Order parameter variation through the $C2/m$-$P2_1/m$ phase transition in cummingtonite

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ABSTRACT

The $C2/m$-$P2_1/m$ phase transition in natural cummingtonites, with different compositions, has been investigated by single-crystal X-ray diffraction and powder absorption IR spectroscopy. Variations in the intensity of type $b$ (superlattice) reflections above room temperature are consistent with the transition being thermodynamically continuous and conform to the solution to a 2-4-6 Landau potential. Parameters extracted from IR spectra collected both above and below room temperature suggest that the local structural evolution differs slightly from the average macroscopic behavior observed by X-ray diffraction. Changes in wavenumber of an isolated absorption band at ∼1130 cm$^{-1}$ and changes in the integrated intensity of a band at ∼760 cm$^{-1}$ can be described by the solution to a 2-4 Landau potential with saturation below room temperature. Absorption bands due to O-H vibration and libration, however, appear to show discontinuities in the variation of their wavenumbers at the transition point. A local mechanism for the transition might involve a framework distortion providing the main driving force, with coupling to an order-disorder process for the protons.

INTRODUCTION

In comparison with framework silicates, phase transitions in chain silicates are relatively rare. Perhaps the best known are the $C2/m$-$P2_1/m$ transition in cummingtonite (Prewitt et al. 1970) and the $C2/c$-$P2_1/c$ transition in pigeonite (Smyth 1969). Geometrical aspects of the structural changes involved in these transitions are well understood. Tetrahedra in the amphibole or pyroxene chains rotate to produce changes in the coordination of cations at the M4 site in cummingtonite and of cations at the M2 site in pigeonite. The M4 or M2 sites are relatively open in the C-face centered structures at high temperatures, but are significantly contracted in the $P$ structures at low temperatures. Renewed interest over the last few years has led to a better characterization of the transition boundaries in pressure-temperature-composition space. Both transitions can be induced by changing pressure or temperature (Angel et al. 1992; Angel and Hugh-Jones 1994; Hugh-Jones et al. 1994; Yang and Smyth 1996; Arlt and Armbruster 1997; Arlt et al. 1998, 2000; Yang et al. 1998; Arlt and Angel 2000a; Boffa Ballaran et al. 2000, 2002; Cámara et al. 2002; Tribaudino et al. 2001, 2002), depending on composition and the degree of non-convergent order of cations between the M sites (Prewitt et al. 1971; Hirschmann et al. 1994; Yang and Hirschmann 1995; Boffa Ballaran 2000, 2001; Cámara et al. 2002).

Although the two $C$-$P$ transitions are closely analogous in many respects, they also show some significant differences. Most notably, the sequence with increasing pressure at room temperature is $C2/m$ → $P2_1/m$ for amphiboles (Yang et al. 1998; Boffa Ballaran et al. 2000), but $P2_1/c$ → $C2/c$ for Fe-, Mn-, and Mg-bearing pyroxenes (Angel et al. 1992; Hugh-Jones et al. 1994; Angel and Hugh-Jones 1994; Arlt et al. 1998, 2000; Tribaudino et al. 2001). In addition, while the $C2/m$ structure of cummingtonites in the high pressure and high temperature stability fields appears to be essentially the same (e.g., compare structural parameters given by Yang and Hirschmann 1995; Yang et al. 1998; Boffa Ballaran et al. 2001), the high pressure $C2/c$ structure of the pyroxenes differs from the high temperature $C2/c$ structure in that the tetrahedral chains are strongly kinked in the former and relatively extended in the latter (Hugh-Jones et al. 1994; Arlt et al. 1998, 2000; Shimobayashi et al. 1998, 2001; Arlt and Angel 2000a, 2000b; Miyake et al. 2002). Another difference relates to the thermodynamic character of the transitions. All the cummingtonite crystals that have been examined at high pressures display continuous variations of spontaneous strains and of the intensities of superlattice ($b + k = 2n + 1$) reflections through the transition. Yang et al. (1998) concluded that the transition is close to tricritical in character, while Boffa Ballaran et al. (2000) found that a 2-4-6 Landau potential provides a good description of the structural evolution. In contrast, the $P2_1/c$ → $C2/c$ transitions in pyroxenes are generally first order in character as a function of increasing pressure (Angel et al. 1992; Hugh-Jones et al. 1994; Angel and Hugh-Jones 1994; Arlt et al. 1998, 2000; Arlt and Angel 2000a, 2000b). However, Tribaudino et al. (2001) reported a continuous variation of lattice parameters through the transition in a Ca-rich clinoenstatite, but they also noted that their sample was not totally homogenous with respect to composition. The $C$-$P$ amphibole transition appears to be thermodynamically continuous as a function of temperature (Sueno et al. 1972; Reece et al. 2000), though experimental data are sparse. The pyroxene transition can be first order or thermodynamically continuous as a function of temperature, depending on the compositions of the crystals being investigated (Smyth...