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First evidence for temperature-induced phase transitions in Pb-lawsonite

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Lawsonite-type compounds $A^{+2}B_2^{+3}[(OH)_2|Si_2O_7]\bullet H_2O$ are high-density (3.09 g/cm^3 for lawsonite) hydrous silicates, which are stable within a broad P-T field (Pawley & Allan, 2001; Schmidt & Poli, 1994). Chains of AlO_6 octahedra plus Si_2O_7 groups build up a framework structure, in which large Ca/Sr/Pb/Ba ions, OH^- groups and H_2O molecules fill the vacancies. Because of the high water content lawsonite is considered a potential carrier of H_2O into the subduction zone of the Earth.

Lawsonite, Sr-lawsonite (itoigawaite) and Pb-lawsonite were synthesized by piston cylinder and multi-anvil techniques at pressures up to 12 GPa and temperatures up to 700 ˚C at GFZ Potsdam, Germany. After synthesis of itoigawaite and Pb-lawsonite the structures where refined on a single-crystal X-ray diffractometer. The used crystals had a size of 60x30x35 μm (itoigawaite) and 20x20x8 μm (Pb-lawsonite) and were twinned. Previously, the structures of itoigawaite and Pb-lawsonite had been refined on powder samples only (Dörsam et al., 2011; Liebscher et al., 2010). The single-crystal refinements correspond well with the data of the powder diffraction results.

At ambient pressure lawsonite shows phase transitions at 150 K and 273 K (Libowitzky & Rossman 1996). These reversible phase transitions are mainly caused by changes of the OH- and H_2O groups from disordered, apparently highly symmetric positions to ordered ones at lower temperatures. The itoigawaite and the Pb-lawsonite seem to have corresponding phase transitions at considerably higher temperatures.

Pb-lawsonite powder for example shows a huge shift of OH and H_2O stretching vibrations in Raman measurements. One band shifts from 3294 cm^{-1} at 83 K to 3468 cm^{-1} at 573 K. This shift reveals clear non-linearities, which indicate two phase transitions at $\sim$ 423 K and $\sim$ 473 K. The latter value is about 200 K higher than the corresponding phase transition in lawsonite at 273 K. Another Raman band, which shifts from 877 cm^{-1} at 83 K to 799 cm^{-1} at 573 K confirms the non-linearities at equal temperatures.

Temperature-dependent birefringence measurements on single-crystals of Pb-lawsonite in the range of 83 K to 573 K reveal only one non-linearity and thus only one phase transition with a second order characteristic at a temperature of 350 K.

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