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

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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