

Site preference and local geometry of Sc in garnets: Part II. The crystal-chemistry of octahedral Sc in the andradite–Ca₃Sc₂Si₃O₁₂ join

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ABSTRACT

Investigation of scandium incorporation in garnets along the synthetic Ca₃Fe₃³⁺Si₃O₁₂–Ca₃Sc₂Si₃O₁₂ (adr–CaSc) join, based on the same multi-technique approach used in the companion paper (Oberti et al. 2006a), shows that (1) Sc is incorporated exclusively at the Y octahedron; (2) the local coordination of Sc is slightly different in Sc-poor than in Sc-rich compositions (Sc–O = 2.06 Å in CaSc₁₀ vs. 2.10 Å in CaSc_{30–90}); (3) the local coordination of Ca is also slightly different in Sc-poor than in Sc-rich compositions [Ca1,2–O are 2.34(2) and 2.48(2) Å in CaSc₁₀ and 2.36(2) and 2.50(2) Å in CaSc₉₀, with Δ fixed at 0.14 Å in all the samples]; (4) the linear increase of the unit-cell edge along the join derives from multiple changes in the geometry of the different polyhedra and from the rotation of the tetrahedron around the 4 axis (α rotation), and cannot be modeled from extrapolation of the behavior observed along the Ca₃Al₂Si₃O₁₂–Ca₃Fe₃³⁺Si₃O₁₂ (grs–adr) join.

CaSc-rich garnets, where a large X dodecahedron coexists with a large Y octahedron and a Z tetrahedron occupied by Si, similar to pyrope-grossular garnets, have the highest α values observed to date in calcium silicate garnets. Slightly lower α values are observed in pyrope and almandine, but correspond to a different structural arrangement, where a small X dodecahedron coexists with a small Y octahedron. These results further confirm the efficiency of a combined short- and long-range approach for understanding the properties of garnet solid solutions.

Keywords: Crystal structure, garnet, XAS, XRD data, trace elements and REE, scandium, crystal synthesis