Cation ordering, twinning, and pseudo-symmetry in silicate garnet: The study of a birefringent garnet with orthorhombic structure

HUIFANG XU1,* , SHIYUN JIN1,2,†, SEUNGYEO LEE1,3,4,‡, and PHILIP E. BROWN4

1Department of Geoscience, University of Wisconsin-Madison, Madison, Wisconsin 53706, U.S.A.
2Gemological Institute of America, 5355 Armada Drive, Carlsbad, California 92008, U.S.A.
3USRA Lunar and Planetary Institute, 3600 Bay Area Boulevard, Houston, Texas 77058, U.S.A.
4Department of Earth and Environmental Sciences, Chungbuk National University, Cheongju 2864, Republic of Korea

ABSTRACT

The crystal structure of a birefringent garnet (~Adr53Gr3Si) 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 I2/a 22d (unconventional setting for Fddd) space group symmetry, with unit-cell parameters of a = b = 11.966(3) Å, c = 11.964(3) Å, a = β = 90°, γ = 90.29(2)°, V = 1713.0(7) Å³, Z = 8. The orthorhombic garnet displays very high birefringence (δ ~0.021) produced by the strong Fe-Al ordering in the octahedral sites, with Fe occupancies of 0.804 and 0.221 in Y1 and Y2 sites, respectively. Diffraction peaks (such as 101 and 103) violating the Ia3d symmetry of cubic garnet are obvious even in powder XRD pattern. The homogenization temperatures of the fluid inclusions suggest that the low-crystallization temperature 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 ~Adr53Gr3Si and ~Adr100) 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. 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 Y-sites with the same occupancies.

Keywords: Orthorhombic garnet, Fe-Al ordering, non-cubic garnet, birefringent garnet, pseudo-merohedral twinning, fluid inclusion

INTRODUCTION

Silicate garnets are common rock-forming orthosilicate minerals that occur in Earth’s crust and mantle, which have a general formula of X3Y2[SiO12], with X representing divalent cations in triangular dodecahedron (distorted cube) (i.e., Ca2+, Fe2+, and Mg2+), and Y representing trivalent cations in regular octahedral site (i.e., Cr3+, Al3+, and Fe3+) (Geiger 2008, 2016; Grew et al. 2013). The tetrahedrally coordinated Si site is known as Z site, which can be occupied by elements such as Al, Fe, or V in non-silicate garnets (Grew et al. 2013). A significant amount of structural OH− (water) may be incorporated in these nominally anhydrous minerals, mostly through the hydrogarnet substitution (Lager et al. 1989; Grew et al. 2013; Geiger and Rossman 2018, 2020). Although silicate garnets generally have cubic (Ia3d) symmetry, birefringence is often observed in the grossular (Grs, Ca3Al2Si3O12) – andradite (Adr, Ca3Fe3+Si3O12) solid solution (grandite garnet). [The IMA-CNMNC approved mineral symbols (abbreviations) are used to describe the garnet compositions in this paper (Warr 2021).] Similar effects have been recently reported in the less-studied uvarovite (Uv, Ca3Cr2Si4O12) – grossular solid solution (Andrut and Wildner 2001, 2002; Wildner and Andrut 2001; Andrut et al. 2002). Fine-scale oscillatory zoning, supposedly related to the anisotropy, is also commonly observed in grandite garnets (Lessing and Standish 1973; Murad 1976; Jamtveit 1991; Jamtveit et al. 1993, 1995; Pollok et al. 2001; Antao 2013b; Antao et al. 2015). Some of the sub-micrometer periodic zoning near the surface can create spectacular iridescent colors similar to those observed in labradorite, making gemstones (Ingerson and Barksdale 1943; Akizuki et al. 1984; Hainschwang and Notari 2006; Nakamura et al. 2017).

Various reasons have been proposed to explain the optical anomaly of the calcium silicate garnets, including plastic deformation (Allen and Buseck 1988), magneto-optical effects from rare-earth elements substituting for Ca (Blanc and Maisonneuve 1973), non-cubic orientation of the OH− groups (Rossman and Aines 1986), or residual strain from chemical zoning or twin boundaries (Chase and Lefever 1960; Lessing and Standish 1973; Foord and Mills 1978; Antao 2013a, 2013b, 2021a, 2021b; Antao and Klincker 2013; Antao et al. 2015). Among all the hypothesized reasons, symmetry reduction due to cation ordering remains the most widely proposed (Takeuchi and Hagai 1976; Takeuchi et al. 1982; Gali 1983; 1984; Akizuki 1984, 1989, 1989; Allen and Buseck 1988; Hatch and Griffen 1989; Kingma...