

s11.m1.o1 On the correlation of optical constants with the crystal structure. R.X. Fischer¹, R.D. Shannon², ¹*Fachbereich Geowissenschaften, Universität Bremen, Klagenfurter Straße, D-28359 Bremen, Germany,* ²*Department of Geological Sciences/CIRES, University of Colorado, Boulder CO 80309 USA.*

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Optical properties such as linear and nonlinear refractive indices, birefringence, and optical activity are important characteristics of minerals and synthetic compounds. Technical crystals in optical industry, and in all applications where specific optical properties are required (e.g., in tooth fillings and replacements to conform to the optical appearance of the enamel) are designed to exhibit specific optical properties. For many decades, optical materials were selected empirically or by experimentally determining the optical parameters on a variety of compounds with different chemical compositions. Although quantum chemical calculations predicting optical properties from crystal structure parameters have improved greatly in the last decade, they are still useful only for simple fluorides and oxides.

Another approach to predicting optical properties is given by multi regression analyses of experimentally determined refractive indices and dispersion from crystals with various compositions. If the experimentally determined data are reliable and if the data set is large enough, electronic polarizabilities can be assigned to the single elements using the ion additivity rule which states that the overall optical properties of an inorganic compound consist of the sum of the individual contributions from the ions in consideration of some additional correction terms.

Here, we present an overview of the approaches to predict refractive indices from the crystal structure with emphasis on the empirical methods, extended by recent work done by us on the multi regression analyses to determine electronic polarizabilities

s11.m1.o2 Phase transitions in minerals: Correlation of spectroscopic and diffraction data. E. Libowitzky, *Institut für Mineralogie und Kristallographie der Universität Wien – Geozentrum, Althanstr. 14, A-1090 Wien, Austria.*

Keywords: dynamic disorder, hydrogen bond, crystal structure.

Phase transitions in minerals lead to various phases with different physical and chemical properties. These mineral phases determine the zones of the Earth's interior. Changes of properties may be also technically applied, e.g. ferroelectric transitions. Hence, structural characterisation of phase transitions is an important task of mineralogical and applied crystallography.

Whereas diffraction methods give a time- and space-averaged image of a structure, spectroscopic methods provide detailed insight into single sites with excellent time resolution. Even if discrimination between displacive and order-disorder transitions is not obvious by the former techniques, the latter provide information even in case of dynamic disorder.

The examples below demonstrate the power of a combined approach using single-crystal X-ray and TOF-neutron diffraction supported by infrared (IR) spectroscopy and crystal optics. The investigated minerals are hemimorphite, lawsonite, and leonite.

Hemimorphite shows a phase transition at 98 K that is characterised by the apparent displacement of hydroxyl groups and water molecules from the mirror plane in the structural channels parallel to the *c* axis. However, the number of IR stretching bands, their orientation, and their stretching frequencies (in relation to hydrogen bond lengths) confirm that the transition is not displacive but of a dynamic disorder-order type^{1,2}.

Lawsonite comprises two low-temperature phase transitions that appear displacive from X-ray diffraction. Rotation of water molecules and hydroxyl groups leads to symmetry reduction in two steps. The transitions are accompanied by the formation of a cooperative hydrogen bond system. Correlation of IR stretching frequencies with hydrogen bond lengths and directions confirms the dynamic disorder-order transition type^{3,4}.

Leonite-type minerals and compounds contain disordered sulfate groups at room temperature. These dynamic groups freeze at low temperatures to an ordered structure. Upon further cooling, the ordered arrangement in Mg- and Mn-leonite switches to another polytype with different sulfate ordering scheme. The arrangement of sulfate groups is controlled by hydrogen bonds within and between the polyhedral layers⁵.

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