American Mineralogist, Volume 87, pages 542–549, 2002

The crystal structures of grossular and spessartine between 100 and 600 K and the crystal chemistry of grossular-spessartine solid solutions

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ABSTRACT

Spessartine ($Mn_3Al_2Si_3O_{12}$)-grossular ($Ca_3Al_2Si_3O_{12}$) solid solutions were synthesized at high pressures and temperatures. Compositionally homogeneous garnets are obtained by crystallizing solid-solution glasses prepared from oxides. The unit-cell parameter, *a*, for the different solid solutions was determined by X-ray powder diffraction methods and the results give positive deviations from ideal volumes of mixing that can be described with a symmetric mixing model with $W^v = 0.80$ (± 0.04) cm^3/mol. The degree of non-ideality is a function of the difference in size between the Ca^{2+} and Mn^{2+} cations and is consistent with the range of those observed for the other aluminosilicate garnet binary joins. The crystal structures of synthetic grossular and spessartine were collected at 50 K intervals between 103 K and 498/648 K using single-crystal X-ray diffraction methods. The rotation of the rigid SiO_4 tetrahedra changes slightly by 0.3(1)° for grossular and 0.2(1)° for spessartine between 103 and 648 K. The volume expansions of the polyhedra were calculated and their distortions in grossular and spessartine were analyzed as a function of temperature. The linear thermal expansion coefficients of the Al-O and two X-O bond were also calculated for almandine, pyrope, grossular, and spessartine. The thermal expansion of spessartine is similar to that of grossular. In terms of polyhedral distortion and bond-valence values, spessartine has the most ideal structure of the aluminosilicate garnets. This could explain its large *P-T* stability field and the ease of synthesis at low pressures.