# Shining light on CuO for exploring high-Tc multiferroics

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Abstract. Searching for a 3D multiferroic material with a strong magnetoelectric coupling and high critical temperature is a major challenge in modern condensed matter research. CuO is the building block of high-temperature superconductors and triggered a new interest when it was established as potential high temperature multiferroic. We have succeeded in growing high quality single crystals of CuO with two different methods, namely the floating zone under high oxygen pressure and the chemical vapor transport growth. The fact that we are able to grow crystals of the same compound by different techniques makes it possible to study the effect of slightly different chemical compositions, various kinds of defects and variable strain on the final properties of the compound. Optical spectroscopy has been deployed to study the optical response of cupric oxide. Thereby we achieved a deeper insight of the optical, electronic and structural properties by measuring the infrared reflectivity under a magnetic field and the Raman shift under hydrostatic high pressure.

## 1. Introduction

According to its definition, a multiferroic material is a solid phase where two or more primary ferroic properties are united. In our case we have focused on magnetoelectric materials where an intrinsic magnetization can be induced by applying an electric field or inversely, where an electric polarization can be created by applying an external magnetic field. For being exploitable multiferroicity must occur at high temperature and CuO appears to be one of the few candidates to show multiferroics properties close to room temperature [1].

Cupric oxide, CuO, is one of the two stable copper oxides, the other being  $Cu_2O$ . Even if its chemical formula is very simple, this material is highly interesting because of its structural, chemical and physical properties. CuO is the only monoxide transition metal who crystalizes in a monoclinic crystal system [2], belonging to space group C2/c [3]. The structure of CuO can be viewed as being composed of two types of zigzag Cu - O chains running along two different crystallographic directions. Cupric oxide recovered a new surge of interest since it was established as a joint-order parameter multiferroic compound, where a non-collinear spiral magnetic order breaks inversion symmetry, thus inducing ferroelectricity. In most cases, this spiral-phase-induced ferroelectricity exists only at low temperature, but it was found that for CuO, magnetic transitions occur at 213 K, 229.3 K and 230 K [4].

# 2. Crystal growth

It is well accepted that the credibility of a result in condensed matter experiments is strongly correlated to the quality of the crystal. We successfully grew our own bulk crystals using two different techniques: the optical floating zone method (OFZ) in an image furnace and the chemical vapor transport (CVT) process in sealed quartz tubes. Thanks to both techniques we obtained high quality macroscopic crystals with facets larger than several squared millimeters.

## 2.1. Optical floating zone method

In the first case, commercial powders of high purity (>99.99%) CuO were hydrostatically pressed into a cylindrical rod under 40 MPa. In order to increase the density of the precursors rod we established a grain size analysis. We found that the density of the rods was a major parameter for finding the more stable conditions during the growth. We sintered the rod at 900°C for 72 hours then the rod was cut into two parts: one being about 6 cm long and the second about 2 cm. The long one was hung on the upper shaft and the short one was held on the lower shaft (in order to be used as a seed) of an infrared radiation furnace equipped with two ellipsoidal mirrors. We used 1000 W halogen lamps as light sources. The rods are inserted inside a quartz chamber filled with 9 bars of O<sub>2</sub> at the common focus of both mirrors. By heating the rod ends with the light emitted by the lamps, a molten zone formed that connected the rods to each other. The strong thermal gradient induced a crystallization front in the lower liquid-solid interface when the two parts travel downwards at a controlled velocity. The homogeneity of the liquid was increased by counter rotating the upper rod at 25 rpm and the lower rod at 20 rpm. A crystallized rod was grown using a slow rate of 5 mm/h. Under these conditions, a crystal rod of 4 cm length and 5 mm in diameter was grown.

## 2.2. Chemical vapour transport process

Using the chemical vapor transport method, a mixture of high purity metallic copper was mixed in stoichiometric ratio with BaO<sub>2</sub> according to the formal reaction:  $Cu + BaO_2 \rightarrow CuO + BaO$ . The transport agent I<sub>2</sub> was added to the mixture, with a ratio I<sub>2</sub>:Cu ranging between 0.01 and 0.4. These reagents were sealed in a quartz ampoule, 12 cm long and 0.8 cm inner diameter, under high vacuum equal to  $10^{-5}$  mbar. The sealed ampoule was placed in a resistive furnace with a specific thermal gradient of approximately 6.5 K/cm. The extremity containing the reagents was heated at 950°C and the other side at 820°C during 10 days. The system was then slowly cooled down to room temperature. After breaking the quartz ampoule, the excess of iodine was washed out by several acetone or ethanol bath and some high purity CuO macroscopic bulk crystals were collected in the cold extremity.

#### 2.3. Characterization

The single crystals were characterized by X-Ray diffraction whose results are presented in Fig. 1.



Figure 1. a) XRD pattern on single crystal grown by OFZ. The inset is the rocking curve. b) XRD pattern on single crystal grown by CVT.

We recognize one single orientation in both spectra. By reproducing the measurement on several crystal, we established that both techniques lead to crystals with high quality of crystallization and a preferred cleavable orientation in [-111] direction.

# 3. Optical spectroscopy

We successfully used optical spectroscopy to study the natural frequencies of cupric oxide. In this work, we achieved a deeper understanding of its optical, electronic and structural properties, by measuring the infrared reflectivity under a magnetic field and the Raman shift under hydrostatic high pressure. A large frequency range was under our control to derive the optical modes and define their behavior at the occurrence of magnetic transitions.

# 3.1. Infrared spectroscopy

We performed reflectivity measurements on a CuO sample, grown by OFZ and cleaved in the [-111], at various temperatures from 200 K until room temperature and external magnetic field up to 7 T in the far infrared range from 50 to 650  $cm^{-1}$ . The sample was mounted on a coldfinger placed in a superconducting magnet which is attached to a Fourier Transform Infrared Spectrometer. The absolute reflectivity, presented in the Fig. 2, was obtained by calculating the ratio between the intensity of the reflected beam on the sample and the reflected intensity of a mirror. Polarized incoming light allows us to extract the reflectivity of different planes in the crystal by interpolating the original data as explained in [5]. Data of reflectivity in the range 50 to 650  $cm^{-1}$ , attributed to two different planes, are showed in Fig. 2 a) and b) and are in good agreement with the literature [6].



**Figure 2.** Reflectivity of one CuO single crystal, extracted for the [010] (panel a) and [001] (panel b) crystallographic planes. Solid lines show spectrum measured at zero magnetic field. Dotted lines show spectra measured at 7T. In panels (c) and (d), the intensity ratio between reflectivity at zero field and at 7T (called *Double ratio*) is shown, for the [010] and [001] plane, respectively.

By plotting the ratio between the intensity measured at 7 T and at zero field for different temperatures, we can probe the effect of the magnetic field on the infrared active optical modes. Result of this analysis is shown in Fig. 2 c) and d). For sake of visibility curves are shifted

on vertical axis. We observed that the active infrared modes are not sensitive to an external mangetic field up to 7 T.

# 3.2. Raman scattering

We performed Raman spectroscopy on single crystals of CuO grown by OFZ. The temperature was ramped from 150 K to room temperature and the evolution of the Raman response with T is shown in Fig. 3. The three expected Raman active modes are clearly visible and show very high sharpness and proper intensity according to [7]. We notice the appearance of two small peaks between 200 and 250  $cm^{-1}$  in the Raman shift below the temperature of the magnetic transition. These two peaks confirm the previous observations by Chen *et al.* [8] and are attributed to zone-folded phonons.



Figure 3. Raman shift spectrum of CuO as a function of temperature from 150 to 250K. Zoom at low frequency in the inset.

A study in high hydrostatic pressure conditions at room temperature was performed on microscopic single crystals grown by OFZ. We used a Diamond Anvil Cell filled with Daphnee oil 7373 to reach 25 GPa as described elsewhere [9]. The results of this study are shown in Fig. 4. The behavior of the optical modes under pressure is in very good agreement with the literature[10].



**Figure 4.** a) Raman shift as a function of pressure. b) Pressure dependence of the three Raman modes. Blue dashed line taken from literature

## 4. Conclusion

We have grown high quality single crystals with two different techniques, the optical floatingzone and the chemical vapor transport. A high purity and high crystallinity have been obtained for samples grown by OFZ. We have carried a study of IR and Raman spectroscopy under pressure, magnetic field and temperature of the crystal face [-111] for different polarizations. We confirm the appearance of extra modes below  $T_N$  as expected for the monoclinic structure of CuO. We confirm that the C2/c phase is stable up the 25 GPa. We also observe that magnetic fields up to 7 T for T = 200 K do not change the multiferroic phase. In particular the phonons shift much less than 5  $cm^{-1}$ , if at all.

## References

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