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Excess mixing volume, microstrain, and stability of pyrope-grossular garnets

Wei Du[1,*], Simon Martin Clark[2,3], and David Walker[1]

[1]Lamont-Doherty Earth Observatory and Department of Earth and Environmental Sciences, Columbia University in the City of New York, Palisades, New York 10964, U.S.A.
[2]Department of Earth and Planetary Sciences, Macquarie University, North Ryde, New South Wales 2109, Australia
[3]The Bragg Institute, Australian Nuclear Science and Technology Organization, Locked Bag 2001, Kirrawee DC, New South Wales 2232, Australia

Abstract

Synchrotron X-ray diffraction (XRD) was used to measure the unit-cell parameters of synthetic pyrope ($Mg_3Al_2Si_3O_{12}$), grossular ($Ca_3Al_2Si_3O_{12}$), and four intermediate garnet solid solutions. Garnets synthesized dry in multi-anvil (MA) apparatus at 6 GPa show irregular asymmetric positive quenchable excess volumes, with binary Margules parameters $W_{V_{\text{grossular}}} = 2.04 \pm 0.14$ cm^3/mol, and $W_{V_{\text{pyrope}}} = 4.47 \pm 0.15$ cm^3/mol. The two-parameter Margules equation is only an approximate description of the excess volumes in the pyrope-grossular garnets from this study and from the literature. The values for intermediate garnets in this report are roughly a factor of ~3 larger than previous literature reports of excess volumes of garnets grown at piston-cylinder (PC) pressures (2–4 GPa) with hydrothermal assistance. The discrepancy between our large dry excess volumes and the smaller hydrothermally assisted syntheses previously reported in the literature may be due in part to the hydrothermal assistance. When we do damp syntheses, we too get small excess volume. Although dampness produces smaller excess volumes, the mechanism by which this is achieved remains to be discovered. Does dampness relieve microstrains to relax excess volumes? Analysis of synchrotron X-ray diffraction profiles by using Williamson-Hall plots to test for microstrain shows that peak width does change with dampness and with garnet composition. Microstrain in the garnet structure, rather than grain size variation, is the principal reason for the observed XRD peak broadening. Damp garnets at $Py_{60}Gr_{40}$ have less microstrain and lower excess volume than dry $Py_{60}Gr_{40}$, in accord with the working hypothesis that dampness is responsible for diminished excess volume through strain relief. However garnets with compositions $Py_{80}Gr_{20}$ and $Py_{20}Gr_{80}$, close to the negligibly strained end-members pyrope (Py_{100}) and grossular (Gr_{100}), have large microstrains but relatively small excess volume. This is in contrast to $Py_{40}Gr_{60}$, which has the largest excess volume but almost no microstrain. (The end-members have no excess volume, by definition, and little microstrain.) This uncorrelated behavior demonstrates that microstrain in general is not directly related to the excess volumes, whatever else dampness may do to a specific composition, for instance introduce a small amount of clinopyroxene into the mode that partitions Ca preferentially away from garnet. Thus the mechanism responsible for the difference between our large excess volumes and the smaller ones in the literature may not be as complete or as simple as dampness relieves microstrain and relaxes excess volume. Our dry intermediate garnets have already been relieved of their microstrain by some other mechanism than dampness and still have large excess volume. The state of Ca-Mg ordering may also change, and we show that this may have a small effect on the excess volume through experiments using variable synthesis time and temperature. A potential test for whether our large, complex excess volumes, of whatever origin, are real (or not) is whether the rise of the solvus with pressure is better described by our large excess volumes or those smaller ones in the literature. We observe garnet phase exsolution at 8 GPa and show it to be reversible, at a temperature consistent with theoretical calculation using the large mixing volume presented in the current study.

Keywords: Pyrope-grossular garnet solid solution, excess volume, microstrain, garnet exsolution