ABSTRACT

In ferroelectric oxides with transition metals have no electrons (d^0 ness) in their d orbitals. There are several materials, in spite having d^0 ness and also having a polar soft mode, yet do not show any ferroelectric phase transition, e.g. $SrTiO_3$, $KTaO_3$, $CaTiO_3$, and TiO_2. They are known as quantum paraelectrics. Recently ferroelectricity is realized in a number of multiferroics without d^0 requirement. In this thesis, we have chosen simple oxides like TiO_2 and CuO and investigated the effect of doping and co-doping on dipolar and magnetic ordering. Doping of (Cr, Nb) pair has induced ferroelectricity. Neutron diffraction results indicated no structural transitions with temperature. A relaxor kind of behavior with a switchable pyroelectric behavior with the electric field was found at low temperatures (around 30 K). DFT studies collaborate with the experimental studies. It is however restricted to the low doping regime as higher concentrations lead to clustering and the loss of polarization. Magnetic studies (MH & MT) indicate that the sample was entirely paramagnetic in the whole temperature range 3- 398 K. Replacing the Cr with a ferromagnetic impurity, i.e., (Fe, Nb) pair, was however, unable to induce either ferroelectric or ferromagnetic interaction in the TiO_2 host. The system remains quantum paraelectric but with enhanced paramagnetic moment, at low temperatures the system shows incipient ferroelectric behavior with antiferroelectric interactions while the magnetic properties show paramagnetic behavior with possible antiferromagnetic interactions at low temperature.

Reports on CuO single crystal showed two CM (230 K) and IC (213 K) antiferromagnetic transitions with ferroelectric behavior between these transitions. We could reproduce the ferroelectric behavior in oxygen annealed CuO bulk samples. Doping of either single ions like Co or Zn and codoping of (Li^+, T^{3+}) T = Cr, Fe, and In has destroyed this multiferroic behavior indicating multiferroicity is vulnerable even to slight doping of either magnetic or nonmagnetic dopants. XPS studies indicate doping leads to multiple oxidation states of Cu and the dopants, which cause a huge dielectric constant and a relaxation around room temperature region in all the samples. The complex magnetic structure of CuO found to be vulnerable to different doping ions and their magnetic nature. The 232 K IC transition seems very stable and found in all except with (Li, Fe). Moreover, the 213 K AFM transition transforms to FM with Co and (Li, Cr), while this behavior was absent in the case of nonmagnetic ion doping.

Keywords: Ferroelectricity, multiferroicity, incipient ferroelectric, paraelectric, codoping