Mn$_3$Al$_2$Si$_3$O$_{12}$ spessartine and Ca$_3$Al$_2$Si$_3$O$_{12}$ grossular garnet: Structural dynamic and thermodynamic properties

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ABSTRACT

The structures of synthetic Mn$_3$Al$_2$Si$_3$O$_{12}$ spessartine and Ca$_3$Al$_2$Si$_3$O$_{12}$ 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 SiO$_4$ tetrahedra and AlO$_6$ octahedra. The amplitudes of vibration of Mn$^{2+}$ in spessartine are similar to those of Fe$^{2+}$ of almandine, in the plane of the longer X-O(4) bonds, and both are about twice that of Ca$^{2+}$ 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.

INTRODUCTION

The garnet group is extremely diverse showing a wide compositional range (e.g., Geller 1967). One class of garnet, the silicate garnets of space group $Ia\overline{3}d$ (Menzer 1928), which occur commonly in nature, are, in addition, thermodynamically stable over very large pressure and temperature regimes. They show, in comparison with most silicate structures, little in the way of phase transitions or instability as a function of pressure and temperature. The aluminosilicate garnets of the general formula X$_3$Al$_2$Si$_3$O$_{12}$, where for the most common end-members X$^{2+}$ (almandine), Ca$^{2+}$ (grossular), Mn$^{2+}$ (spessartine), and Mg$^{2+}$ (pyrope), are a good example for such phase stability. As a group, they are stable from 1 atm up to several 10s of GPa from roughly 400 °C to very high temperatures. The aluminosilicate garnets also possess the ability to form extensive solid solutions, as shown by the mixing of different cations on the dodecahedral X-site, Wycoff position 24(c).

The static structural description of garnet, largely based on room temperature diffraction experiments, is well known since its initial structure determination by Menzer (1928). Recently, the dynamic properties of the polyhedral units and the X-site cations of some of the end-member silicate garnets (almandine, pyrope, and andradite-Ca$_3$Fe$_2$Si$_3$O$_{12}$) have been investigated by temperature-dependent, X-ray single-crystal refinements between 100 and 500 K (Geiger et al. 1992; Armbruster et al. 1992; Armbruster and Geiger 1993). An analysis of the atomic mean-square difference displacement parameters (Bürgi 1989) as a function of temperature shows that the SiO$_4$ tetrahedra and the AlO$_6$ octahedra can be considered as rigid bodies over this temperature range, thus confirming the static polyhedral description of the structure (Zemann 1962). The divalent X-site cations show, in contrast, substantial anisotropic dynamic disorder in the large irregular dodecahedral site (Geiger et al. 1992; Armbruster et al. 1992; Armbruster and Geiger 1993). Recognition of this dynamic disorder allows new insight into the garnet structure and has enabled, for example, several unusual and previously not understood spectroscopic features to be elucidated (Geiger et al. 1992; Quartieri et al. 1997; Kolesov and Geiger, in press).

In addition, thermodynamic properties such as heat capacity could depend on the dynamic properties of the X-site cations. The relatively large heat capacity of pyrope at low temperatures (Haselton and Westrum 1980), for example, may be related to the large amplitude, low energy vibrations of the Mg cations. The phonon density of states of the silicate garnets is unknown. Only a few