Acoustic dissipation associated with phase transitions in lawsonite, CaAl₂Si₂O₇(OH)₂·H₂O

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ABSTRACT

Resonant ultrasound spectra of a single crystal and a polycrystalline sample of lawsonite [CaAl₂Si₂O₇(OH)₂·H₂O] have been measured at room temperature and at low temperatures in the region 20–300 K. The influence of known phase transitions at 125 and 270 K is seen in the frequency variations of the resonance peaks, which are indicative of elastic stiffening, and in values for the quality factor QQF, which are indicative of dissipation. Two dissipation peaks, at ~250 and ~210 K, are interpreted as being due to the proton order-disorder processes associated with the two species of hydrogen atoms in the structure: one in hydroxyl OH groups and one in the H₂O molecules. These occur below the \textit{Pmcn} ↔ \textit{P}₂\textit{cn} transition point but coincide with changes in the shear elastic constants and in features of IR spectra reported elsewhere. A third, much smaller, dissipation peak occurs immediately below the \textit{P}₂\textit{cn} ↔ \textit{P}₂\textit{cn} transition point. The combination of these anomalies in acoustic dissipation and in elastic constants is consistent with the view that the \textit{Cmcm} ↔ \textit{Pmcn} transition is driven both by displacive and proton ordering effects. For the \textit{Pmcn} ↔ \textit{P}₂\textit{cn} transition, dissipation and the transition are more closely related, consistent with the view that the transition is driven essentially by proton ordering.

Keywords: Lawsonite, resonant ultrasound spectroscopy, dissipation, proton ordering

INTRODUCTION

Lawsonite [CaAl₂Si₂O₇(OH)₂·H₂O] is of interest in Earth sciences due to its unusually high water content (~11.5 wt% H₂O) and high density. It is formed from hydration of the anorthite component of rocks in regions of high-pressure, low-temperature metamorphism, and has a wide degree of shear anisotropy, resulting in a distinctive seismic signature when it is present in abundance at depth in the Earth (Sinogeikin et al. 2000).

Lawsonite undergoes two reversible phase transitions at low temperature associated with rearrangement of hydrogen bonds within the structure (Libowitzky and Armbruster 1995; Libowitzky and Rossman 1996). At 270 K, there is a transition from the room temperature orthorhombic \textit{Cmcm} structure, with dynamically disordered hydroxyl OH groups and H₂O molecules, to the \textit{Pmcn} phase in which H₂O and OH groups are systematically rotated within the (100) plane, thus strengthening some hydrogen bonds and weakening others. The \textit{Pmcn} structure persists to 125 K in a natural sample (155 K in a deuterated sample), where there is a transition to a polar (ferroelectric) \textit{P}₂\textit{cn} structure due to unidirectional shifts of the hydrogen atoms of the H₂O and OH groups along the x axis (Libowitzky and Armbruster 1995; Carpenter et al. 2003). The 270 K transition is tricritical in character and the 125 K transition is second order, but the thermodynamic properties do not follow exactly the expected behavior for classical tricritical and second-order transitions (Sondergeld et al. 2000a, 2000b, 2005; Meyer et al. 2000, 2001; Martin-Ollala et al. 2001; Hayward et al. 2002; Carpenter et al. 2003; Schranz et al. 2005).

The symmetry changes at the two phase transitions have been investigated in great detail using X-ray diffraction (Libowitzky and Armbruster 1995) and FTIR spectroscopy (Libowitzky and Rossman 1996). Further works on lawsonite using X-ray diffraction (Sondergeld et al. 2005; Schranz et al. 2005), strain analysis (Carpenter et al. 2003), calorimetry (Martin-Ollala et al. 2001; Hayward et al. 2002), transmission electron microscopy (Cámara et al. 2001), and optical, elastic, and dielectric studies (Sondergeld et al. 2000b, 2005) have confirmed the occurrence of these phase transitions and the anomalies observed due to changes in the hydrogen bonds within the structure. Powder neutron diffraction studies (Meyer et al. 2001; Carpenter et al. 2003) and infrared spectroscopy experiments (Meyer et al. 2000) have shown that displacive components involving framework distortions and proton ordering may contribute differently to the two phase transitions.

The temperature dependencies of the elastic constants of single crystals of lawsonite have been examined using Brillouin spectroscopy and plane wave resonance (Sinogeikin et al. 2000; Schilling et al. 2003; Sondergeld et al. 2005; Carpenter 2006). As a result of the phase transitions, the elastic constants show a complex pattern of softening and stiffening that depends on the...