

Dispersion analysis of arbitrarily cut uniaxial crystals



Sonja Höfer^{a,*}, Reinhard Uecker^b, Albert Kwasniewski^b, Jürgen Popp^{a,c},
Thomas G. Mayerhöfer^{a,c}

^a Leibniz-Institut für Photonische Technologien e.V., Albert-Einstein-Straße 9, D-07745 Jena, Germany

^b Leibniz-Institut für Kristallzüchtung, Max-Born-Straße 2, D-12489 Berlin, Germany

^c Institut für Physikalische Chemie und Abbe Center of Photonics, Helmholtzweg 4, D-07743 Jena, Germany

ARTICLE INFO

Article history:

Received 14 July 2014

Received in revised form 13 March 2015

Accepted 16 March 2015

Available online 17 March 2015

Keywords:

Dispersion analysis

Uniaxial single crystals

IR reflectance spectra

Determining orientation

ABSTRACT

We modified the measurement and evaluation scheme developed for the dispersion analysis of triclinic crystals to perform dispersion analysis of arbitrarily cut uniaxial crystals. In addition to the dispersion parameters, we determine the orientation of the optical axis and can distinguish between degenerate and non-degenerate vibrational modes. The investigated crystals comprise quartz, calcite and lithium niobate, which exhibit different levels of difficulty to evaluate the dispersion parameters and the correct orientation.

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1. Introduction

Dispersion analysis was first defined by Spitzer and Kleinman in 1961 [1] and is described as the determination of dispersion parameters of a single crystal based on the evaluation of polarized reflection spectra. Oscillator parameters and the dielectric background tensor are required to compute the dielectric tensor function of a crystal in the investigated spectral range. Both oscillator parameters and dielectric tensor function build the bridge between the structural and the optical properties of the crystals.

In [2] and [3] we developed a scheme to perform dispersion analysis on triclinic crystals. With $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ we investigated a representative of a triclinic crystal which shows almost orthorhombic-like behavior in the IR spectral region due to only weakly distorted SO_4^{2-} tetrahedrons. In contrast, $\text{K}_2\text{Cr}_2\text{O}_7$ single crystals show much stronger anisotropic behavior as there are no high symmetry structural elements like, e.g., tetrahedrons or octahedrons.

Triclinic crystals do not have any preferred orientations in contrast to optically uniaxial and other optically biaxial crystals. If dispersion analysis is able to determine the orientations of the transition moments in the triclinic crystals, as was shown in [2] and [3], it should be possible to do the same also for crystals with higher symmetry. Since in such crystals the transition moments

are oriented parallel to certain symmetry elements (rotation axes and mirror planes), it should be possible to find out by dispersion analysis not only the dispersion parameters, but simultaneously the crystal orientation and symmetry (certainly not the full symmetry, since e.g. the tetragonal, trigonal, and hexagonal crystal structures cannot be distinguished by optical methods; on the other hand, it is just necessary in this case to know that a crystal is optically uniaxial to perform dispersion analysis). Therefore, dispersion analysis should be possible without prior knowledge of structure and orientation, and, of course, without the necessity to orient the crystal prior to dispersion analysis. This kind of generalized dispersion analysis that we contemplate would have a number of interesting applications.

Our vision is, e.g., the in-situ examination of phase-transitions induced by changing the thermodynamic variables [4]. The modified crystal structure after the phase transition will be identifiable by generalized dispersion analysis and dispersion analysis of such altered phases would be possible even if the orientation of the new phase would not be known a priori.

For example, the crystal trimyditite (SiO_2) belongs to the triclinic crystal system at room temperature, while it changes to the orthorhombic system above 100 °C [5]. Another example is tungsten trioxide (WO_3) which has two phase transitions. At room temperature the crystal is monoclinic, at around 17 °C it transforms to triclinic and at −40 °C it becomes monoclinic again [6]. $\text{LiHf}_2(\text{PO}_4)_3$ is an example for a crystal with a phase transition from a uniaxial symmetry at room temperature to triclinic symmetry at low temperatures [7].

* Corresponding author. Tel.: +49 3641 948351.

E-mail address: sonja.hoefer@uni-jena.de (S. Höfer).

The orthorhombic and trigonal crystal systems are distinguishable from each other by the occurrence of degenerate oscillators in the trigonal crystal system, which are no longer present in the orthorhombic system. What is more, even if the starting point is a principal cut of an optically uniaxial or orthorhombic crystal, it is obvious that under a phase change to monoclinic or triclinic structure the advantage of allowing to separate dielectric tensor components with linear polarized radiation of this particular cut would necessarily cease to exist.

In the end, we aim at being able to differentiate between cubic, uniaxial, orthorhombic, monoclinic and triclinic crystal symmetry by adapting the measurement and evaluation scheme developed by [2,3] to the respective crystal class. As a first step in this direction, we need to evaluate how reliable we can perform dispersion analysis for the individual crystal classes while being able to determine crystal structure and orientation. To do this for uniaxial crystals is the aim of this paper.

2. Experimental and characterization of crystals

In order to assess reliability and limits of generalized dispersion analysis in the uniaxial system we handpicked a number of different crystals with different spectral properties (i.e. optical anisotropy, number of bands etc.) in the infrared.

We gave preference to crystals grown in the laboratory to avoid impurity effects occurring in case of naturally grown crystals that might disturb the measured reflectance spectra.

The investigated crystals are quartz (SiO_2), calcite (CaCO_3) and lithium niobate (LiNbO_3), which all three belong to the trigonal crystal system. The optically uniaxial crystal systems include crystals of hexagonal, trigonal and tetragonal symmetry. These crystals exhibit two species of transition moments: One species is non-degenerate and is aligned along the c -axis (the optical axis), the other species is twofold degenerate and is located on a plane normal to the c -axis. Consequences of this degeneracy are the same values for resonance wavenumber, oscillator strength and damping constant for each pair, and a mutually orthogonal orientation. Due to the identical arrangement of transition moments the three uniaxial crystal classes cannot be distinguished by IR spectroscopy, including that the orientation of the a -axes cannot be determined.

To ensure that the crystals used for the measurements possess three orthogonal crystal faces (these are not necessarily required

by the measurement scheme [2], but of advantage), the crystal samples were cut into a cube and the faces got optically polished with $1\ \mu\text{m}$ DP diamond paste purchased by Stuers.

Of each of the three crystals SiO_2 , CaCO_3 and LiNbO_3 two samples were investigated, one in an arbitrary cut and one in a principal cut to check the results obtained from the arbitrary cut. To perform conventional dispersion analysis for uniaxial crystals usually two spectra are sufficient if one spectrum is recorded with the polarization direction of the incoming light parallel to the optical axis and the second spectrum is recorded with polarization direction of the incoming light normal to the optical axis. This implies using a so-called principal cut of the crystal, with a face having the c -axis parallel to it, usually oriented parallel to one edge of the cut.

The quartz crystal and one calcite crystal in form of a cleavage rhombohedron were purchased from Zeiss, Jena, and were grown by hydrothermal synthesis. The cleavage rhombohedron was used to prepare a cube in an arbitrary cut. To prepare a principal cut of calcite we used a naturally grown calcite crystal provided by the Mineralogische Sammlung, Jena, and polished off the tip of the crystal and prepared a face normal and parallel to the c -axis. The lithium niobate samples were cut out of a bar grown by the Czochralski-method by the Leibniz-Institut für Kristallzüchtung, Berlin.

The orientation of the c -axes of the arbitrary cut crystal cubes were determined by Laue method. The IR spectra were recorded with a Bruker V80v FT-spectrometer with a resolution of $2\ \text{cm}^{-1}$ for both the MIR ($4000\ \text{cm}^{-1}$ – $360\ \text{cm}^{-1}$) and FIR ($500\ \text{cm}^{-1}$ – $100\ \text{cm}^{-1}$) spectral region. To obtain linear polarization we used an Al/KRS-5 polarizer in the MIR region and a polyethylene polarizer for in the FIR region. The crystal cubes were mounted on an 8° reflection unit from Harrick Scientific.

2.1. Crystal structure of quartz

The structure of quartz has already been resolved 90 years ago by Huggins [8] and Bragg and Gibbs. [9]. The α -quartz we investigated is the low temperature modification of quartz and has trigonal symmetry with space group D_3^6 or $P3_221$.

The unit cell contains 3 SiO_2 molecules, which form connected SiO_4 tetrahedra. The SiO_4^{2-} tetrahedra are only slightly distorted, the deviation of the Si–O bond angles from the tetrahedron angle is less than one degree, also are the Si–O and O–O bond lengths

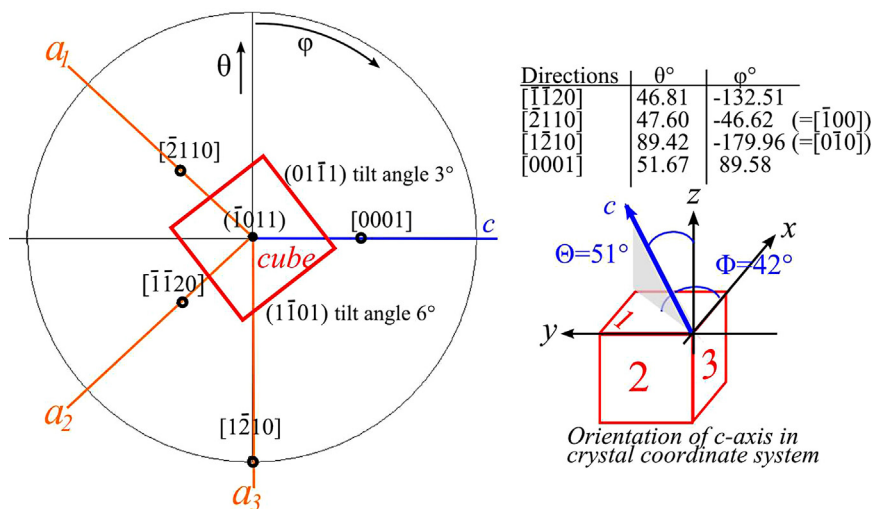


Fig. 1. Stereographic projection of quartz. For the projection four Miller indices and the four axes system with three equal a -axes is used, which is the usual convention for trigonal (and hexagonal) crystals. Due to the bulky shape of the original crystal only the orientation of the cube is shown. The face in top view is the $(\bar{1}011)$ face, the side faces are a $(01\bar{1}1)$ face that is tilted by 3° to the cube face, and a $(1\bar{1}01)$ face that is tilted by 6° to the cube face.

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