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Cation order/disorder behavior and crystal chemistry of pyrope-grossular garnets: An ^{17}O 3QMAS and ^{27}Al MAS NMR spectroscopic study

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Abstract

The thermodynamic mixing properties of the pyrope-grossular solid solution show large deviations from ideality, which could be partly related to Ca-Mg order/disorder. In this study, synthetic pyrope-grossular garnets with X_{Mg} = 1.00, 0.91, 0.75, 0.50, 0.24, 0.10, and 0.00 are observed using ^{17}O 3QMAS, ^{27}Al MAS, and ^{29}Si MAS NMR to examine Ca-Mg order/disorder behavior and crystal chemical variations. The ^{17}O 3QMAS NMR spectra show four distinct resonances, assigned to four different local oxygen coordination environments; two resemble end-member garnets (oxygen bonded to two Mg or two Ca) and two are intermediate (oxygen bonded to one Ca and one Mg), indicating that there are two distinct bond distances for the Mg-O and/or Ca-O bonds through the entire solid solution. Noticeable changes in the NMR peak position for two of the oxygen sites suggest that as X_{Mg} increases, the longer Ca-O bond shortens. The relative areas for the different oxygen sites are close to those predicted using a model of random Ca/Mg mixing. The maximum allowed reduction in configurational entropy from first neighbor Ca-Mg ordering is insignificant relative to other configurational entropy reductions and excess vibrational entropy. These conclusions are not inconsistent with published theoretical calculations suggesting some Ca-Mg ordering that involves correlations beyond the first neighbor, as suggested by published theoretical calculations. Even at 18.8 Tesla, the ^{27}Al MAS NMR spectra do not resolve different local Al sites with varying combinations of X cation neighbors. The ^{29}Si MAS NMR spectra have resonance broadening, probably caused by the addition of 0.15 wt% Fe_2O_3 in the synthetic samples, and are consistent with published results suggesting a small degree of Ca-Mg ordering that is not reflected in the ^{17}O NMR spectra.

Keywords: NMR spectroscopy, pyrope, grossular, order-disorder, garnet, oxygen-17, aluminum-27, silicon-29