A.8: Colossal dielectric permittivity and mechanism of AC conduction in bulk delafossite $CuFeO_2$

As a type II multiferroic, and a member of delafossite family, $CuFeO_2$ (CFO) has received substantial attention due to the presence of structural, magnetic phase transitions and spontaneous spin-lattice coupling properties. It is a well known magneto-electric (ME) multiferroic which has attracted attention as a distinct class of ME multiferroic because of the discovery of ferroelectricity in the first magnetic field induced phase. Recently there has been a great interest for large dielectric constant materials due to their demand in the electronic industry for various applications, such as memory devices, capacitors and energy storage devices. Dielectric properties of CFO system are reported only in the immediate vicinity of magnetic transitions i.e. T<30 K only. Dielectric dispersion mechanism, well above the magnetic ordering temperatures, is yet to be explored for this system. Hard X-ray Application Laboratory (HXAL) of Synchrotrons Utilization Section (SUS) RRCAT has undertaken the present study of details of dielectric properties and mechanism of conduction of CFO system in the vicinity of room temperature. Our results show that this system exhibits a colossal dielectric behavior. Different conduction mechanism dominates at low and high temperatures.

Poly crystalline sample of CFO was synthesized via solid state reaction method. X-ray diffraction (XRD) measurement confirmed phase purity of the prepared sample. XANES measurements suggested Cu in +1 oxidation state, while Fe is in mixed state of +2 and +3, shown in Figure A.8.1(a).

Dielectric measurements (Figure A.8.2(a)), show high value ($>10^4$) of dielectric permittivity with weak temperature dependence accompanied by the peak in the loss tangent data is typically a colossal dielectric permittivity (CDP) behavior observed for CFO system. Two dielectric relaxation processes are observed at low and high temperature regions. Activation energy for low temperature relaxation process has been found to be 0.08 eV. Such low activation energy has been attributed to the interplay between lattice and polaronic defects such as oxygen vacancies, in literature. Mixed oxidation state of Fe^{2+} and Fe^{3+}, is expected to give rise to the oxygen vacancy in the sample. Activation energy for high temperature dielectric relaxation was found to be 1.8 eV, which corresponds to motion of oxygen ions. It is expected that Maxwell-Wagner relaxation is responsible for the observed large dielectric permittivity in CFO system, resulting from the difference in the resistance of grain and grain boundary.

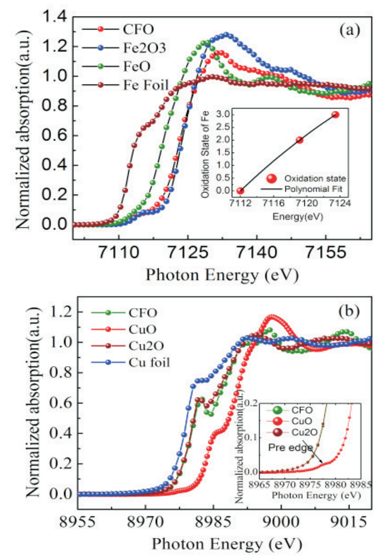

Fig. A.8.1: (a) XANES spectra for CFO measured at (a) Fe, and, (b) Cu edges, respectively.

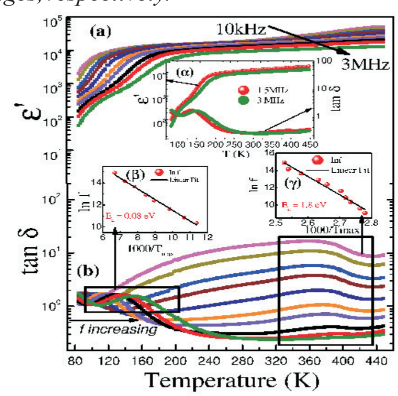

Fig. A.8.2: (a) Variation of dielectric permittivity and (b) loss tangent as a function of temperature at different frequencies. Inset (α) Dielectric permittivity and loss tangent. Inset (β) and (γ) are Arrhenius plots corresponding to the relaxation peak at low temperature and high temperature, respectively.

A comparison of imaginary part of impedance (Z”) and imaginary part of electric modulus (M”) spectra indicates that there are both short and long-range motions of charge carriers in the sample, with short range motion dominating at low temperatures and long range motion dominating at high temperatures. Thus, it can be concluded that CFO material, which is well known for its multiferroicity at low temperatures, also shows the presence of large dielectric permittivity surrounding room temperature. For more details, please see *J. Appl. Phys. 125, 164101 (2019).*

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