

The crystal chemistry of birefringent natural uvarovites: Part II. Single-crystal X-ray structures

MANFRED WILDNER* AND MICHAEL ANDRUT

Institut für Mineralogie und Kristallographie, Universität Wien, Geozentrum, Althanstrasse 14, A-1090 Wien, Austria

ABSTRACT

The crystal structures of six birefringent uvarovite-grossular garnets from three localities (Saranov, Veselovsk, and Saranka, Ural Mountains, Russia) were investigated using single-crystal X-ray CCD diffraction data. The intensity and lattice parameter data attest to the violation of the cubic garnet space group $Ia\bar{3}d$ and the symmetry reduction to subgroups with triclinic ($I\bar{1}$), monoclinic ($I2/a$), or at most orthorhombic symmetry ($Fddd$). Careful structure refinements starting in space group $I\bar{1}$ reveal that partial long-range Cr^{3+}/Al ordering on the octahedral sites is the most prominent non-cubic feature. For each crystal, a nearly perfect linear correlation of the individual octahedral size with its Cr occupancy is observed. Considering the dependence on the bulk Cr mole fraction, the individual octahedral size in non-cubic uvarovite-grossular solid solutions is represented by $\langle \text{Cr}/\text{Al}-\text{O} \rangle$ (\AA) = $1.9247 + 0.0147 X_{\text{Cr}(\text{bulk})} + 0.0534 X_{\text{Cr}(\text{individual})}$. These uvarovites also structurally incorporate traces of hydrous component (<1 wt% H_2O) as O_4H_4 “hydrogarnet” substitution in a non-cubic way, thus leading to further subtle deviations from cubic symmetry. Within the range of these low water contents, the refined Si-O bond length, averaged over crystallographically different tetrahedra, correlates with the total integral OH absorption coefficient α_i through the equation $\langle \langle \text{Si}-\text{O} \rangle \rangle$ (\AA) = $1.6455 + 1.0074 \cdot 10^{-7} \alpha_i$ (cm^{-2}). Although the Si and Ca atoms occupy general positions in $I\bar{1}$, they deviate little from their respective special positions in $Ia\bar{3}d$.

Consistent with the respective angular lattice distortions, the refined Cr^{3+}/Al site distribution pattern is definitely triclinic in the Saranka sample, somewhat less pronounced triclinic (pseudomonoclinic) in the Veselovsk sample, and distinctively pseudo-orthorhombic or orthorhombic in all four samples from the Saranov locality. Considering crystal chemical evidence, three of the pseudo-orthorhombic Saranov samples with elevated water content appear to have triclinic symmetry as well, while one low-water uvarovite is classified as orthorhombic. These results are in good agreement with those of optical and UV-VIS-IR spectroscopic investigations reported in Part I of the present study (Andrut and Wildner 2001).

Previous structure data for birefringent garnets reported in the literature as non-cubic are compared and discussed. Special emphasis is also drawn to structural and crystal chemical details exhibiting a non-ideal mixing behavior along the uvarovite-grossular join. Evidence for and against the cation ordering models postulated in the literature are discussed.