Generalized dispersion analysis of arbitrarily cut monoclinic crystals

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ABSTRACT

Dispersion analysis is applicable to arbitrarily cut monoclinic crystals of unknown orientation in order to find the symmetry axis. By this it is possible to differentiate between the transition moments oriented parallel and normal to the *b*-axis and to determine the dielectric tensor functions of those two principal directions. Dispersion analysis of arbitrarily cut monoclinic crystals is based on an extension of the evaluation scheme developed for arbitrarily cut orthorhombic crystals. We present dispersion analysis of monoclinic crystals exemplarily on spodumene ($LiAl(SiO_3)_2$) and yttrium orthosilicate (Y_2SiO_5).

1. Introduction

Dispersion analysis is the determination of oscillator parameters of a material (e.g. a crystal), mainly based on the evaluation of polarized reflection spectra [1]. With the oscillator parameters the dielectric tensor function for the investigated spectral region is calculated and by that the optical properties like absorption or transmission are derived.

Usually, if the crystal orientation is unknown, the crystal gets oriented via X-ray investigation. Then a principal cut of the crystal can be prepared, so that the reflection of the symmetry axis (crystal *b*-axis) and the *a-c* plane can be measured independently. Yet, if the crystal is too small, too brittle or too precious to be cut appropriately, no principal cut of such a crystal will be available. Many organic crystals usually grow only in small sizes, furthermore, as own experience showed, the accurate cutting of a sample into a certain orientation can be a time-consuming procedure. If an arbitrarily oriented sample is not allowed to be cut since it will be used for further investigations, also no principal cut will help to determine the oscillator parameters. If a sample is not cut in principal orientation, reflection spectra will exhibit bands of both the *b*-axis and *a-c* plane, which leads to false results for the dielectric tensor function, if the mixing of the oscillators is not taken into account.

Therefore, we show how to perform dispersion analysis correctly and gain the dielectric tensor function for monoclinic crystals regardless of the orientation of the *b*-axis within the sample.

Characteristic for a monoclinic crystal is that it has two types of transition dipole moments. The first type is oriented parallel to the monoclinic *a-c* plane, but, since the *a-c* axes are not perpendicular to each other, transition dipole moments can have any orientation in this plane. In contrast, the second type of transition moments is oriented parallel to the crystallographic *b*-axis, which itself is perpendicular to the *a-c* plane. Furthermore, the orientation of the transition dipole moments of the *a-c* plane is frequency dependent, while the transition dipole moments parallel to the *b*-axis remain in this orientation, independent of frequency, and by this creating the crystal symmetry axis in the first place. As the monoclinic crystal (like the orthorhombic crystals) have no plane created by twofold degenerate transition dipole moments as it is the case for uniaxial crystals, the monoclinic crystal (like the orthorhombic crystals) belong to the optically biaxial crystals. For more information to the absorption and fluorescence angular distributions in polarized light of monoclinic crystals and corresponding tensor properties the reader is referred to the work of Petit et al. in [2].

Towards our final goal of determining the dielectric tensor function, symmetry, and the orientation of an arbitrarily cut crystal with unknown symmetry, we present in this paper the generalized dispersion analysis of (the last remaining crystal family to be investigated) the monoclinic crystals. By orientation we mean the mutual relation between the crystallographic axes and the morphology of the investigated crystal at disposal. Although with lowest symmetry, the measurement and evaluation scheme for triclinic crystals was the easiest one to develop [3]. This experience was the basis for the development of the more demanding evaluation scheme, in order to perform dispersion analysis on arbitrarily cut uniaxial crystals [4], which had to take into
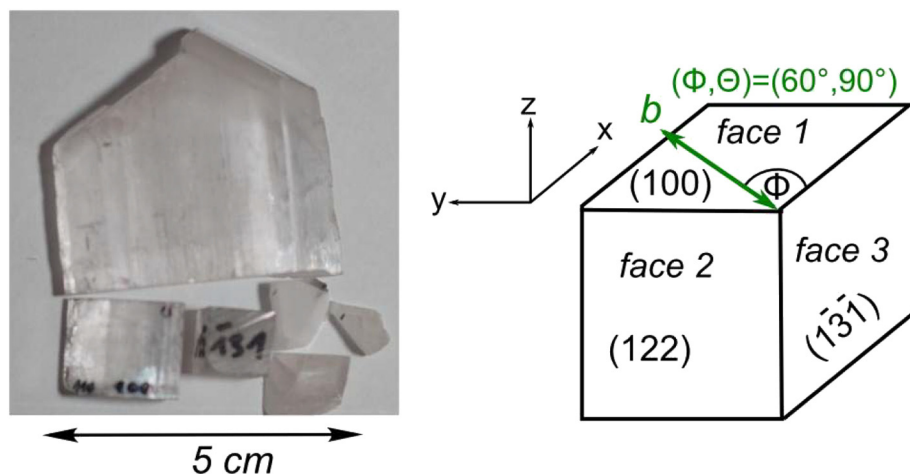
Fig. 1. Spodumene bulk crystal and initial orientation of the b-axis and Miller indices of the faces. Faces 1, 2 and 3 are the investigated faces. Since the IR-beam is incident from below the investigated face 1 is the bottom face. The term initial orientation refers to the orientation of the internal coordinate system (x,y,z) to the crystal faces for the first measurement.

consideration the twofold degenerated transition moments characterizing them. The evaluation scheme for the uniaxial crystals [4] in turn was the basis for dispersion analysis of arbitrarily cut orthorhombic crystals [5], by introducing the necessity to further include the cross-polarization spectra into the calculus. In this work, the method was extended to perform dispersion analysis on arbitrarily cut monoclinic crystals. Our investigation main focus was the reliability and the reproducibility of the results obtained using the generalized dispersion analysis, thus abstaining from refining the previously reported band assignments.

2. Experimental

We chose the corresponding crystal samples in order to have different structural and spectral properties in the infrared region (4000–100 cm^{-1}) and thus to cover the different levels of difficulty as explained in the following. The structure of spodumene and therefore its spectra are dominated by the barely distorted SiO$_4$ tetrahedra, the Y$_2$SiO$_5$ single crystal was chosen for its comparably high number of infrared active bands (45 in total). Both investigated crystals have space group C_{2h}^6, No. 15 in the International Tables of Crystallography [6]. The Y$_2$SiO$_5$ crystal was grown by Czochralski method by the Leibniz-Institut für Kristallzüchtung, Berlin. The spodumene crystal was purchased from a private mineral collection. From both crystals, cubes with an edge length of 5 mm and 10 mm were cut. The crystal faces were polished with 1 μm diamond paste on a silk cloth, the diamond paste was diluted in Lubricant Yellow purchased from Struers.

The reflectance spectra were recorded with a Bruker V80v FT-spectrometer with a resolution of 4 cm^{-1}, while the samples were mounted on an 8° incidence angle reflection unit from Harrick scientific. Of each sample 24 spectra with polarized incident light were recorded, following the measurement scheme and nomenclature introduced for the triclinic crystals [3]. 12 of the 24 spectra were recorded with an additional analyzer inserted into the beam path as described in [7]. We call the spectra recorded with both the polarizer and analyzer "cross polarization spectra", while the spectra recorded with only polarized incident

light are called "one polarizer spectra". To polarize the incident beam we used an Al/KRS-5 wire grid polarizer for the MIR region (5000–360 cm^{-1}) and a polyethylene polarizer for the FIR region (600–80 cm^{-1}). The measured spectra were fitted with a self-written program in Matlab [8] based on the "fminunc" [9] and "fminseach(bnd)" [10] algorithms. To rate the fitted dispersion parameters we compared them to the parameters gained from samples of the same crystals in principal cut.

2.1. Crystal Morphology and Structure

Spodumene belongs to the pyroxene group [11] with unit cell parameters $a = 9.45$ Å, $b = 8.37$ Å, $c = 5.21$ Å and $\beta = 110.10°$ [12]. The orientation of the b-axis (needed for further comparison with dispersion analysis results) was found with the help of a stereographic projection created of the crystal face angles. The crystal consists of infinite SiO$_4$ tetrahedra chains and are not connected directly to each other but by interstitial AlO$_6$ octahedra. The sites between adjacent SiO$_4$ tetrahedra are occupied by Li ions [12]. A detailed figure of the structure can be found in [13] or [14]. The bond lengths of the SiO$_4$ tetrahedra are between 2.53 and 2.74 Å, the bond angles range from 104.2 to 116.5°. The bond lengths of the AlO$_6$ octahedra have a similar range from 2.5 to 2.78 Å, whereas the bond angles deviate up to 11° from the ideal angles 90° and 180° [15].
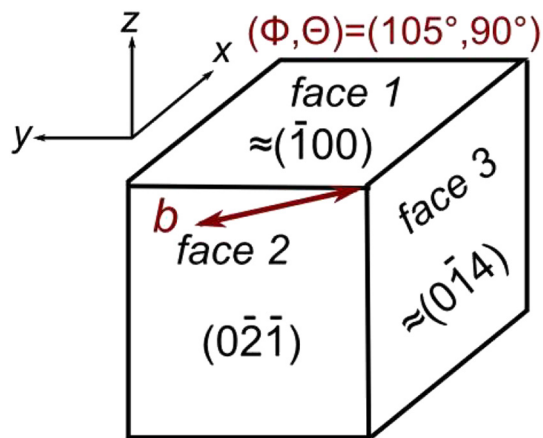

Fig. 2. Initial orientation of the faces of the Y$_2$SiO$_5$ cube. Face 1 and 3 of the Y$_2$SiO$_5$ sample have very high Miller indices and are therefore approximated by $(\bar{1}00)$ and $(0\bar{1}4)$, the face normal to $(\bar{1}00)$ has the orientation angles $(\Phi,\Theta) = (164°, 5°)$, the face normal to $(0\bar{1}4)$ is oriented with $(\Phi,\Theta) = (170°, 82°)$.

Table 1
Nuclear site group analysis for spodumene, space group C_{2h}^6, Z = 4.

Ion	Wyckoff position	Contributed vibrations per ion
1 × Li, 1 × Al	4e	$A_g + A_u + 2B_g + 2B_u$
1 × Si, 3 × O	8f	$3A_g + 3A_u + 3B_g + 3B_u$
Raman active: $14A_g + 16B_g$		$\Sigma 14A_g + 14A_u + 16B_g + 16B_u = 60$ modes
Acoustic: $A_u + 2B_u$		Total IR active: $13A_u + 14B_u$