

Temperature-induced phase transitions in Pb/Sr-lawsonites

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Pb-lawsonite and itoigawaite ($\text{SrAl}_2[(\text{OH})_2\text{Si}_2\text{O}_7]\cdot\text{H}_2\text{O}$) were synthesised using either oxides [1,2], spinel phases with quartz, feldspars or glasses with stoichiometric compositions. The achieved crystal sizes reached 20 μm in maximum for the Pb-lawsonite and about 60 μm for itoigawaite.

For the syntheses a piston cylinder press at GFZ Potsdam, Germany was used. Experimental conditions were 600°C and 3-4 GPa for Pb-lawsonite and 700°C and 4 GPa for itoigawaite. Using Raman spectroscopy temperature-induced shifts of different bands were analysed. For Pb-lawsonite the most interesting one was a band at about 860 cm^{-1} , which probably arises from an AlO_6 stretching vibration [3]. It shows a minimum of two discontinuities, which could be interpreted as phase transitions at about 350 and 445 K (Fig. 1). Analyses of a band arising from a $\nu_{\text{as}} \text{SiO}_3$ stretching vibration [3] reveal a minimum of one phase transition for itoigawaite at about 225 K.

These reversible phase transitions are comparable to those of lawsonite and are mainly caused by changes of OH and H_2O groups from disordered, apparently highly symmetric positions to ordered ones at lower temperatures [4].

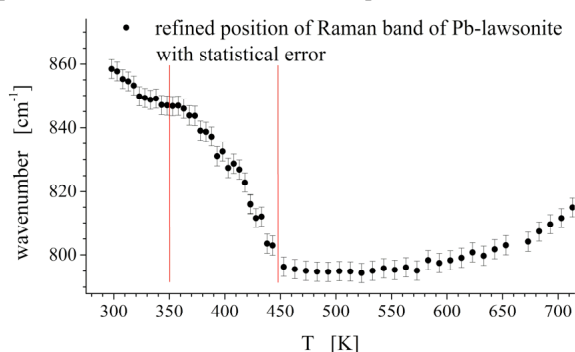


Figure 1: Raman band positions vs. temperature for Pb-lawsonite. Discontinuities probably reveal phase transitions.

[1] Dörsam *et al.* (2011) *N. Jb. Miner. Abh.* **188/2**, 99-110 [2] Liebscher *et al.* (2010) *Am. Mineral.* **95**, 724-735 [3] Le Cléac'h & Gillet (1990) *Eur. J. Mineral.* **2**, 43-53 [4] Libowitzky & Armbruster (1995) *Am. Mineral.* **80**, 1277-1285

Pressure-dependent change of ultraviolet absorption cross section of SO_2 isotopologues and S-MIF

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Photolysis of SO_2 is known to produce anomalous sulfur isotope fractionation (S-MIF). The mechanism of the photochemical S-MIF is important for reconstructing chemistry of paleoatmosphere, though has been still poorly understood. It is important to determine isotopologue-specific UV absorption cross section accurately for estimating fractionation factor of the SO_2 photolysis. We used a dual beam monochromator in order to obtain higher accuracy cross section that is complementary to high spectral resolution Fourier transform spectrometer [1]. The results show the peak position for heavier isotopologue is red shifted relative to the lightest $^{32}\text{SO}_2$ isotopologue, though rotational structures cannot be seen due to low spectral resolution. The observed cross sections systematically changed depending on the gas pressure at certain specific wavelengths. This may suggest that S-MIF can occur when SO_2 is photolyzed even under optically thin condition and thus not by self-shielding effect in the Archean atmosphere. Also, the observed pressure dependence of cross sections may indicate S-MIF can be changed as a function of atmospheric pressure.

[1] Danieleche *et al.* (2008) *J. Geophys. Res.* **113**, 1-14.