

INFLUENCE OF Ca-Mg SUBSTITUTION ON THE Cr³⁺ CRYSTAL FIELD PARAMETERS IN NATURAL GARNET SOLID SOLUTIONS

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Electronic absorption spectra of a series (19 samples) of natural Mg,Ca-garnets with constant amount of octahedral Cr³⁺, $^{[8]}(\text{Mg}_{1-x}\text{Ca}_x)_3^{[6]}(\text{Al}_{0.67}\text{Cr}_{0.33})_2^{[4]}\text{Si}_3\text{O}_{12}$, from deep-seated xenoliths in kimberlite pipes of Siberia and South Africa were measured and evaluated. It was established that increasing of x_{Ca} from 0.02 to 0.745 results in decreasing of: (i) $10Dq_{\text{Cr}^{3+}}$ from 17800 cm⁻¹ to 16580 cm⁻¹, (ii) β parameter, reflecting the ionicity of the Cr-O bond, from 0.714 to 0.682, and (iii) FWHM values of ν_1 and ν_2 absorption bands of Cr³⁺. The above dependences are represented by two distinct linear trends (a) ($x_{\text{Ca}} < x_{\text{Cr}}$) ($10Dq = 17845 - 2469.5 \cdot x_{\text{Ca}}$, $r = 0.992$) and (b) ($x_{\text{Ca}} > x_{\text{Cr}}$) ($10Dq = 17583.3 - 1361.1 \cdot x_{\text{Ca}}$, $r = 0.995$) with the boundary between these trends that corresponds to the composition $x_{\text{Ca}} = x_{\text{Cr}}$.

The observed character of variation of the Cr³⁺ crystal field parameters along the garnet solid solution studied reflects, most probably, different stages of the Ca and Cr³⁺ ordering in the shared X- and Y-sites of the structure, respectively. Such ordering is caused by the mechanism of the optimization of Ca and Cr³⁺ local environment (BOSENICK et al., 2000). The presence of large Cr³⁺-centered octahedra in the pyrope host structure is energetically favourable when Ca replaces Mg if Ca and Cr³⁺ are placed in adjacent (shared) X and Y sites, respectively (UNGARETTI et al., 1995).

In garnets with ratio $x_{\text{Ca}} < x_{\text{Cr}}$, two types of Cr³⁺-centers occur: (i) Cr³⁺-ions in a pure pyrope matrix, that is octahedral Cr³⁺ surrounded by six next-next-neighbour Mg atoms (Mg₆-Cr³⁺); (ii) Cr³⁺-ions in "mixed" X-cation surrounding, that is (Mg_{6-x}Ca_x)-Cr³⁺, where $\lim(x) \rightarrow 6$.

In garnets with $x_{\text{Ca}} > x_{\text{Cr}}$ ratio only Ca₆-Cr³⁺ centers ("uvarovite like" clusters) exist.

In both cases the mentioned change of Cr³⁺ crystal field parameters is caused by an increase of the Ca amount and as result of increasing Cr-O distances and their covalency. However, in the first case (trend (a)) Ca atoms replace Mg in local environment of Cr³⁺ and in the second one (trend (b)) – in the Cr-free parts of the garnet structure.

References

- BOSENICK, A., DOVE, M.T. & GEIGER, C.A. (2000): *Phys. Chem. Minerals*, **27**: 398-418.
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