Raman Spectroscopy Investigation of the Polar Vibrational Modes in CuB2O4

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Abstract. We report results of polarized Raman spectroscopy of piezoelectric copper metaborate CuB2O4 (space group I̅42d, Z = 12) in the range from 80 to 1300 cm⁻¹. Due to the dense population of the phonon spectra we carried out angular-dependent measurements by rotating the sample in different crystallographic planes thus performing gradual transitions from one polarization configuration to another. The different angular dependence of the scattering intensities of vibrational modes of different symmetries allowed us to obtain Raman signal from some transversal optical (TO) modes of E-symmetry and to demonstrate the single-mode behavior of the B2 modes by means of transition from TO character to longitudinal optical (LO) character of these phonons.

1. Introduction
Copper metaborate CuB2O4 is an intriguing system with interesting magnetic, acoustic, dielectric, and magnetooptical properties. The complex crystal structure with magnetic Cu²⁺ ions in symmetrically nonequivalent positions leads to a variety of magnetic phases at low temperatures starting with an antiferromagnetic ordering below T_N = 21 K [1]. Commensurate and incommensurate magnetic structures arise as a result of interactions within and between the different copper sublattices. In connection to its interesting magnetic behavior, this material also demonstrates a rich variety of linear and nonlinear optical properties. A couple of examples are magnetic-field-induced second harmonic generation [2, 3] recently reported magnetic-field induced chirality [4], and magneto-electric dichroic signals [5].

Below 1.35 eV, CuB2O4 is transparent. A complex absorption band is seen in the range of 1.35–2.5 eV related to electronic transitions between crystal-field-split levels within two different 4b and 8d copper sublattices [6]. Above 2.5 eV, CuB2O4 becomes again transparent up to 3.8 eV where the fundamental absorption due to charge-transfer (CT) transitions begins [6]. This window defines a dark blue color of CuB2O4.

The study of low-temperature optical absorption spectra and second harmonic generation spectra established six zero-phonon (ZP) lines with exceptionally rich structure of phonon sidebands [6] which seems exotic for a 3d compound as CuB2O4. Motivated by the challenge to rationalize this rich vibronic structure, several thorough studies of the lattice dynamics and the vibronic spectra of CuB2O4 appeared recently [7, 8]. Detailed infrared (IR) and Raman investigations identified almost all zone-center optical phonon modes [7, 8]. Especially, in the Raman measurements of polar phonons the emphasize was mainly put on longitudinal optical (LO) modes.
In this study we exploit the abilities of polarized Raman spectroscopy combined with rotation of the sample about various crystal axes. This enabled us to obtain from Raman measurements the frequencies of several transversal optical (TO) phonons that were so far known only from IR studies. We also confirm the belonging of TO and LO components to each other for some polar modes with a larger LO/TO splitting.

2. Experimental

CuB$_2$O$_4$ single crystals were successfully grown by the high-temperature solution growth method. The starting materials CuO and B$_2$O$_3$ were taken in 1:20 molar ratio, B$_2$O$_3$ being used as a flux. The mixture was first homogenized for 48h at 980 °C and then cooled to 750 °C at a cooling rate of 1 °C/h. The crystals were grown in a platinum crucible and the process took place in a resistive heating oven in air atmosphere. The size of the crystals synthesized at the bottom and walls of the crucible was up to 7 × 3 × 3 mm$^3$.

The crystallographic characterization of the crystals was carried out by X-ray single-crystal diffractometry. A single crystal was mounted on a glass capillary and diffraction data were collected at room temperature by an ω -scan technique, on an Agilent Diffraction SuperNova dual four-circle diffractometer equipped with an Atlas CCD detector. A mirror-monochromatized Mo Kα radiation from a microfocus source was used (λ = 0.7107 Å). The determination of the cell parameters, data integration, scaling, and absorption correction were carried out using the program package CRYSTALS [9]. The structure was solved by direct methods (SHELXS -97) [10] and refined by full-matrix least-square procedures on F2. The single-crystal x-ray diffraction confirmed the $\Gamma$ -42d crystal structure with lattice parameters a = 11.4972 Å and c = 5.6290 Å and atomic site positions close to those of [11, 12].

For the spectroscopic measurements single crystals with elongated shapes along the Z axis with naturally grown {100} and {001} surfaces were selected which additionally displayed well shaped {110} surfaces. The Raman spectra were measured in the range of (80 - 1300) cm$^{-1}$ on a HORIBA Jobin Yvon Labram HR visible spectrometer equipped with a Peltier-cooled CCD detector. The 1.95 eV line of a He-Ne laser was used for excitation, the absolute accuracy being 0.5 cm$^{-1}$. At this energy there is an absorption band due to crystal-field induced transitions. Therefore this excitation energy was chosen to minimize the path length of the laser light inside the crystal in order to avoid possible birefringence effects.

3. Results and Discussion

Copper metaborate CuB$_2$O$_4$ crystallizes in a noncentrosymmetric tetragonal structure with the point group symmetry 42m, the space group $I\bar{4}2d$ (No. 122).2,3,5,30 [13]. The unit cell contains 12 formula units and the lattice parameters are a = b = 11.484 Å and c = 5.620 Å. The structure comprises a strongly coupled three-dimensional (3D) network of BO$_4$ tetrahedrons with cavities between them occupied by copper ions in the 4b and 8d positions. There are two types of boron atoms B1(16e) and B2(8d) positioned at the centers of tetrahedrons, and the bond lengths B-O vary between 1.44 and 1.48 Å. The tetrahedrons’ vertices are linked by common oxygen ions. There are four nonequivalent oxygen positions in the unit cell, O1(16e), O2(8d), O3(8d), and O4(16e).

The primitive unit cell contains 42 atoms, which results in 126 normal modes. After subtracting acoustic and silent modes one ultimately obtains the distribution of the Raman active modes as follows:

$$\Gamma_{\text{Raman}} = 13A_1 + 14B_1 + 17B_2(z) + 31E(x,y).$$ (1)

The modes $B_2$ and E are polar. $B_2$ modes vibrate along the z-axis and the vibrational patterns of the E modes lie in the (x,y) plane. The Raman tensors for the pertinent modes have only the following non-zero elements:
A_1: \alpha_{xx} = \alpha_{yy} = a, \alpha_{zz} = b; \\
B_1: \alpha_{xx} = c, \alpha_{yy} = -c; \\
B_2(z): \alpha_{xy} = \alpha_{yx} = d; \\
E(x): \alpha_{yz} = \alpha_{zy} = e; \\
E(y): \alpha_{xz} = \alpha_{zx} = e.

For the polarized Raman measurements we use the notations X (100), Y (010) and Z (001) for the main crystal axes as well as X' (110) and Y' (-110). The spectra were measured by irradiating the crystal along the Z axis and along different directions in the in the XY plane as a function of the azimuthal angle in the XY plane and the pertinent rotational angle, respectively. We used the following scattering configurations in Porto notations:

(i) Z(x_\phi y_\phi)Z, where x_\phi and y_\phi are orthogonal variable directions in the XY plane, the azimuthal angle \phi being the angle between X and x_\phi;

(ii) x_\phi(Z y_\phi)x_\phi, where x_\phi and y_\phi are orthogonal variable directions in the XY plane, the rotational angle \phi being again the angle between X and x_\phi.

(iii) x'_\phi(Y'Y')x'_\phi, where x'_\phi is a variable direction in the X'Z plane, depending on the rotational angle \phi between X' and x'_\phi.

Figure 1. Azimuthal-angle dependence of the Raman spectra in Z(x_\phi y_\phi)Z configuration. Frequencies of B_1 (B_2) modes are given in blue (red). Spectra in well defined scattering configurations are plotted in blue (B_1 modes allowed) and red (B_2 modes allowed).

The scattering intensity is |\mathbf{e}_i \cdot \mathbf{R} \cdot \mathbf{e}_s|^2, where \mathbf{e}_i and \mathbf{e}_s are unit vectors in the directions of the incident and the scattered radiation, respectively, and \mathbf{R} is the corresponding Raman tensor. The theoretically
predicted Raman intensity dependence on the angle $\phi$ for the examined vibrational modes is given in table 1.

Table 1. Theoretical Raman intensities, variable configurations dependent on the rotational angle $\phi$.

|          | $Z(x_0y_0)Z$ | $x_0(Zy_0)x_0$ | $X'(Y'Y')X'$ | $Z(Y'Y')Z$ |
|----------|--------------|----------------|---------------|-------------|
| $B_1$    | $|c|^2\sin^2 2\phi$ | 0              | 0             | 0           |
| $B_2$    | $|d_{LO}|^2\cos^2 2\phi$ | 0              | $|d_{TO}|^2$   | $|d_{LO}|^2$ |
| E(TO)    | 0            | $|e_{TO}|^2\sin^2 2\phi$ | 0             | 0           |
| E(LO)    | 0            | $|e_{LO}|^2\cos^2 2\phi$ | 0             | 0           |

With figure 1 we exemplify the advantage of the azimuthal-angle dependent polarized measurements in $Z(x_0y_0)Z$ configuration. The doublet at $386 - 390$ cm$^{-1}$ consists of a $B_1$ mode at $386$ cm$^{-1}$ [7, 8] and a symmetry forbidden E(TO) mode at $390$ cm$^{-1}$ with comparable intensity. Due to the relatively weak Raman intensity of this particular $B_1$ mode, its correct assignment in one fixed polarization configuration would be difficult. By means of the azimuthal-angle dependence of its intensity, however, it can be reliably assigned because the intensity of the forbidden mode remains constant.

![CuB$_2$O$_4$ rotation about Z in crossed polarization](image)

**Figure 2.** Raman spectra with intensity transfer from the TO to the LO component and vice versa (only E modes allowed by selection rules). Spectra in well defined scattering configurations are plotted in blue (LO allowed: $\phi = 0^\circ$) and red (TO allowed: $\phi = \pm 45^\circ$).
Figure 2 displays Raman spectra in scattering configurations $x_0(Z_{y_0})x_0$ selecting the E modes at different values of the rotational angle about the Z axis. This illustrates the gradual intensity transfer between the TO and the LO component of the E modes and facilitates identifying components with weak intensity as well as TO/LO pairs with larger splitting. In this way we provided a Raman verification of the TO/LO pair at 390 – 397 cm$^{-1}$, respectively, and of the TO components at 908, 979, 1083, 1122 and 1176 cm$^{-1}$ which were so far only detected with IR spectroscopy [7].

The first-order Raman spectrum of CuB$_2$O$_4$ is densely populated with 75 modes distributed between 100 and 1250 cm$^{-1}$. Assignment of nondegenerate polar B$_2(z)$ modes with larger TO/LO splitting is therefore particularly difficult because they appear at different frequencies in different scattering configurations. We therefore measured a series of Raman spectra in configurations gradually passing from $X'(Y'Y')X'$, where B$_2$ modes are TO, to $Z(Y'Y')Z$, where B$_2$ modes are LO vibrations. This was accomplished by rotating the sample about the $Y'$ direction. B$_2$ modes of tetragonal CuB$_2$O$_4$ as a function of the angle $\phi$ between the Z axis and incident laser direction $K_i$ are depicted in figure 3. The spectra at different values for several elevated B$_2$ modes demonstrate a monotonic migration of the B$_2$ frequency from the TO to the LO value thus additionally confirming the belonging of TO and LO components to each other.

The spectra at different rotation-angle values for several elevated B$_2$ modes are depicted in figure 3 and demonstrate an approximately linear migration of the B$_2$ frequency from the TO to the LO value thus additionally confirming the belonging of TO and LO components to each other.

![Figure 3](image_url) **Figure 3.** Raman spectra gradually passing from $X'(Y'Y')X'$ to $Z(Y'Y')Z$ scattering configuration (as shown by green arrows) by rotating the sample about the $Y'$ direction. The rotation angle goes from 90 deg to zero from top to bottom.
4. Conclusion
We obtained polarized Raman spectra of CuB$_2$O$_4$ single crystals in different scattering configurations dependent on rotational angles with respect to the main crystal axes. The different angular dependence of scattering intensity of vibrational modes with different symmetries enabled us to verify the belonging to each other of the TO/LO components of several polar modes and to confirm the frequency of some low-intensity TO components with Raman spectroscopy. These results demonstrate the power of Raman spectroscopy in characterization of crystal structures with lower symmetry.

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6. References
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