Ordering and elasticity associated with low-temperature phase transitions in lawsonite

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ABSTRACT

The two low-temperature phase transitions of lawsonite have been studied using single-crystal X-ray diffraction from 86 to 318 K and a single-crystal high-frequency continuous-wave resonance technique from 323 to 102 K. While recently published data of the variations of strains, birefringence, and IR line widths are consistent with the (271 K) Cmcm-Pmcn transition being simply tricritical, our investigation of critical X-ray reflections and the six diagonal elastic constants of lawsonite reveals, consistently, a more complex crossover pattern in the temperature range of 205–225 K. Below 205 K the overall pattern is again in good agreement with a tricritical solution of the Cmcm-Pmcn transition and a second-order behavior of the (120 K) Pmcn-P2₁,cn transition. The structure determination from single-crystal X-ray data at 215 K reveals a possible orientational disorder of some of the hydroxyl groups in the Pmcn phase. From this and a recent strain analysis of deuterated and hydrogenated lawsonite we conclude that down to 205 K the Cmcm-Pmcn transition is driven by a displacive component, as observed in strain and birefringence data, plus an order/disorder component or dynamical effects associated with proton ordering. Below 205 K only the displacive component plays a role, and the (120 K) Pmcn-P2₁,cn transition is driven by a single order parameter. The remarkable elastic softening of C⁶₆ ahead of the Cmcm-Pmcn transition indicates another orthorhombic-monoclinic transition, which is suppressed on cooling through the low-temperature phase sequence Cmcm-Pmcn-P2₁,cn, but can be applied on applying pressure to the mineral.

INTRODUCTION

Lawsonite, CaAl₃[Si₂O₇](OH)₂·H₂O, is seen as an essential component in the geological water cycle (Pawley 1994) due to the high water content of ~11 wt% and the occurrence in high-pressure, low-temperature metamorphic environments. Figure 1 shows the room-temperature structure of lawsonite at ambient pressure. The framework consists of infinite linear chains of [AlO₆] octahedra bridged via [Si₂O₇] building blocks. The cavities are occupied by Ca²⁺ ions, water molecules, and hydroxyl groups. The polymorphism of lawsonite has attracted considerable interest over the last few years. To date five different phases of lawsonite are known with two low-temperature phase transitions around ~271 K (T₁) and ~120 K (T₂) at ambient pressure and two high-pressure phase transitions around ~4 and ~9.5 GPa at room temperature (Daniel et al. 2000; Boffa Ballaran and Angel 2003). Libowitzky and Armbruster (1995) have determined the structures of both low-temperature phase and the two low-temperature phases. These differ from one another mainly with respect to the arrangement of the hydrogen-bearing components and thus the hydrogen bond system. Both low-temperature phase transitions are accompanied by changes of the special-site symmetry of the water molecules, and the one at lower temperature (T₂) also affects the special-site symmetry of the hydroxyl groups. The authors deduce that the water molecules are dynamically disordered at room temperature. It follows that the two phase transitions involve ordering processes of the water molecules. The hydroxyl groups are affected by this via the hydrogen bond system. In addition, neutron diffraction experiments have shown that some of the hydroxyl groups remain disorder at 20 K (Lager et al. 1998).

A closer inspection of the ordering processes has recently been initiated (Meyer et al. 2000, 2001; Sondergeld et al. 2000a, 2000b; Carpenter et al. 2003), involving studies of the temperature dependence of physical properties such as birefringence, lattice parameters, and IR line widths that are correlated with the macroscopic order parameters. All these data are consistent with a rather simple tricritical Cmcm-Pmcn transition, while the Pmcn-P2₁,cn transition associated with T₁ appears to be second order.

Nevertheless, the birefringence data and recent calorimetric studies (Martín-Olalla et al. 2001), in particular, indicate signifi-

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