Role of water molecules in the phase transitions in lawsonite

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Lawsonite: $CaAl_2[Si_2O_7](OH)_2.H_2O$

T

orthorhombic, *Cmcm* space group – centrosymmetric

T_{c1} = 273 K

Structural phase transition; order-disorder, antiferrodistortive, Brillouin zone folding, i.e., unit cell multiplication

orthorhombic, *Pmcn* = *Pnma* space group – centrosymmetric. Rotation of water molecules and OH groups within the (100) plane; anomalous increase in lattice parameter *a* upon cooling

T_{c2} = 124 K

Improper ferroelectric phase transition, 2nd-order, "co-elastic"

orthorhombic, space group $P2_1cn$ = $Pna2_1$

Spontaneous polarization: P_s || a, up to 3 μC/cm² @40 K

Aims:

- Studying lattice vibrations with respect to the two phase transitions
- Determining the role of static and dynamic orientations of water molecules in the symmetry changes

Expectations—two soft modes:

- Raman-active soft mode observable below T_{c1} at the antiferrodistortive transition
- Ferroelectric soft mode observable below T_{c2} in both IR and Raman spectra (A_1 symmetry) and above T_{c2} in IR spectra only (B_{3u} symmetry)

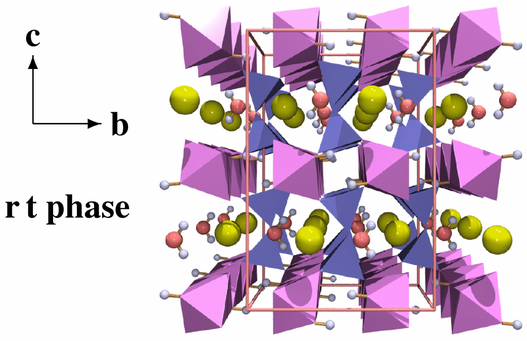
Note: Partial order-disorder character of the transitions may lead to increased damping and difficulties in observing the soft mode.

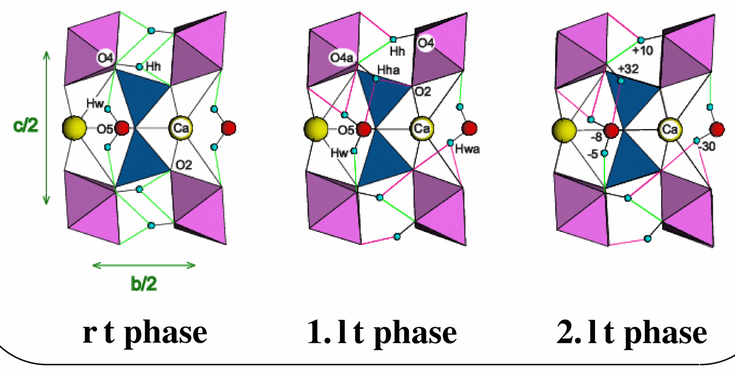
Experimental techniques:

- Micro-Raman spectrometer Renishaw RM 1000, (10 – 4000 cm^{-1}, 20–300 K)
- Fourier-transform infrared spectrometer Bruker IFS 113v (50–650 cm^{-1}, 20–300 K)
- Custom-made THz time-domain spectrometer based on a Coherent Mira fs laser (7−60 cm^{-1}, 10−300 K)

Structural changes

Libowitzky & Armbruster (1995):
Am. Min. **80**, 1277-1285.

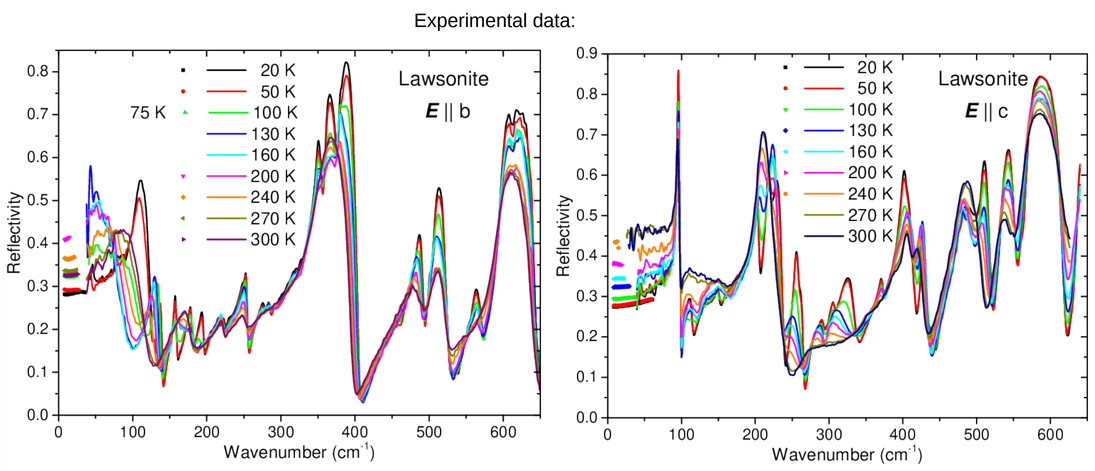




— OH bonds H(h/w) from OH/water ±numbers: shifts along *a* [Å*100]

Infrared and THz spectroscopies

Experimental data:



Spectra modeling

Complex permittivity due to phonon modes:

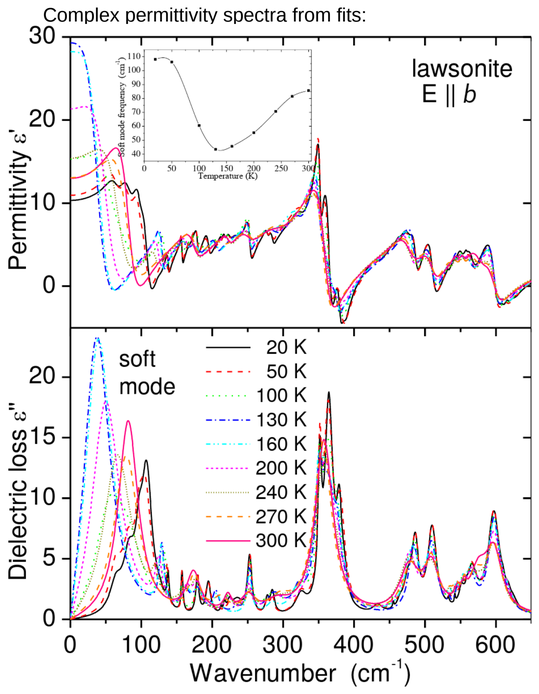
$$\varepsilon^*(\omega) = \sum_{j=1}^{n} \frac{\Delta\varepsilon_j \omega_j^2}{\omega_j^2 - \omega^2 + i\omega\gamma_j} + \varepsilon_\infty$$

(*n* is limited by the factor-group analysis, see below)

FTIR reflectance:

$$R(\omega) = \left| \frac{\sqrt{\varepsilon^*(\omega)} - 1}{\sqrt{\varepsilon^*(\omega)} + 1} \right|^2$$

Complex permittivity spectra from fits:

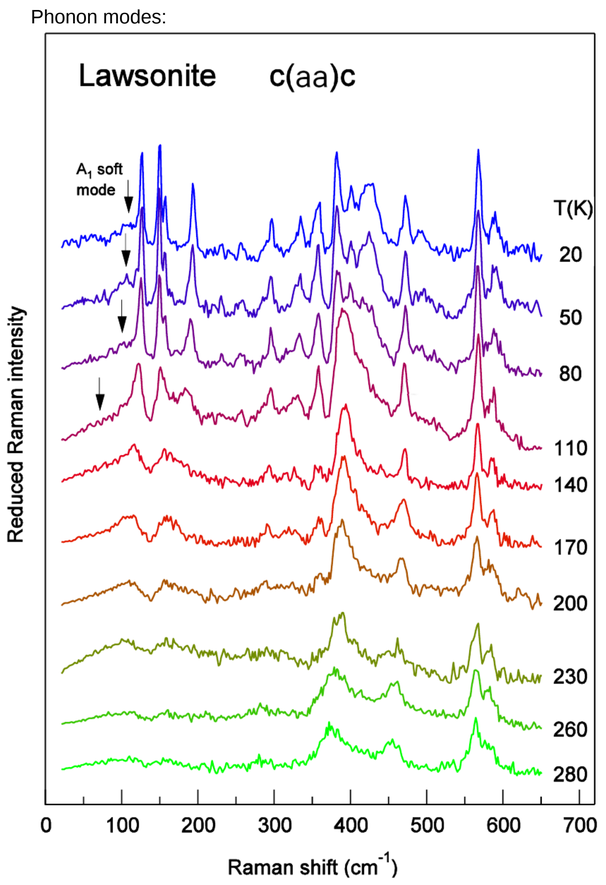


Factor-group analysis, yielding the maximum numbers of phonon modes allowed by symmetry in the three crystallographic phases:

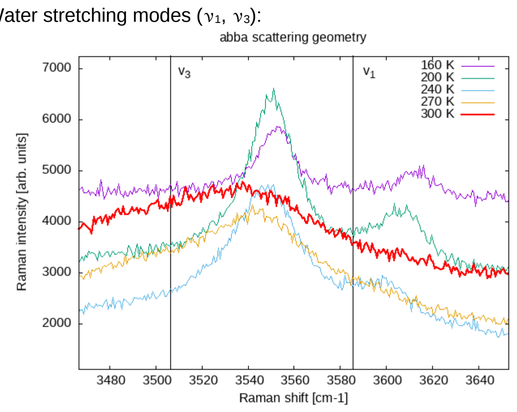
C_{mcm}	→ P_{mcn}	→ P_{2_1cn}
16 A_g (*aa, bb, cc*)	32 A_g	
11 A_u -	25 A_u	57 A_1 (*a; aa, bb, cc*)
11 B_{1g} (*ab*)	19 B_{1g}	
19 B_{1u} (*c*)	38 B_{1u}	57 A_2 (*bc*)
8 B_{2g} (*ac*)	19 B_{2g}	
19 B_{2u} (*b*)	38 B_{2u}	57 B_1 (*b; ab*)
16 B_{3g} (*bc*)	32 B_{3g}	
14 B_{3u} (*a*)	25 B_{3u}	57 B_2 (*c; ac*)

Raman spectroscopy

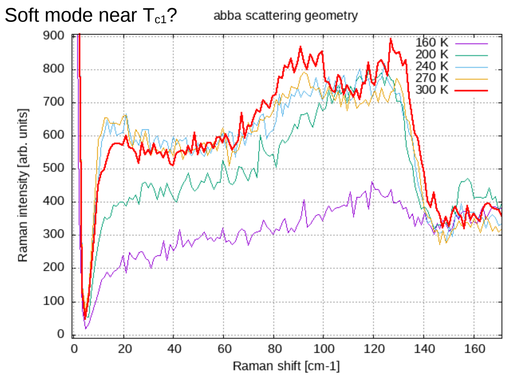
Phonon modes:



Water stretching modes (ν_1, ν_3):



Soft mode near T_{c1}?



Conclusions:

- Polarized infrared and Raman spectra of lawsonite were taken in its all three crystal phases and compared with the factor group analysis of lattice vibrations. Room-temperature data are in agreement with earlier studies [1].
- Antiferrodistortive phase transition at T_{c1} is accompanied by H_2O rotation and proton ordering [2], as manifested in Raman scattering by quasi-elastic scattering (overdamped low-frequency mode) which disappears far below T_{c1}. No phonon soft mode connected with this transition can be identified in Raman spectra below T_{c1} (order-disorder transition). Doubling of unit cell (Brillouin zone folding) below T_{c1} causes activation of **new modes in both IR and Raman spectra.**
- Both phase transitions at T_{c1}, T_{c2} are connected with a loss of inversion centre → activation of new modes in IR and Raman spectra.
- **E||b** IR spectra show a **ferroelectric soft mode** near ferroelectric phase transition at T_{c2}. This soft mode is also observed in A_1(*aa*) Raman spectra at lowest temperatures. Since a dielectric relaxation was observed in radio-frequency region [3], the phase transition displays a **crossover between order-disorder and displacive type**.

References

[1] A. Le Cleac'h, P. Gillet, *Eur. J. Mineral.* **2**, 43 (1990).
[2] E. Libowitzky, T. Armbruster, *American Mineralogist*, **80**, 1277 (1995).
[3] H. Sondergeld, W. Schranz et al. *Phys. Rev.* B **64**, 024105 (2001).