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Dispersion analysis of arbitrarily cut orthorhombic crystals

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ABSTRACT

We developed a measurement and evaluation scheme to perform dispersion analysis on arbitrarily cut orthorhombic crystals based on the schemes developed for triclinic and uniaxial crystals. As byproduct of dispersion analysis the orientations of the crystal axes are found.

In contrast to the spectra of arbitrarily cut uniaxial crystals, where the fit routine has to separate two independent principal spectra, the spectra of arbitrarily cut orthorhombic crystals are a combination of three independent spectra and the evaluation scheme gets more complex. Dispersion analysis is exemplary performed on two different crystals, which show different spectral features and different levels of difficulties to evaluate. Neodymium gallate ($NdGaO_3$) has broad overlapping reflections bands while topaz (Al_2SiO_4 [F, OH]$_2$) has a quite high total number of infrared active bands.

1. Introduction

Dispersion analysis is defined as the determination of dispersion parameters of a material based on polarized spectra [1]. The dispersion parameters are the resonance wavenumber, oscillator strength, damping constant and orientation angles of the oscillators visible in the spectra, plus the dielectric background. The dispersion parameters allow computing the dielectric tensor function of the material in the investigated spectral region. To perform a correct dispersion analysis on orthorhombic crystals the crystal orientation has to be taken into account, since for orthorhombic crystal the dielectric axes are orthogonal to each other and fixed by the crystals symmetry elements.

By now, dispersion analyses on orthorhombic crystals have only been performed on crystals in principal cuts (the symmetry elements are parallel or normal to the crystal faces), which of course implies that the crystal orientation is known. The usual way to orient crystals is X-ray analysis, but even if the crystal orientation is determined by X-ray analysis, the crystals must be cut in principal orientation by a qualified person. Producing a specified cut out of a crystal can be a very time-consuming task. If the crystal is not large enough to be cut, or too brittle to produce a certain cut, or must not be cut since the crystal is e.g. precious or is needed unaltered for further investigations, the described method of generalized dispersion analysis is the only way to gain the complete set of dispersion parameters.

The matter of size concerns especially organic crystals, of which the fewest grow into crystals that are large enough to be cut. In the described method dispersion analysis goes hand in hand with the determination of the crystal orientation, which can be considered as a byproduct of dispersion analysis, which makes the orientation of orthorhombic crystals via X-ray redundant.

One possible application of generalized dispersion analysis is e.g. the in-situ examination of phase transitions induced by changing the thermodynamic variables [2]. 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 is not known a priori.

A vast amount of phase transitions have been investigated during the past decades For actinide diphosphates phase transition at high temperatures, depending on the acitinide ion, between the cubic and triclinic system takes place [3]. The perovskite-like system $PbZr_{1-x}Ti_xO_3$ changes from tetragonal to monoclinic structure at about 300 K [4]. Sodium potassium niobate perovskites, which are monoclinic at room temperature, undergo monoclinic-tetragonal and tetragonal-cubic transitions with increasing temperature [5].

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1386-1425/

	Face 1:	Face 2:	Face 3:
One polarizer	R_s 0 0 0	R_s 0 90 0	R_p 90 90 90
	R_p 0 0 0	R_p 0 90 0	R_s 90 90 90
	R_p 45 0 0	R_s 0 90 45	R_s 90 90 45
	R_s 45 0 0	R_p 0 90 45	R_p 90 90 45
Polarizer + analyzer	R_{sp} 0 0 0	R_{sp} 0 90 0	R_{ps} 90 90 90
	R_{ps} 0 0 0	R_{ps} 0 90 0	R_{sp} 90 90 90
	R_{ps} 45 0 0	R_{ps} 0 90 45	R_{sp} 90 90 45
	R_{sp} 45 0 0	R_{sp} 0 90 45	R_{ps} 90 90 45

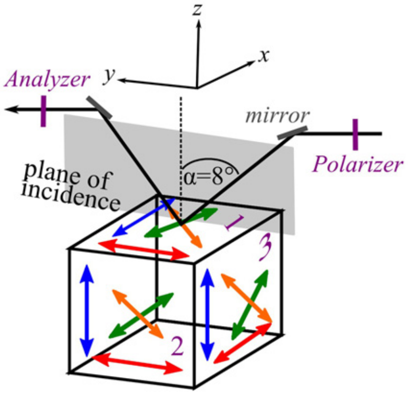

Fig. 1. To perform dispersion analysis on orthorhombic crystals 12 spectra with one polarizer and 12 spectra with a polarizer and analyzer with crossed transmission direction are recorded. A set of 12 spectra comprises four spectra of each of three non-coplanar crystal faces (not necessarily orthogonal to each other), of which for two spectra the plane of incidence is parallel to a face edge (blue and red double arrows), and for tow spectra the plane of incidence is at 45° to the face edges (orange and green double arrows). In the real setup the light in incidence from below. The label of the spectra is a combination of the orientation of the sample in the spectrometer and the employed polarization direction of the incident light.

Tetracyanoethylene is an example for a crystal, which has a cubic (at about 4 K) and monoclinic phase (above 318 K) [6]. All these could favorably be investigated by generalized dispersion analysis.

The measurement and evaluation scheme is the subject of this paper, avoiding any detailed band assignment, but focusing on the results of the evaluation scheme instead.

2. Experimental and characterization of crystals

The investigated crystals are neodymium gallate ($NdGaO_3$) and topaz ($Al_2SiO_4[F, OH]_2$). The space group of both crystals is Pnma or D_{2h}^{16}, with four formula units per unit cell ($Z = 4$). The $NdGaO_3$ crystal was grown by Czochralski method by the Leibniz-Institut für Kristallzüchtung, Berlin. From the originally bar-shaped crystal a cube with an edge length of 5 mm was cut. The topaz crystal is a naturally grown sample and provided by the Mineralogische Sammlung, Jena. On each sample three non-coplanar faces were optically polished with 1 μm diamond paste (Stuers) on a silk cloth.

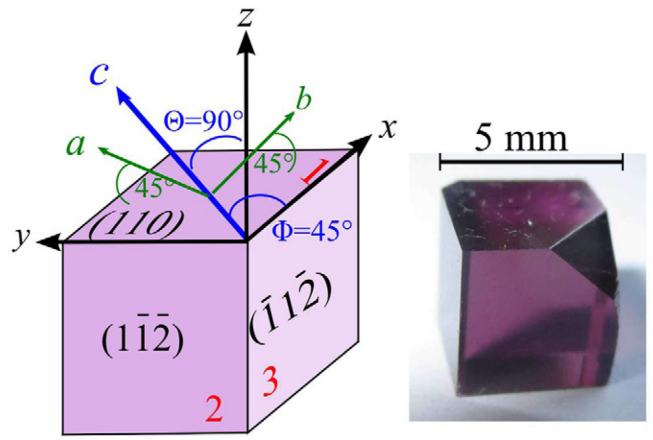

Fig. 2. Left: Orientation of the crystal axes of the $NdGaO_3$ cube cut out of the Czochralski-grown bar and Miller indices of the cube faces. The numbers in red indicate the measured sample faces; face 1 is the projection from the bottom face as the beam is incident from below. Right: The sample is a purple transparent crystal.

The IR spectra were recorded with a Bruker V80v FT-spectrometer with a resolution of 2 cm^{-1} for both the MIR (4000 cm^{-1}–360 cm^{-1}) and FIR (500 cm^{-1}–100 cm^{-1}) spectral region. To obtain linearly polarized incident light we used an Al/KRS-5 wire grid polarizer in the MIR region and a polyethylene polarizer for the FIR region. The crystal cubes were mounted on an 8° reflection unit from Harrick scientific. The spectra were recorded and named according to the measurement scheme for the triclinic crystals as described in [7,8]. Due to the not-cubic shape of the topaz, however, the Euler angles for the third face were $(\varphi\ \theta\ \Psi) = (95°\ 90°\ 90°)$, $(95°\ 90°\ 45°)$ instead of $(\varphi\ \theta\ \Psi) = (90°\ 90°\ 90°)$, $(90°\ 90°\ 45°)$. However, we found during the optimization process of the 12 measured reflection spectra that the orthogonality condition in Eq. (3) is necessary, yet not sufficient to find the crystal axes unambiguously. The fitted spectra had a very good agreement to the measured spectra, but yielded incorrect orientation angles for the transition moments, partly far off the correct values. This is consequence of the still extremely high dimensional parameter space, which is not reduced sufficiently by the orthogonality condition. Therefore, to support the fit routine, additional so-called cross polarization spectra were recorded by inserting an analyzer into the beam path, so that the sample holder is sandwiched between a polarizer and analyzer. The polarizer and analyzer have crossed transmission directions. With this setup, 12 reflection spectra are recorded in the same way as given in Fig. 1.

Fig. 1 illustrates the positions of the polarizer and analyzer, the polarization directions of the incident light represented by the differently colored double arrows, and the name of the respective spectrum. The indices *s* and *p* describe the polarization direction of the incident light normal and parallel to the plane of incidence, respectively. When spectra labels consist of two indices, the first describes the transmission direction of the polarizer and the second describes the transmission direction of the analyzer with respect to the plane of incidence. The three-angle labels are a combination of the polarization directions of the incident light and the rotation of the sample in the spectrometer.

To allow reproducibility of the measured spectra with other samples of the same crystal kind and to rate the results gained by dispersion analysis the orientation of the crystal axes in the employed samples was identified with X-ray analysis in the case of $NdGaO_3$. For topaz information about the orientation of the axes was provided by the Mineralogische Sammlung, Jena.