Static disorders of atoms and experimental determination of Debye temperature in pyrope: Low- and high-temperature single-crystal X-ray diffraction study

AKIHKO NAKATSUKA,1,* MAMI SHIMOKAWA,1 NORIAKI NAKAYAMA,1 OSAMU OHTAKA,2 HIROSHI ARIMA,3 MAKI OKUBE,4 AND AKIRA YOSHIASA5

1Graduate School of Science and Engineering, Yamaguchi University, Ube 755-8611, Japan
2Graduate School of Science, Osaka University, Toyonaka 560-0043, Japan
3J-PARC Center, Japan Atomic Energy Agency, Ibaraki 319-1195, Japan
4Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan
5Graduate School of Science and Technology, Kumamoto University, Kumamoto 860-8555, Japan

ABSTRACT

Low- and high-temperature single-crystal X-ray diffraction studies of synthetic pyrope garnet have been conducted at 20 temperature-points over a wide temperature range from 96.7 to 972.9 K. From precise structure refinements, the possibility of static disorder and anharmonic thermal vibration of Mg in the dodecahedral site, which has long been under debate, has been assessed together with the thermal expansion behavior. Application of the Debye model to the temperature dependence of the resulting mean square displacements (MSDs) of atoms shows that they clearly include significant static disorder components in all the constituent atoms, of which Mg has the most dominant static disorder component. The residual electron density analyses and the structure refinements based on the split-atom model at a low temperature of 96.7 K provide direct proof of the Mg static disorder. Anharmonic structure refinements applying the Gram-Charlier expansion up to the fourth-rank tensor show that the anharmonic contribution to atomic thermal vibrations begins to appear in all atoms except Si at a high temperature of \( T > 800 \) K. However, at lower temperatures, anharmonic refinements show no sign of anharmonic thermal vibrations on any atom and instead provide an indication of their static disorder.

Keywords: Garnet, static disorder, Debye temperature, anharmonic thermal vibration, thermal expansion, single-crystal X-ray diffraction

INTRODUCTION

Garnets have attracted much attention in various research fields from solid-state physics to Earth science. Since silicate garnets are major constituents of the Earth’s crust, upper mantle, and transition zone, they are important to elucidate physical properties, phase relations, and dynamics in the Earth’s interior. Although most natural garnets occur commonly as complex multi-component solid solutions, the most significant component in garnets of mantle origin is pyrope (Mg\(_2\)Al\(_2\)Si\(_3\)O\(_{12}\)), composed of the major elemental components of the mantle. Therefore, the investigation of the structural, physical, and thermodynamic properties of pyrope is important for the understanding of the Earth’s mantle.

Pyrope crystallizes in cubic symmetry with the highest space group \( Ia\overline{3}d \). The cubic garnets \( X_3Y_2Z_4O_{12} \) have three symmetrically distinct cation sites (Fig. 1): the eightfold-coordinated \( X \) site [Wyckoff position 24e at \((0.125, 0, 0.25)\)], the sixfold-coordinated \( Y \) site [Wyckoff position 16a at \((0, 0, 0)\)], and the fourfold-coordinated \( Z \) site [Wyckoff position 24d at \((0.375, 0, 0.25)\)]. The \( X, Y, \) and \( Z \) cations are coordinated dodecahedrally, octahedrally, and tetrahedrally by \( O \) atoms, located at the Wyckoff position 96h at \((x, y, z)\), respectively. These three types of coordination polyhedra link in a complex manner; a \( \text{ZO}_3 \) tetrahedron shares edges with two \( \text{XO}_4 \) dodecahedra, a \( \text{YO}_6 \) octahedron with six \( \text{XO}_4 \) dodecahedra, and a \( \text{XO}_6 \) dodecahedron with two \( \text{ZO}_4 \) tetrahedra, four \( \text{YO}_6 \) octahedra, and four other \( \text{XO}_6 \) dodecahedra. The linkage between tetrahedra and octahedra is made by mutually sharing all corners. In pyrope, which is stable only at high pressure as confirmed by geological occurrence and synthetic experiments, the dodecahedral, octahedral, and tetrahedral sites are occupied by Mg, Al, and Si, respectively. In terms of crystal chemistry, this coordination environment of Mg is apparently unreasonable because the dodecahedral cavity size is too large for the ionic radius of Mg, which would fit better into the octahedral site as expected from Pauling’s first rule (Pauling 1929). This geometric anomaly implies the possibility of positional disorder (static disorder) or large thermal vibration (dynamic disorder) of Mg (including the possibility of anharmonic contribution to the thermal vibration). Indeed, structural and thermodynamic studies of pyrope have reported the following experimental observations suggesting these possibilities: (1) anomalously large atomic displacement parameters (ADPs) of Mg in pyrope observed by diffraction method (Gibbs and Smith 1965; Novak and Gibbs 1971; Armbruster et al. 1992; Pavese et al. 1995; Artioli et al. 1997); (2) an anomalously high heat capacity at low temperature observed in pyrope (Haselton and Westrum 1980; Kieffer 1980; Hofmeister and Chapelas 1991) and a positive excess entropy observed in its solid solutions with