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Incorporation of Y and REEs in aluminosilicate garnet: Energetics from atomistic simulation

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ABSTRACT

Yttrium and the rare-earth elements (Y+REEs) are incorporated into aluminosilicate garnet as trivalent ions replacing divalent Mg, Fe, Mn, or Ca (“M^{2+}”) in dodecahedral sites, which requires some form of coupled substitution to maintain electroneutrality. We compare the energetic costs of competing coupled-substitution schemes, using lattice dynamics calculations to assess defect energies and exchange energies for each scheme. Substitutions with relatively low energetic costs introduce menzerite-like components via the exchange vector $[\mathrm{YM}_{-1}\cdot(\mathrm{Mg,Fe})\mathrm{Al}_{-1}]$, or alkali components via the exchange vector $[\mathrm{Y(Na,Li)M}_{-2}]$. Substitutions with substantially higher energetic costs introduce a vacancy component via the exchange vector $[\mathrm{Y}_2\square\mathrm{M}_{-3}]$, or the yttrogarnet (YAG) component via the exchange vector $[\mathrm{YM}_{-1}\cdot\mathrm{AlSi}_{-1}]$, or a component with octahedral Li via the exchange vector $[\mathrm{Y}_2\mathrm{M}_{-2}\cdot\mathrm{LiAl}_{-1}]$. Energetic costs decrease significantly as the host-garnet unit-cell dimension expands, decrease very modestly as temperature rises or pressure falls, and decrease substantially with the contraction in ionic radius across the lanthanide series. These results, combined with critical re-examination of arguments cited in favor of each substitution scheme in natural occurrences, suggest that Y+REE incorporation in natural garnet is dominated by coupled substitutions that introduce menzerite and alkali components, that the YAG substitution plays only a subsidiary role, and that the other schemes are likely to be of very minor importance.

Keywords: Garnet, yttrium, rare-earth elements, lattice dynamics, atomistic simulation