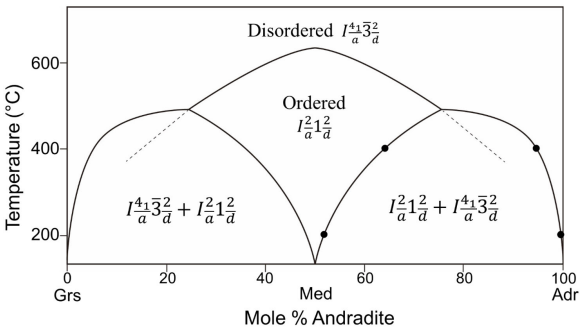
Goldschmidt 2023 Abstract
https://doi.org/10.7185/gold2023.16993

Cation ordering, phase transformation and miscibility gaps in silicate garnet ugrandite ternary system

HUIFANG XU[1], SHIYUN JIN[2], SEUNGYEOL LEE[3] AND PHILIP E BROWN[1]

[1]University of Wiscosin-Madison
[2]Gemological Institute of America
[3]Chungbuk National University
Presenting Author: hfxu@geology.wisc.edu

The crystal structure of a birefringent garnet (~$Adr_{53}Grs_{47}$) that occurs as a late-stage rim on andradite from Stanley Butte, Graham County, Arizona is analyzed and refined using single-crystal XRD. The structure has an orthorhombic (unconventional setting for *Fddd*) space group symmetry, with unit cell parameters of $a = b = 11.966(3)$ Å, $c = 11.964(3)$ Å, $\alpha = \beta = 90°$, $\gamma = 90.29(2)°$, $V = 1713.0(7)$ Å^3, $Z = 8$. The orthorhombic garnet displays very high birefringence ($\delta \sim 0.021$) produced by the strong Fe-Al ordering in the octahedral sites, with Fe occupancies of 0.804 and 0.221 in Y_1 and Y_2 sites, respectively. Diffraction peaks (such as 101 and 103) violating the symmetry of cubic garnet are obvious even in powder XRD pattern. The homogenization temperatures of the fluid inclusions suggest that the low crystallization temperature (~ 200 °C) is responsible for the ordered orthorhombic structure. The strong ordering state of the structure and the sharp boundaries in the chemical zoning in the crystal (between ~$Adr_{53}Grs_{47}$ and ~Adr_{100}) indicate the orthorhombic intermediate grandite garnet is a thermodynamically stable phase at low temperature, separated by wide miscibility gaps from the pure end members (grossular and andradite) with cubic structures. The solvi between orthorhombic Al-Cr garnet and its end-members (grossular & uvarovite) will be narrower than the solvi in the grossular-andradite binary system, because the difference between Al^{3+} and Cr^{3+} is smaller than the difference between Al^{3+} and Fe^{3+} in their ionic radii and chemical hardness (Xu et al. 2017). Most of the previously reported triclinic garnet structures are likely artifacts produced by pseudo-merohedral twinning of less ordered orthorhombic structure, as indicated by the characteristic pairing pattern of different octahedral Y-sites with the same occupancies.



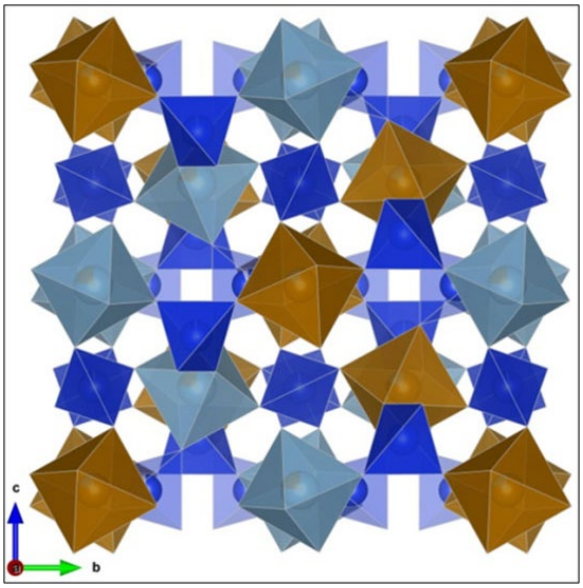


Figure 1: A phase diagram showing stability field for the ordered orthorhombic garnet with symmetry at low temperature.

Figure 2: Crystal structure of the Al-Fe ordered orthorhombic garnet showing ordered octahedra and tetrahedra.

References:

Xu, H., Xu, D.C., and Wang, Y. (2017) ACS Omega, 2, 7185–7193, https://doi.org/10.1021/acsomega.7b01039.

Xu, H., Jin, S., Lee, S., and Brown, P. E. (2023) American Mineralogist, 108, 572-583, https://doi.org/10.2138/am-2022-8455.