

Atomic displacement behavior of pyrope

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Introduction

Pyrope garnet ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) is an important mineral as constituents in the Earth's upper mantle. This garnet crystallizes in cubic symmetry ($Ia\bar{3}d$), and Mg, Al and Si occupy dodecahedral, octahedral and tetrahedral sites, respectively. 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. This geometric anomaly is reminiscent of the possibility of positional disorder (static disorder) of Mg, together with the possibility of its large thermal vibration (dynamic disorder). Indeed, it is well known that the displacement parameter of Mg in pyrope is much larger than those in other silicate garnets. However, conclusive evidence for the Mg static disorder has not yet been provided although its presence has long been debated [1, 2]. In the present study, we investigate temperature dependence of the mean square displacements (MSD) of atoms in pyrope to examine the possibility of the Mg static disorder.

Experimental

Single crystal of pyrope ($0.14 \times 0.11 \times 0.11 \text{ mm}^3$ in size) synthesized at 5 GPa and 1573 K was used in the present study. The crystal was put into a silica-glass capillary for X-ray diffraction intensity measurements. Intensity data were collected at 20 temperature-points in the range of 97–973 K. The data collections at 97–273 K were performed in the wavelength $\lambda = 0.70 \text{ \AA}$ using a vertical-type four-circle diffractometer at BL-10A, Photon Factory, KEK, Japan. The data collections at 295–973 K were performed using a Rigaku AFC-7R four-circle diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). All the data collections were carried out within $2^\circ \leq 2\theta \leq 100^\circ$. After the corrections for L_p factors, absorption effects and thermal diffuse scattering, the intensity data were averaged in Laue symmetry $m\bar{3}m$. Consequently, independent reflections between 211 and 328 with $F_o > 6\sigma(F_o)$ were used in the structure refinements at each temperature. The correction for extinction effects was made during the refinements.

Results and discussion

The U_{eq} data, corresponding to the mean square displacements (MSD) of atoms averaged over all

directions, were fitted to the following equation based on the Debye model to extract the contribution of static disorder to MSD (Fig. 1):

$$\text{MSD} = \langle u^2 \rangle_{\text{static}} + \langle u^2 \rangle_{\text{dynamic}} = \langle u^2 \rangle_{\text{static}} + \frac{3\hbar^2 T}{mk_B \Theta_D^2} \left[\Phi\left(\frac{\Theta_D}{T}\right) + \frac{1}{4} \frac{\Theta_D}{T} \right]$$

$$\Phi\left(\frac{\Theta_D}{T}\right) = \frac{T}{\Theta_D} \int_0^{\frac{\Theta_D}{T}} \frac{x}{\exp(x)-1} dx$$

where $\langle u^2 \rangle_{\text{static}}$ is the temperature-independent static disorder component, $\langle u^2 \rangle_{\text{dynamic}}$ the temperature-dependent dynamic disorder component, m the mass of atoms, k_B the Boltzmann constant, \hbar the Planck constant, Θ_D the Debye temperature and T the absolute temperature. The resulting $\langle u^2 \rangle_{\text{static}}$ are $1.43(10) \text{ \AA}^2$ for Mg, $0.64(5) \text{ \AA}^2$ for Al, $0.68(6)$ for Si and $0.57(4) \text{ \AA}^2$ for O, which have significantly positive values with the high reliability levels of 11–14 σ for each atom. In particular, the $\langle u^2 \rangle_{\text{static}}$ value of Mg is the most dominant. The resulting Θ_D values, corresponding to characteristic vibrational frequencies, are 482(2) K for Mg, 723(3) K for Al, 754(4) K for Si and 789(2) for O; these become larger in order of Mg \ll Al $<$ Si $<$ O. This relationship in the cations is reasonably consistent with bonding stiffness expected from the thermal expansion of the bond lengths.

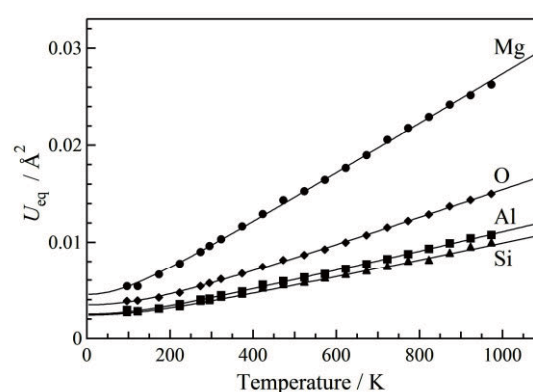


Fig. 1. Variation of U_{eq} as a function of temperature.

References

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