

## **The crystal chemistry of birefringent natural uvarovites: Part I. Optical investigations and UV-VIS-IR absorption spectroscopy**

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### **ABSTRACT**

Six garnet crystals with compositions close to the uvarovite-grossular binary from three different localities (Saranov, Veselovsk, and Saranka, Ural Mountains, Russia) were investigated by optical methods, electron microprobe analysis, and polarized UV-VIS-IR micro-spectroscopy. Under crossed polarizers the crystals display “strong” birefringence in the order of 0.006 and formation of domains, aligned parallel to the crystal faces of the form  $\{110\}$ . Referring to the cubic cell,  $Y$  is always parallel to a principal lattice direction, e.g.,  $[010]_{\text{cub}}$ , whereas  $X$  and  $Z$  are then parallel to  $[101]_{\text{cub}}$  and  $[10\bar{1}]_{\text{cub}}$ , respectively.

The garnets are uvarovite-grossular solid solutions with 48 to 71 mol% uvarovite component and traces of Ti, Fe, Mn, and Mg, and exhibit no compositional zoning.

Polarized single crystal infrared absorption spectra in the region of the OH stretching vibration display 14 discernible, partly superimposing, and strongly anisotropic absorption bands between 3470 and 3680  $\text{cm}^{-1}$ , which are caused by structurally incorporated hydroxyl groups. The polarization behavior observed for individual samples complies with orthorhombic, monoclinic, and triclinic crystal symmetry, respectively. The water content calculated using an integral extinction coefficient,  $\epsilon = 43800 \text{ L/cm}^2 \cdot \text{mol}$ , ranges from 0.07 to 0.34 wt%. Annealing experiments indicate that the incorporation of hydroxyl groups is not the primary cause for the anisotropic behavior. Instead, cation ordering on octahedral positions may play an important role. This assumption is substantiated by single crystal X-ray diffraction investigations reported in Part II of the present study (Wildner and Andrut 2001).

Contrary to the IR spectroscopic data, single-crystal electronic absorption spectra show no significant polarization behavior in the UV-VIS-NIR spectral region. The observed absorption bands are caused by  $d-d$  transitions of  $\text{Cr}^{3+}$  cations in octahedral coordination. The linear extinction coefficients of the investigated uvarovites strongly indicate that the  $\text{Cr}^{3+}$  cations occupy centrosymmetric sites, regardless of the exact symmetry reduction from  $Ia\bar{3}d$ .