr garnet. The order seems more nearly correct for the Mn group of germanate garnets. For the In garnet, MILL' gives two different values 12.62 and 12.59 Å. The first was obtained for a hydrothermally synthesized garnet, the second for one prepared by solid state reaction. Inasmuch as the values MILL' obtained for his hydrothermally synthesized garnets are generally high by about 0.03 Å, I would speculate that the lower one is the more nearly correct one for the pure garnet.

Among the cadmium garnets, again the value for the V compound looks high, while the value for the Ga compound seems low.

I think it worth emphasizing that in the case of some of the germanates, there may be a question regarding ideal stoichiometry and some of the differences in lattice constant may be reflections of difficulties in this regard. Even when there is no difference between investigators, the garnet phase could still not be of the ideal stoichiometry.

#### Rare-earth aluminum, iron and gallium garnets

Lattice constants for these garnets are listed in Table 5. The lattice constant value given by YODER and KEITH<sup>40</sup> for the first known aluminum garnet is  $12.01 \pm 0.02$  Å, BERTAUT and FORRAT<sup>58</sup> give 12.02 Å, GILLES and GELLER<sup>59</sup>, 12.003 Å, and EULER and BRUCE<sup>12</sup>,

<sup>56</sup> M. L. KEITH and R. ROY, Structural relations among double oxides of trivalent elements. *Amer. Mineral.* **39** (1954) 1–23.

<sup>57</sup> S. J. SCHNEIDER, R. S. ROTH and J. L. WARING, Solid state reactions involving oxides of trivalent cations. *J. Res. Nat. Bur. Standards* **65A** (1961) 345–374.

<sup>58</sup> F. BERTAUT et F. FORRAT, Étude des combinaisons des terres rares avec l'alumine et la galline. *Compt. Rend. Acad. Sci. [Paris]* **243** (1956) 1219–1222.

<sup>59</sup> M. A. GILLES and S. GELLER, Magnetic and crystallographic properties of substituted yttrium-iron garnet  $3\text{Y}_2\text{O}_3 \cdot x\text{M}_2\text{O}_3 \cdot (5-x)\text{Fe}_2\text{O}_3$ . *Physic. Rev.* **10** (1958) 73–78.

Table 5. Rare earth aluminum, iron and gallium garnets

A <sup>3+</sup>	B <sup>3+</sup> , C <sup>3+</sup>	a [Å]	
Y	Al	12.01 <sup>40,56</sup> , 12.02 <sup>58</sup> , 12.000 <sup>12</sup> , 12.003 <sup>59</sup>	
Gd		12.11 <sup>58</sup> , 12.113 <sup>12</sup> , 12.111 <sup>60</sup>	
Tb		12.074 <sup>61</sup>	
Dy		12.06 <sup>58</sup> , 12.042 <sup>61</sup>	
Ho		12.011 <sup>61</sup>	
Er		11.98 <sup>58</sup> , 11.981 <sup>61</sup>	
Tm		11.957 <sup>60</sup>	
Yb		11.929 <sup>60</sup>	
Lu		11.912 <sup>60</sup>	
Y		Fe	12.376 <sup>4,62</sup>
La*			12.767 <sup>63</sup>
Pr*			12.646 <sup>63</sup>
Nd*			12.60 <sup>62</sup> , 12.596 <sup>64</sup> , 12.600 <sup>63</sup>
Pm*			12.57 <sup>62</sup> , 12.561 <sup>63</sup>
Sm	12.524 <sup>62</sup> , 12.530 <sup>64</sup> , 12.528 <sup>65</sup> , 12.529 <sup>63</sup>		
Eu	12.518 <sup>62</sup> , 12.498 <sup>63</sup>		
Gd	12.479 <sup>62</sup> , 12.472 <sup>64</sup> , 12.471 <sup>63</sup>		
Tb	12.447 <sup>62</sup> , 12.436 <sup>63</sup>		
Dy	12.414 <sup>62</sup> , 12.405 <sup>63</sup>		
Ho	12.380 <sup>62</sup> , 12.375 <sup>63</sup>		
Er	12.349 <sup>62</sup> , 12.347 <sup>64</sup>		
Tm	12.325 <sup>62</sup> , 12.323 <sup>63</sup>		
Yb	12.291 <sup>62</sup> , 12.302 <sup>63</sup>		
Lu	12.277 <sup>62</sup> , 12.283 <sup>63</sup>		
Y	Ga	12.30 <sup>58</sup> , 12.273 <sup>59</sup> , 12.280 <sup>12</sup> , 12.275 <sup>57</sup> , 12.274 <sup>66</sup>	
Pr		12.57 <sup>58</sup> , 12.545 <sup>45</sup>	

\* Hypothetical.

<sup>60</sup> C. B. RUBENSTEIN and R. L. BARNES, Crystallographic data for rare-earth aluminum garnets: Part II. *Amer. Mineral.* **50** (1965) 782–785.

<sup>61</sup> C. B. RUBENSTEIN and R. L. BARNES, Crystallographic data for rare-earth aluminum garnets. *Amer. Mineral.* **49** (1964) 1489–1490.

<sup>62</sup> F. BERTAUT et F. FORRAT, Étude des paramètres des grenats. *Compt. Rend. Acad. Sci. [Paris]* **244** (1957) 96–99.

<sup>63</sup> G. P. ESPINOSA, Crystal chemical study of the rare-earth iron garnets. *J. Chem. Physics* **37** (1962) 2344–2347.

<sup>64</sup> S. GELLER, H. J. WILLIAMS and R. C. SHERWOOD, Magnetic and crystallographic study of neodymium substituted yttrium and gadolinium iron garnets. *Physic. Rev.* **123** (1961) 1692–1699.

<sup>65</sup> S. GELLER and D. W. MITCHELL, Rare earth ion radii in the iron garnets. *Acta Crystallogr.* **12** (1959) 936.

<sup>66</sup> G. P. ESPINOSA, A crystal chemical study of titanium (IV) and chromium (III) substituted yttrium iron and gallium garnets. *Inorg. Chem.* **3** (1964) 848–850.