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Crystal chemistry of $Fe_3^{2+}Cr_2Si_3O_{12}$–$Fe_3^{2+}Fe_2^{3+}Si_3O_{12}$ garnet solid solutions and related spinels

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ABSTRACT

Garnet solid solutions have been synthesized across the skiagite–Fe-knorringite ($Fe_3^{2+}Fe_2^{3+}Si_3O_{12}$–$Fe_3Cr_2Si_3O_{12}$) binary join. Such compositions reflect a simple Cr-Fe^{3+} exchange on the octahedral sites, with Fe^{2+} occupying the adjacent dodecahedral sites. Solid solution is complete across the join and the correct stoichiometry was verified by Mössbauer spectroscopy. A symmetric fit to the molar volume data yields 119.77(2) cm^3/mol [unit-cell parameter a_o =11.6736(7) Å] for the Fe-knorringite end-member and a small negative excess volume, W_V = –0.76(15) cm^3/mol. Combining this result with literature data reveals that binary joins involving octahedral site substitutions exhibit significantly different behavior than those where substitution occurs on the dodecahedral sites. In the former case, W_V is usually negative, whereas the latter joins have positive deviations from ideal behavior. Therefore, we conclude that the garnet structure responds in a fundamentally different way when accommodating different cations on the dodecahedral or octahedral sites. Mössbauer spectra of skiagite–Fe-knorringite garnets do not exhibit any significant asymmetry in the $^{[8]}Fe^{2+}$ doublet. $Fe^{3+}/\Sigma Fe$ values determined at room temperature and 80 K confirm the general applicability of the recoil-free fraction correction factors reported by Woodland and Ross (1994) for mixed-valence garnets. Coexisting spinels in some samples are either binary Fe_3O_4–Fe_2SiO_4 or Fe_3O_4–$FeCr_2O_4$ solid solutions. Very little mutual solubility is apparent suggesting a significant solvus may exist between the silicate and Cr-bearing spinel series.

Keywords: Fe-knorringite, Fe-Cr garnet, skiagite, molar volume, Mössbauer spectroscopy, excess thermodynamic properties, Fe-Cr spinel