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Microscopic strain in a grossular-pyrope solution anti-correlates with excess volume through local Mg-Ca cation arrangement, more strongly at high Ca/Mg ratio

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Abstract

Unit-cell volume and microstrain of $Py_{40}Gr_{60}$ garnets vary with synthesis temperature and annealing time, showing a strong *negative* correlation, as is also seen in another garnet solid solution, $Py_{20}Gr_{80}$. This anti-correlation is explained by local Ca-Mg cation arrangement in which Ca-Ca and Mg-Mg third-nearest-neighbor (Same 3NN = S3NN) pairs form at rates other than those expected from random Ca-Mg distribution. S3NN pairs cause microstrain (Bosenick et al. 2000) but allow more efficient packing than random Ca-Mg pairings that contribute to excess volume, hence smaller cell volumes correlate with more microstrain. Both longer annealing time and higher heating temperature cause more S3NN formation, larger microscopic strain, and smaller unit-cell volume. The anti-correlation of microstrain and excess volume is weaker in our previous study of pyrope-rich solutions (i.e., $Py_{80}Gr_{20}$, Du et al. 2016) because excess volume varies little from Ca-Ca S3NN pairings in pyrope-rich solutions, whereas Mg-Mg S3NN pairings in grossular-rich solutions studied here are effective at reducing excess volume. Heating to 600 °C under room pressure or cold hydrostatic compression to 10 GPa does not reset microstrain.

Margules' formulations for microstrain and volume as a function of Ca/Mg ratio captures these features, especially the two-peaked distribution of microstrain with composition discovered by Du et al. (2016). The similar two-peaked distributions of microstrain and excess energies derived from ab initio calculation with short-range ordering of Mg and Ca cations (Vinograd and Sluiter 2006) indicate that the macroscopic thermodynamic mixing properties of solid solutions are directly related to arrangement of cations with large size misfit. The observed changes of microstrain with annealing temperature suggest that mixing properties measured from our pyrope-grossular garnet solid solutions synthesized at same temperature can serve as better experimental constrains for computational work.

Keywords: Pyrope-grossular garnet solid solution, high temperature, FWHM, microstrain, unit-cell volume