High Temperature Multiferroicity in Cupric Oxide

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Abstract. Multiferroic materials where magnetic and electrical orders coexist have been subject of extensive studies during last few years. Non-collinear/spiral magnetic structures are expected to exhibit concurrent ferroelectricity. CuO which adopts the structure as mineral Tenorite, with monoclinic structure (space group C2/c), has been reported to possess two high temperature antiferromagnetic (AFM) transitions, $T_{N1} \sim 213$ K & $T_{N2} \sim 230$ K. Below the first AFM transition, magnetic structure is reported to be collinear while below later one magnetic structure is non-collinear . In the present study observation of strong anomalies in dielectric and heat capacity measurements around both the $T_N$'s confirm magnetically induced ferroelectricity in CuO.

1. Introduction

Materials which exhibit co-existence of magnetic and electrical orderings foresee tremendous technological applications and have attracted considerable attention in recent years [1]. Magnetic order and ferroelectric polarization in spiral magnets are expected to exhibit strong magneto-electric (ME) coupling effects; recent observation of large magneto-electric and magneto-capacitive effects in TbMnO$_3$ that provides a novel approach to the mutual control of magnetization and electric polarization in magnetic ferroelectrics (FE) materials [2]. However, the multiferroicity in these materials typically occurs at low temperatures, at $\sim 40$K. Recently, significant progress has been achieved in some hexaferrites, where spiral magnetic order (SMO) induced multiferroics and ME effects were discovered at or near room temperature [3]. In addition to the complex compounds mentioned above, a prominent exception was recently discovered in the very well-known oxide, cupric oxide CuO, where SMO-induced polarization is observed in the temperature range of 215-230K [4-5]. Such discoveries extend the family of high-temperature multiferroics. Copper (II) oxide, occurs in nature as the mineral Tenorite, and has a monoclinic structure with the space group C2/c [6].

There are two well-established magnetic transitions in CuO, one at $T_{N1} \sim 213$ K and another at $T_{N2} \sim 230$K [4-5]. A commensurate (CM) collinear magnetic structure develops below $T_{N1}$. In this phase, magnetic moments are aligned collinear along the $b$-axis, such as parallel and anti-parallel zigzag chains of Cu-O along the [101] and [101̅], respectively. With increasing temperature, an incommensurate (ICM) spiral magnetic structure develops, exists between $T_{N1}$ and $T_{N2}$, due to the competition between antiferromagnetic (AFM) and ferromagnetic (FM) interactions. This noncollinear structure results in a net electric polarization through the inverseDzyaloshinskii-Moriya (D-M) interaction and transverse spin-lattice coupling [7]. Above $T_{N2}$, the magnetic susceptibility of CuO undergoes an anomalous continuous rise, instead of a peak at its Néel temperature, and rises to a broad
maximum at about 540K [5]. Even in the strongest magnetic field, the transition temperatures and the associated dielectric anomalies were found to be unaffected by Wang et al.[8]. Considering the SMO as very robust, these authors concluded that the ME effects are nominal in CuO at both $T_{N1}$ and $T_{N2}$. In the present work we have performed structural, dielectric spectroscopy and heat capacity, measurements and investigated the above mentioned transitions.

**Experimental Details**
High-purity CuO (99.995%) powder was pelletized and then heat treated at 800°C for few hours. Phase purity of sintered material was checked by powder X-ray diffraction (XRD) at room temperature using Cu Kα radiation by Bruker D-8 advanced diffractometer. The dielectric measurements were performed using Novo control Alpha-A High Frequency Analyzer, with a homemade test-cell, across 10Hz-10MHz, from room temperature down to 10K. Heat capacity was measured using Modulated Differential Scanning Calorimeter (MDSC) from TA-2910 instruments with temperature range 150-300K in Nitrogen atmosphere, with the scanning rate of 10K/min.

**Results and Discussions**
Figure 1 shows the room temperature Rietveld fitted XRD pattern of CuO, confirming the sample having monoclinic structure with the space group C2/c. A small unavoidable secondary phase of cubic Cu$_2$O was detected (a small peak at ~ 36.4deg.) during Rietveld fitting. Wang et al. [8] also observed the small quantity of same secondary phase. Lattice parameters of synthesized CuO, obtained from fitting, are as follows; $a = 4.6878\,\text{Å}$, $b = 3.4228\,\text{Å}$, $c = 5.1316\,\text{Å}$, $\alpha = 90^\circ$, $\beta = 99.51^\circ$, $\gamma = 90^\circ$. These are similar to those reported elsewhere [8].

Further, we explored the dielectric behaviour of this material in wide frequency range, across magnetic transitions reported in CuO. Zhenget al. [9] reported both the AFM transitions ($T_{N1}$&$T_{N2}$), and unlike other antiferromagnets, they found that its magnetization increases with temperature above $T_{N2}$, and transformation to proper paramagnetic state occurs only at higher temperatures ($630K >> T_{N2} = 230K$). Fig. 2 (a) shows the temperature dependence of real part of dielectric permittivity in the temperature region 200-250K, at two different high frequencies (0.6 &0.8 MHz).

![Room temperature Rietveld fitted XRD pattern of CuO.](image-url)
The dielectric constant shows small FE-like peak at $T_{N2}$ and a decreasing step-like behaviour at $T_{N1}$. It shows no substantial ferroelectric polarization ($P$) exists below $T_{N1}$ and above $T_{N2}$. Observation of a finite $P$ between $T_{N1}$ and $T_{N2}$ is a signature of magnetically induced ferroelectricity. It is to be highlighted here that in an earlier study on CuO single crystal, though the existence of magnetically induced polarization was confirmed in between $T_{N1}$ and $T_{N2}$ through pyroelectric current measurement [4], but the anomaly in dielectric constant around $T_{N1}$ was not as evident as here.

The manifestation of these transitions is also clear in our heat capacity measurement and it show sharp peak at both the commensurate-incommensurate antiferromagnetic transition temperatures (fig.2b). The anomalies observed in the heat capacity are reported here for the first time. Also the anomalies observed here in the dielectric data are much clearer than the previous reports [4, 9].

**Conclusions**

Dielectric anomalies across the incommensurate magnetic phase boundaries, at $T_{N2} \sim 230$K and $T_{N1} \sim 213$K in CuO evidence magnetically-induced ferroelectricity. Anomalies in the heat capacity are observed for the first time, confirming the AFM transitions.

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