

Local Ca-Mg distribution of Mg-rich pyrope-grossular garnets synthesized at different temperatures revealed by ^{29}Si MAS NMR spectroscopy

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ABSTRACT

Pyrope-grossular solid solutions, $(\text{Mg,Ca})_3\text{Al}_2\text{Si}_3\text{O}_{12}$, of composition $\text{Py}_{85}\text{Gr}_{15}$ and $\text{Py}_{75}\text{Gr}_{25}$ were synthesized at 1000, 1200, and 1400 °C and 30 kbars in a piston-cylinder device. The synthetic garnets were characterized using optical, microprobe, and X-ray methods and their Ca-Mg distributions were investigated using ^{29}Si MAS NMR spectroscopy. The syntheses produced 100% garnet except for those undertaken at 1000 °C, where small amounts (up to 3%) of clinopyroxene were present. X-ray powder refinements showed differences up to 0.01 Å in the unit-cell dimension of the garnets synthesized at the three different temperatures. A general decrease of the X-ray diffraction line widths with increasing synthesis temperature is observed. The ^{29}Si NMR spectra of $\text{Py}_{85}\text{Gr}_{15}$ show little change as a function of synthesis temperature. In the spectra of $\text{Py}_{75}\text{Gr}_{25}$ small but measurable changes in the relative peak intensities, depending upon synthesis temperature, were observed with a more random cation distribution corresponding to a higher synthesis temperature. None of the garnets investigated has a completely random Ca-Mg distribution. The reduction in configurational entropy compared to the disordered state is estimated to be less than 2 J/mol·K.