

## Comparison of peak fitting and autocorrelation analysis on temperature-dependent Raman spectra

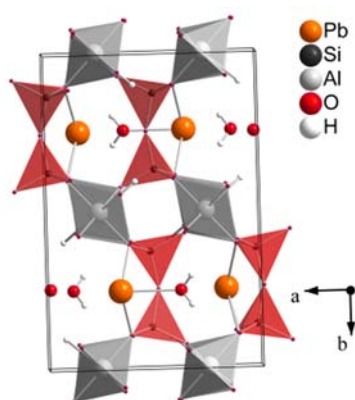
Ende, M.\* , Libowitzky, E.

University of Vienna, 1090 Vienna, Austria

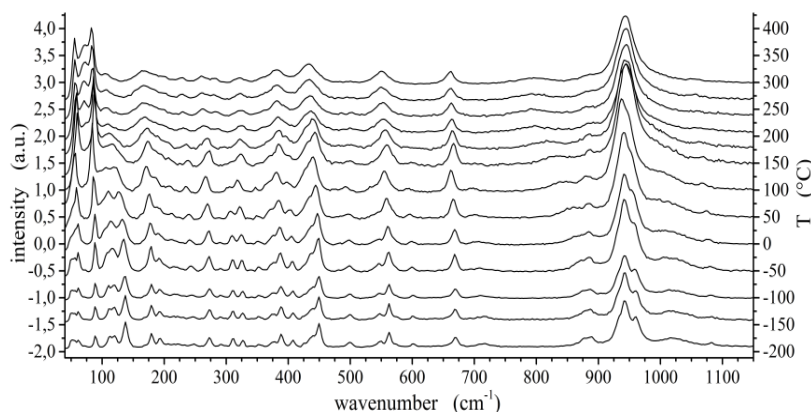
E-mail: martin.ende@univie.ac.at

Raman spectroscopy is a powerful tool for the investigation of phase transitions and chemical mixing phenomena (Hertweck and Libowitzky, 2002; Watenphul et al., 2010). The structural change, whether physical or chemical leads to a change of the spectrum in form of band shifts or bandwidth variations. In the cases of structural phase transitions or cation ordering the thermodynamic order parameter  $Q$  could be determined. This can give insights into the thermodynamic behaviour of materials undergoing phase transitions. For phases with high symmetry and small unit cell a standard peak fitting procedure is sufficient for getting quality data. However, most silicate minerals give complex spectra with multiple overlapping peaks (Salje et al. 2000).

In this work Raman spectra of Pb-lawsonite ( $\text{PbAl}_2[(\text{OH})_2\text{Si}_2\text{O}_7]\cdot\text{H}_2\text{O}$ ; Fig. 1) powder samples were acquired at temperatures ranging from 25 °C to as high as 450 °C. These spectra had relatively complex patterns and low intensities (Fig. 2). A standard peak fitting procedure was applied on the bands between 750  $\text{cm}^{-1}$  and 1150  $\text{cm}^{-1}$ .



**Fig. 1.** The  $Pbnm$  structure of Pb-lawsonite at 295 K.



**Fig. 2.** Temperature-dependent Raman spectra of Pb-lawsonite powder in the range of 40  $\text{cm}^{-1}$  to 1150  $\text{cm}^{-1}$ .

Due to the low intensities and the complexity of the Raman spectra autocorrelation analysis was used as well. This procedure has the advantage that it does not require any peak fitting of the primary spectrum and it can be applied to individual bands or groups of bands. The autocorrelation function  $\text{Corr}(\alpha, \omega')$  has the following form:

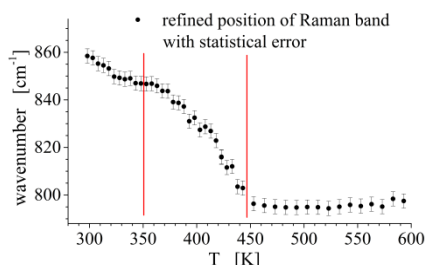
$$\text{Corr}(\alpha, \omega') = \int_{-\infty}^{\infty} \alpha(\omega + \omega') \cdot \alpha(\omega) d\omega$$

With  $\alpha$  for the absorbance in the case of absorption spectra or intensity in case of Raman spectra and  $\omega$  for the frequency. Therewith  $\alpha(\omega)$  is the spectrum itself and  $\alpha(\omega + \omega')$  is the same spectrum with an offset in frequency by  $\omega'$ . Thus using the autocorrelation function each segment of a spectrum is correlated with itself (cf. pages 538–539 in Press et al., 1992; Salje et al., 2000).

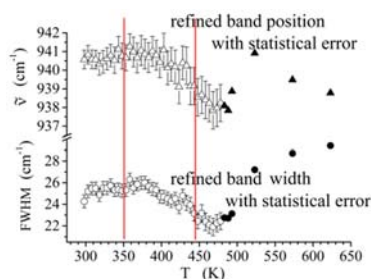
For the standard peak fitting process the most interesting band was a small but strongly shifting one at about 860  $\text{cm}^{-1}$ , which probably arises from an  $\text{AlO}_6$  stretching vibration (Le Cléac'h and Gillet, 1990). It shows a minimum of two discontinuities, which could be interpreted as phase transitions at about 350 K and 445 K (Fig. 3). All the other bands between

100  $\text{cm}^{-1}$  and 1200  $\text{cm}^{-1}$  were useless for band shift analysis, because their small intensities reveal discontinuities within the error or pseudo-discontinuities caused by band overlapping. Band width analyses reveal the same behaviour (Fig. 4).

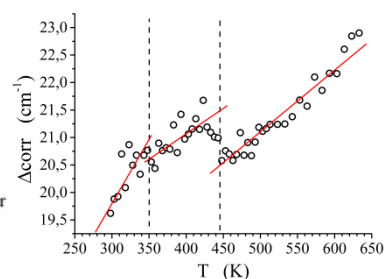
Autocorrelation analyses were done in different parts of the Raman spectra. The result of the region between 730  $\text{cm}^{-1}$  and 1200  $\text{cm}^{-1}$  can be seen in Fig. 5. For comparison Fig. 4 shows the band width analyses with standard peak fitting of the highest band in this region, which arises from a  $\nu_{\text{as}}(\text{SiO}_3)$  stretching vibration.



**Fig. 3.** Temperature-dependent Raman band shift analysis on a small but strongly shifting band at 860  $\text{cm}^{-1}$  in the Pb-lawsonite spectra. The two discontinuities can be interpreted as phase transitions.



**Fig. 4.** Fitted band widths (FWHM) and positions of the strongest band at a wavenumber ( $\tilde{\nu}$ ) of ca. 940  $\text{cm}^{-1}$ . Black data points are based on not properly converged refinements.



**Fig. 5.** Temperature-dependent autocorrelation analysis of the Pb-lawsonite spectra in the region of 730  $\text{cm}^{-1}$  to 1200  $\text{cm}^{-1}$ . This analysis is mostly influenced by three bands around 940  $\text{cm}^{-1}$ .

The discontinuity at about 350 K could also be seen with a birefringence analysis on a single crystal of Pb-lawsonite. The possible phase transition of Pb-lawsonite at 445 K has been located only by Raman spectroscopy. If the strongly shifting band at 860  $\text{cm}^{-1}$  would not exist the only reasonable way for analysis of the Raman spectrum would be autocorrelation analysis. To illustrate this, the possible phase transition temperatures of Fig. 3 are plotted in Figs. 4 and 5.

However, autocorrelation analysis has its own problems. For example, in noisy spectra the analysis could react on the noise and not on the true absorption peaks. This can be shown with variations within the autocorrelation routine. In addition, a wrong background handling for a measurement with bad signal to noise ratio is equally harmful for autocorrelation analysis as for standard peak fitting methods. Nevertheless the autocorrelation function achieves a clear advantage on handling Raman spectroscopic data with band overlapping for phase transition detection. In addition, autocorrelation analysis can be automated easier than usual peak fitting methods.

**Acknowledgments:** We are very grateful to M. Koch-Müller and B. Wunder, Helmholtz Centre Potsdam, GFZ (German Research Centre for Geoscience) for providing the equipment for high-pressure synthesis of the Pb-lawsonite crystals. We also thank the Austrian Science Fund, since the present work was financially supported by FWF project P23108-N19.

## References:

- Hertweck B, Libowitzky E, (2002) Vibrational spectroscopy of phase transitions in leonity-type minerals. *Eur J Mineral* 14:1009–1017
- Le Cléac'h A, Gillet P (1990) IR and Raman spectroscopic study of natural lawsonite. *Eur J Mineral* 2:43–53
- Press WH, Teukolsky SA, Vetterling WT, Flannery BP (1992) *Numerical Recipes in Fortran 77 – The art of scientific computing*. 2<sup>nd</sup> ed, vol 1, Cambridge University Press
- Salje EKH, Carpenter MA, Malcherek T, Ballaran TB (2000) Autocorrelation analysis of infrared spectra from minerals. *Eur J Mineral* 12:503–519
- Watenphul A, Libowitzky E, Wunder B, Gottschalk M (2010) The OH site in topaz: an IR spectroscopic investigation. *Phys Chem Miner* 37:653–664