

Mn₃Al₂Si₃O₁₂ spessartine and Ca₃Al₂Si₃O₁₂ grossular garnet: Structural dynamic and thermodynamic properties

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ABSTRACT

The structures of synthetic Mn₃Al₂Si₃O₁₂ spessartine and Ca₃Al₂Si₃O₁₂ grossular garnet have been refined using single-crystal X-ray diffraction methods at 100 K, 293 K, and 500–550 K. The divalent X-site cations, located in large dodecahedral sites, show measurable anisotropic dynamic disorder in contrast to the rigid vibrational behavior of the SiO₄ tetrahedra and AlO₆ octahedra. The amplitudes of vibration of Mn²⁺ in spessartine are similar to those of Fe²⁺ of almandine, in the plane of the longer X-O(4) bonds, and both are about twice that of Ca²⁺ in grossular, despite the lighter mass of the latter. Heat capacities measured between 300 and 1000 K on synthetic polycrystalline spessartine and two natural nearly end-member spessartine crystals are similar to those of almandine. In addition, the IR active modes of spessartine at low frequencies are very similar to those of almandine suggesting that their heat capacities are also similar at lower temperatures. The low-energy phonon spectra of pyrope and grossular are probably considerably distinct from the two transition metal-containing garnets as suggested by their different low frequency IR active modes, reflecting the different bonding properties for Mg and Ca in garnet. The large pressure-temperature stability field of spessartine, relative to the other aluminosilicate garnets, does not appear to be due to any sort of intrinsic entropy stabilization.