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Phase transitions in lawsonite and KDP-type ferroelectrics: Comparisons of proton ordering mechanisms

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Both the $Cmcm - Pm\bar{c}n$ ($T_C = 273$ K) and $Pm\bar{c}n - P2_1cn$ ($T_C = 130 - 143$ K) phase transitions in lawsonite involve the ordering of protons and displacive changes in the structure of the surrounding aluminosilicate framework. However, the interactions of these two processes are radically different for the two transitions. These differences are revealed by comparisons of the specific heat anomalies.

For the $Cmcm - Pm\bar{c}n$ transition, the excess entropy only correlates with other measures of the order parameter ($\Delta S \propto Q^2$) in the situation where an ordered lawsonite is heated very slowly. However, the total excess entropy associated with the phase transition does not appear to vary significantly with the rate or direction of the temperature ramp. The transition temperature is independent of the degree of deuteration. The initial driving force for this phase transition is therefore the displacive instability in the framework; the proton ordering follows this as a coupled process.

For the $Pm\bar{c}n - P2_1cn$ transition, the various experiments give mutually consistent results, implying that the transition behaviour is limiting second order without kinetic anomalies. There is a strong isotope effect; the transition temperature is 13 K higher in deuterated lawsonite than in hydrogen-lawsonite.

Further insights are gained by comparing these results with those for the ferroelectric phase transition in KH_2PO_4 . Like the lower temperature transition in lawsonite, this transition also shows a strong isotope effect, and no kinetic effects. In both these cases, the transitions are driven by the dynamics of the proton ordering, which causes a coupled distortion of the surrounding framework.

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Transformation twinning in minerals: A credible source of anelasticity in crustal and mantle rocks?

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As seismologists develop a detailed picture of seismic attenuation throughout the Earth's crust, mantle, and core, it becomes essential that we understand the physical processes responsible for anelasticity in minerals. In the mantle, anelasticity is normally attributed to the mechanism of grain-boundary sliding, whereas in crustal rocks anelasticity is normally attributed to the presence of fluids. A potential source of anelasticity that has yet to be considered by seismologists is the presence of transformation twinning. Many minerals develop twinning as a result of a displacive phase transition. The time-dependent displacement of twin walls in response to a seismic-frequency stress leads to both a dramatic mechanical softening and a large increase in attenuation. This effect has been studied in detail using a combination of dynamical mechanical analysis, stroboscopic X-ray diffraction, and in-situ optical microscopy.

The mechanical properties of several oxides with perovskite structure have been studied in order to determine the possible influence of transformation twinning on lower-mantle $MgSiO_3$ perovskite. Massive attenuation due to twin-wall motion was observed below the cubic to rhombohedral phase transition in $LaAlO_3$ and the cubic to tetragonal transition in $(Ca, Sr)TiO_3$. Both phases display anelastic relaxation below 200 °C, attributed to the gradual pinning of twin walls by lattice defects. Activation energies for twin-wall motion were found to be of the order 0.8-1 eV, revealing that twin walls are extremely mobile in these phases. Simple extrapolation to lower mantle conditions implies that massive mechanical softening due to twin wall motion would be observed, but that the relaxation times would be far too small to be a significant source of seismic attenuation. However, very different behaviour was observed in $(Ca, Sr)TiO_3$ on cooling below the tetragonal to orthorhombic phase transition. On entering the orthorhombic phase (which has the same space group symmetry as $MgSiO_3$) there is a sudden decrease in the mobility of the twin walls. Our latest measurements reveal that this effect is not a consequence of the low spontaneous strain of the intermediate orthorhombic phase, as initially thought, but a common feature of the orthorhombic phase across the entire solid solution. The consequences of this observation for the credibility of twin walls as a source of anelasticity in the lower mantle will be discussed.