Non-ideal solid-solution in garnet: crystal-structure evidence and modelling

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Abstract: Crystal-chemical characterization of 281 garnets, representative of most geologic environments, has allowed distortion of the X, Y and Z polyhedra to be examined as a function of chemical composition, allowing us to understand the reasons for compositional preferences in nature. Pyralspites [with Σ(Mg,Fe,Mn) as the dominant X cations] and ugrandites (with Ca as the dominant X-cation) are separated by a significant compositional gap (1.5 to 2.1 Ca apfu). The existence and width of this gap have been explained on the basis of two different configurations for the X and Y polyhedra, corresponding to mainly ionic and mainly covalent bonding schemes, respectively. In the former configuration, occurring in pyralspitic garnets, the shared X-X and X-Y edges are shorter than the unshared ones; in the latter configuration, occurring in ugrandites, the opposite situation is present.

Most structural parameters within (Mg,Fe,Mn) - Ca garnet solid-solutions show non-linear variations: this fact, together with spectroscopic (XANES) data, rules out the presence of domains with either pyralspitic or grossular configurations; thus, the same X cation shows a different bonding behaviour, depending on the garnet structure (pyralspitic or ugranditic) in which it occurs.

The unit-cell edge and the fractional coordinates of the oxygen atom have been modelled along the PYR-ALM, ALM-GRO and PYR-GRO joins. Positive excess volumes of mixing (ΔV) are present along all three solid-solutions. The ΔV value increases, and its compositional dependence is progressively more symmetric, with increasing size difference between the component X cations.

The maximum calculated ΔV of mixing along the PYR-GRO join (~ 7.5 Å³ per unit cell) is mainly due to the excess volume increase of the XO₆ polyhedron with increasing Ca substitution (~ 5.5 Å³ per unit cell). The YO₆ octahedron also shows an excess volume, but its contribution to the ΔV of mixing is just enough to compensate for the negative ΔV shown by the ZO₄ tetrahedron (~ 0.3 Å³ per unit cell).

Key-words: garnet, crystal-chemistry, excess volume of mixing, non-ideal behaviour, structure modelling

1. Introduction

Merli et al. (1995) have shown how the unit-cell edge and the fractional atomic coordinates of the oxygen in the garnet structure change as a function of the composition of X,Y and Z sites. It was shown that the oxygen coordinates follow three well-defined trends which correspond to substitutions occurring at the X, Y and Z sites. Structure-refinements of a large number of samples covering as much as possible the compositional range of garnet should allow us to unravel the contribution of each isomorphous species to the geometric changes of the structure (i.e., to the variations of the unit-cell edge and of the x,y,z fractional coordinates of the oxygen

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