

## ORDER-DISORDER PHASE TRANSITIONS IN LAWSONITE AND HEMIMORPHITE

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Single-crystals of lawsonite and hemimorphite were investigated by infrared (IR) spectroscopy, optics, X-ray diffraction (lawsonite), and neutron diffraction (hemimorphite) at temperatures between 20° and 500°K. Both minerals show phase transitions at low temperatures which are related to order-disorder in the proton positions (in the form of OH groups and H<sub>2</sub>O molecules). The driving force for the phase transitions is found in reduced thermal vibration at low temperatures which leads to the formation of cooperative hydrogen bonds across the structure.

Lawsonite, CaAl<sub>2</sub>[Si<sub>2</sub>O<sub>7</sub>](OH)<sub>2</sub> · H<sub>2</sub>O, shows reversible phase transitions at 273° and 155°K which are characterized by lowering in space group symmetry (from ambient to low temperatures) from *Cmcm* via *Pmcn* to *P2<sub>1</sub>cn*. Whereas the silicate frame work behaves rigidly, the water molecules rotate off their highly symmetric positions. In addition, the hydroxide groups rotate into two different positions which leads to reduced symmetry in two steps. The phase transitions can be monitored by sudden changes of certain X-ray intensities, by non-linearities in the lattice parameters, and by discontinuities in the birefringence curves of lawsonite.

In contrast, single-crystal IR spectra between 82° and 325° K do not show sudden changes at all. They constantly exhibit four OH stretching modes which are assigned to two different OH groups and to two OH vectors of the water molecule. It is interesting that the frequencies of the low-energy bands shift up to 150 cm<sup>-1</sup> in the temperature range between 82° and 325°K. The shift to lower frequencies at low temperatures is in good agreement with the observed shortening of hydrogen bonds in the structure. However, agreement between IR frequencies and O-H...O distances is only found at lower temperatures, whereas differences between IR data and distances from X-ray refinements exist at room temperature.

These observations suggest a structure with dynamically disordered hydrogen positions at room temperature. The long time scale of X-ray experiments results in intermediate proton positions which lead to the apparently high space group symmetry at room temperature. The extremely short time scale of IR spectroscopy reveals the single, disordered hydrogen sites of the dynamic disorder. These results are also confirmed by preliminary data from neutron diffraction and proton-NMR. Similar phase transitions (even though at higher temperatures) were also observed in the isotopic mineral henomartinite, SrMn<sub>2</sub>[Si<sub>2</sub>O<sub>7</sub>](OH)<sub>2</sub>·H<sub>2</sub>O, which shows an additional monoclinic distortion and twinning in its room-temperature structure.

Hemimorphite, Zn<sub>4</sub>[Si<sub>2</sub>O<sub>7</sub>](OH)<sub>2</sub>·H<sub>2</sub>O, belongs to space group *Imm2*. The polar framework contains structural channels running parallel to *c* which are occupied by the water molecules and the hydroxide groups. Hemimorphite shows a reversible phase tran-

sition at 98°K which is indicated by a discontinuity in birefringence curves. As in case of lawsonite, the phase transition is not directly visible in single-crystal IR spectra. However, strong temperature-dependent shifts in the band positions of the OH stretching modes also indicate an order-disorder relation of the protons. Additional IR bands are assigned to a twisting motion of the water molecule, but also suggest an additional OH position which cannot be derived from the room-temperature structure. The OH stretching bands are generally observed at higher frequencies than those in lawsonite. This is in agreement with the weaker (and longer) hydrogen bonds in hemimorphite.

Single-crystal neutron diffraction experiments at 20°K (using the »Time-Of-Flight« method at the »Intense Pulsed Neutron Source« at Argonne National Laboratory, IL, USA) showed the appearance of additional super-reflections which lead to a doubling in the *b* and *c* lattice parameters. An additional test at 120°K showed that these super-reflections disappear above the transition temperature. The low-temperature super-structure has space group *Cc*, but it can be described more conveniently in a superposition of space groups *Ac* and *Ad* which retains the orthogonal metric. During the phase transition, the silicate framework behaves quite rigid, whereas ordering of protons (i.e. of hydroxide groups and water molecules) in the channels leads to the formation of a super-structure. Cooperative hydrogen bonds form an ordered arrangement of OH groups and H<sub>2</sub>O molecules which results in doubling of the *c* lattice parameter. Ordering of the channels across the structure results in a doubled *b* lattice parameter.

As in case of lawsonite, the long time scale of previous room-temperature X-ray and neutron experiments lead to intermediate, highly symmetric atom positions which represented only diffuse centers of dynamically disordered atom positions. The short time scale of IR spectroscopy, however, revealed the individual positions of the disorder. After the transition to an ordered arrangement at low temperatures, the individual positions could be accessed and refined by neutron diffraction.

An additional investigation of dehydrated hemimorphite showed statistically disordered proton positions in the channels of the framework. Neither optics, nor X-ray, nor IR experiments indicated a phase transition between 82° and 500°K. These observations are explained by the missing water molecule and missing hydrogen bonds. The two refined, disordered proton positions in the channels are in good agreement with electrostatic and crystal chemical considerations.