

$\{\text{Na}_3\}[\text{Al}_2](\text{Li}_3)\text{F}_{12}$, $a = 12.41 \text{ \AA}$, cryolithionite. According to MENZER⁷¹, the ionic distribution is in accordance with this formula.

2. Na^+ : A number of garnets other than cryolithionite contain Na ions in c sites.

$\{\text{NaCa}_2\}[\text{Mn}_2](\text{As}_3)\text{O}_{12}$ ⁷² (berzeliite) $a = 12.49 \text{ \AA}$
 $\{\text{Na}_3\}[\text{Al}_2](\text{P}_3)\text{O}_{12}$ ⁷³ a , not reported
 See also 1, 3, 4, 8, 25, 27

Group I B

3. Cu^{2+} : a and c sites

$\{\text{NaCa}_2\}[\text{Cu}_2](\text{V}_3)\text{O}_{12}$ ⁷⁴ $a = 12.423 \text{ \AA}$
 $\{\text{CuGd}_2\}[\text{Mn}_2](\text{Ge}_3)\text{O}_{12}$ ⁴³ (tentative) 12.475
 See also 1.

Group II A

4. Mg^{2+} : c and a sites

$\{\text{Mg}_3\}[\text{Al}_2](\text{Si}_3)\text{O}_{12}$ ^{16,28} $a = 11.459 \text{ \AA}$
 $\{\text{Gd}_3\}[\text{Mg}_2](\text{GaGe}_2)\text{O}_{12}$ ⁴³ 12.425
 $\{\text{MgGd}_2\}[\text{Mg}_2](\text{Ge}_3)\text{O}_{12}$ ⁴³ 12.31
 $\{\text{MnGd}_2\}[\text{MgMn}](\text{Ge}_3)\text{O}_{12}$ ⁴³ (probable distribution) 12.395
 $\{\text{Ca}_3\}[\text{TiMg}](\text{Ge}_3)\text{O}_{12}$ ⁴³ 12.35
 $\{\text{Ca}_3\}[\text{ZrMg}](\text{Ge}_3)\text{O}_{12}$ ⁴³ 12.514
 $\{\text{NaCa}_2\}[\text{Mg}_2](\text{V}_3)\text{O}_{12}$ ⁷⁴ 12.446
 $\{\text{Y}_3\}[\text{Mg}_x\text{Fe}_{2-x}](\text{Fe}_{3-x}\text{Si}_x)\text{O}_{12}$ ⁷
 $\{\text{Gd}_3\}[\text{Mg}_x\text{Fe}_{2-x}](\text{Fe}_{3-x}\text{Si}_x)\text{O}_{12}$ ⁷⁵

See also 1, 17, 25, 33a.

⁷¹ G. MENZER, Die Kristallstruktur von Kryolithionit. Z. Kristallogr. 73 (1930) 265–287.

⁷² F. MACHATSCHKI, Berzeliit, ein Arsenat vom Formel- und Strukturtypus Granat ($\text{X}_3\text{Y}_2\text{Z}_3\text{O}_{12}$). Z. Kristallogr. 73 (1930) 123–140.

⁷³ E. THILO, Über die Isotypie zwischen Phosphaten der allgemeinen Zusammensetzung $(\text{Me}_1)_3(\text{Me}_2)_2[\text{PO}_4]_3$ und den Silikaten der Granatgruppe. Naturwiss. 29 (1941) 239.

⁷⁴ A. DURIF, Sur quelques composés non silicates isomorphes des granats. Int. Conf. on Physics of the Solid State and Application to Electronics and Telecommunications. Brussels, Belgium (1958) pp. 500–502.

⁷⁵ S. GELLER, H. J. WILLIAMS, R. C. SHERWOOD and G. P. ESPINOSA, Magnetic and crystallographic studies of substituted gadolinium iron garnets. J. Appl. Physics 36 (1965) 88–100.

5. Ca^{2+} : thus far, all evidence points to preference for c sites.

There is some indication that Ca^{2+} ions may enter a sites: RINGWOOD and SEABROOK⁷⁶ have reported a pressure induced CaGeO_3 with garnet structure, i.e. $\{\text{Ca}_3\}[\text{CaGe}](\text{Ge}_3)\text{O}_{12}$. We have performed high-pressure experiments on this system and have not obtained a cubic material in any case. The powder photograph of one of the specimens appears to be indexable on a tetragonal cell with $a = 12.51$, $c = 12.36 \text{ \AA}$. The structure does appear to be closely related to that of the garnet. Thus far, we have not obtained single crystals which are required for a structure determination. For examples of Ca^{2+} ion in the garnets, see Tables 3–5 and the many other examples in this survey.

6. Sr^{2+} : c sites

In the earlier survey⁸, I had said, “enters c sites but there is no known garnet in which Sr^{2+} ions fill the c sites”. This was misinterpreted by MILL⁴⁹ to mean that I had said that “ Sr^{2+} is too large to fill all the dodecahedral positions and can only replace other cations partially...”. He then counters this by giving examples of hydrogarnets, which he writes $3\text{SrO} \cdot \text{Ga}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ and $3\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$. Leaving aside the misinterpretation of my remark, I do not consider the hydrogarnets to be *isostructural* with the garnets. Thus at the time I wrote the earlier paper, the statement was correct. Since then MILL⁷ has produced a number of interesting garnets with Sr^{2+} ions filling the c sites; these are listed in Table 4. Nevertheless, the first indications that substantial amounts of Sr^{2+} ion would enter c sites were given in 1960:

$\{\text{Sr}_{0.5}\text{Y}_{2.5}\}[\text{Fe}_2](\text{Fe}_{2.5}\text{Ge}_{0.5})\text{O}_{12}$ ⁴³ $a = 12.414 \text{ \AA}$
 $\{\text{Sr}_{0.5}\text{Y}_{2.5}\}\text{Sn}_{0.5}\text{Fe}_{4.5}\text{O}_{12}$ ⁷⁷ 12.49
 $\{\text{SrY}_2\}\text{SnFe}_4\text{O}_{12}$ ⁷⁷ 12.61

7. Ba^{2+} : small amounts are known to enter c sites⁷⁷

⁷⁶ A. E. RINGWOOD and M. SEABROOK, High pressure phase transformations in germanate pyroxenes and related compounds. J. Geophys. Res. 68 (1963) 4601–4609.

⁷⁷ S. GELLER, R. M. BOZORTH, M. A. GILLES and C. E. MILLER, Crystal chemical and magnetic studies of garnet systems $\text{M}_3^2+\text{Fe}_2\text{Sn}_3\text{O}_{12}-\text{Y}_3\text{Fe}_2\text{Fe}_3\text{O}_{12}$. J. Physics Chem. Solids 12 (1959) 111–118.