b. Fe³⁺: a and d sites

See the numerous examples in Tables 3-5 and throughout the survey.

c. Fe4+: d sites 94

 $\{Y_{2,9}Ca_{0.1}\}[Fe_2](Fe_{2.9}^{3+}Fe_{0.1}^{4+})O_{12}\ ^{45}$

a = 12.378 Å

Magnetic measurements have not as yet been made on the material. The formula is written in accord with the Tcherney paper.

32. Ru⁴⁺: probably a sites

 $\{Y_{2.8}Ca_{0.2}\}[Ru_{0.2}Fe_{1.8}](Fe_3)O_{12}\ ^{82}$

a = 12.383 Å

33a. Co²⁺: c, a and d sites

{MnGd₂}[CoMn](Ge₃)O₁₂ 43 a = 12.437 Å12.402 {CoGd₂}[Co₂](Ge₃)O₁₂ 43 12.300 {CoY₂}[Co₂](Ge₃)O₁₂ 43 12.446 {Gd₃}[Co₂](GaGe₂)O₁₂ 43 12.5443, 12.52845 {Ca₃}ZrCoGe₃O₁₂ {Ca₃}[SnCo](Ge₃)O₁₂ 43 12.47 $\mathrm{Y_2MgCo_2Ge_3O_{12}}~^{95}$ 12.23 12.35 ${CaY_2}[Co_2](Ge_3)O_{12}$ 95 $\{{\rm Ca}_3\}[{\rm Zr}_{0.4}{\rm Sc}_{1.6}]({\rm Co}_{0.2}{\rm Ge}_{2.8}){\rm O}_{12}\ ^{45}$ 12,533

 ${Y_3}Fe_{5-2x}Co_xSi_xO_{12}$ ${P_{6,97}}$ ${Y_3}Fe_{5-2x}Co_xGe_xO_{12}$ ${P_{7}}$

See also 1, 16, Table 3, and discussion section on ionic-sit preference.

b. Co^{3+} a and d sites

 $\begin{aligned} &\{\mathrm{Ca_3}\}[\mathrm{Sc_{1.8}Co_{0.2}}](\mathrm{Ge_3})\mathrm{O_{12}}^{\ 45} & a = 12.501 \text{ Å} \\ &\{\mathrm{Ca_3}\}[\mathrm{Sc_{1.8}Zr_{0.2}}](\mathrm{Co_{0.2}Ge_{2.8}})\mathrm{O_{12}}^{\ 45} & 12.518 \end{aligned}$

94 D. I. TCHERNEV, Frequency-dependent anisotropy in Si- and Co-dop: YIG and LuIG. J. Appl. Physics 37 (1966) 1318—1320. See also D. L. Wood at J. P. Remeika, Optical transparency of rare-earth iron garnets. J. Applysics 37 (1966) 1232—1233.

95 D. Reinen, Die Lichtabsorption des Co²⁺ und Ni²⁺ in oxidischen Ferkörpern mit Granatstruktur I. Z. anorg. allg. Chem. 327 (1964) 238—252.

⁹⁶ S. Geller, H. J. Williams, R. C. Sherwood and G. P. Espinosa, Substitutions of divalent transition metal ions in yttrium iron garnet. J. App. Physics 33 (1962) 1195—1196.

⁹⁷ S. Geller, H. J. Williams, G. P. Espinosa and R. C. Sherwood, Sustitution of divalent cobalt in yttrium iron garnet. Physic. Rev. 136 (196 A1650—A1656.

After calcining these specimens for half an hour at $1215\,^{\circ}\mathrm{C}$ in oxygen, the first was fired at $1200\,^{\circ}\mathrm{C}$ for 24 hours in O_2 then quenched. The second was fired at $1220\,^{\circ}\mathrm{C}$ for 2 hours in O_2 , then reground, recompacted and refired at $1225\,^{\circ}\mathrm{C}$ for 16 hours in O_2 . The first specimen, i.e. with the $\mathrm{Co^{3+}}$ ions presumably in octahedral sites is canary yellow; the second is yellow-green.

34. Rh $^{3+}$: a sites

See Table 4 for end-members.

35. Ni²: a sites

 $\begin{aligned} &\{\mathrm{MnGd}_2\}[\mathrm{MnNi}](\mathrm{Ge}_2)\mathrm{O}_{12}^{\ 43} & a = 12.413 \text{ Å} \\ &\{\mathrm{Gd}_3\}[\mathrm{Ni}_2](\mathrm{GaGe}_2)\mathrm{O}_{12}^{\ 43} & 12.401 \\ &\{\mathrm{Ca}_3\}[\mathrm{ZrNi}](\mathrm{Ge}_3)\mathrm{O}_{12}^{\ 43,45} & 12.50 \\ &\{\mathrm{Y}_3\}[\mathrm{Fe}_{2-x}\mathrm{Ni}_x](\mathrm{Fe}_{3-x}\mathrm{Si}_x)\mathrm{O}_{12}^{\ 55} \\ &\{\mathrm{Y}_3\}[\mathrm{Fe}_{2-x}\mathrm{Ni}_x](\mathrm{Fe}_{3-x}\mathrm{Ge}_x)\mathrm{O}_{12}^{\ 55} \end{aligned}$

See also 1 and 16.

Note: Wherever a system is given in the above survey, lattice constants for various compositions are given in the references.

Ionic site preference

In our earlier work on the garnets, it appeared that the octahedral and tetrahedral sites preferred cations with spherical or pseudospherical ground-state electronic configurations. I should emphasize that we did not assert this rule; rather we indicated that experiments designed to synthesize garnets with ions not satisfying this rule were unsuccessful. However, even though we were aware of the paper (see Ref.⁸), we somehow missed the synthesis by Durif ⁷⁴ of the garnet {NaCa₂}[Cu₂](V₃)O₁₂ in 1958. This alone would be enough to negate this rule because the Cu²⁺ ion has one of the largest Jahn-Teller distortions. But subsequently ⁵⁵ we managed to replace a small amount of Fe³⁺ by Mn³⁺ ion in YFe garnet. Because it was only about ²⁹ erplacement, we could not be absolutely sure of it, even though the powder photograph indicated a single-phase material and the moment per formula unit was significantly higher than that of pure YFe garnet as it should have been.

More recently, garnets in which Mn^{3+} ions fill the a sites have been ynthesized ⁴⁷. The Mn^{3+} ion, of course, is the other 3d ion with a very large Jahn-Teller distortion. Further, a silicate garnet (goldmanite)