ABSTRACT

This thesis describes the experimental investigations of the multiferroic properties of geometrically frustrated swedenborgite $CaBaCo_4O_7$ (CBCO), $CaBaCo_{4-x}B_xO_7$ (B= Ni and Zn: $0 < x \leq 0.10$) and $Dy(Y)BaCo_4O_7$ compounds. They receive special attention for having noncentrosymmetric space group, the large structural distortions, crystal structures build with geometrically frustrated kagome and triangular layers and the magnetic structure of represented with k=0 propagation vector, which is one of the essential symmetry condition for the multiferroic or magnetoelectric coupling. In CBCO the multiferroic properties are reported, however there are no such studies were established in $ABaCo_4O_7$ (A=Y and Rare earth) materials. Having necessary symmetry condition, a set of bonds in kagome layer (couples the c-axis bitetrahedral Co-chains), kagome layer distortion, Co-charge ordering and c-axis anisotropy plays a major role to induce the electric polarization and polarization switching. The CBCO shows different dielectric and heat capacity anomalies compared to magnetic transition and the reason behind the magnetic origin dipolar ordering (pyroelectric) is unclear. Present ac magnetization study on CBCO has revealed a kink at 66 K apart from a frequency independent peak at 60 K (T_C) andthese transitions match closely with the dielectric and heat capacity anomalies. A pyroelectric current measurement shows a nonswitchable electric polarization and neutron powder diffraction (NPD) confirms noncolinear ferrimagnetic ordering with net magnetization along the b-axis. The competing magnetic interactions in CBCO changes drastically upon doping and modifies the multiferroic ground states. Magnetic ion, i.e., Ni^{2+} substitution in kagome layer shows multiple magnetic and dielectric transitions at 60 K and 80 K and switching from pyroelectric to ferroelectric state. Particularly, NPD studies on 10% Ni doped sample showed a transition from noncolinear magnetic structure to the collinear magnetic structure with ↑↑↓↓ ordering in the kagomé planes, further, an increase in c-axis parameter and negative thermal expansion below 80 K. The 3% nonmagnetic Zn doping at Co site in CBCO showed competing magnetic phases and coexistence of magnetic glassy state with the ferroelectric state at low temperatures. With increasing Zn % to 10% a collinear spin structure like in the case of Ni doping was observed, however, the ferroelectric behaviour disappears. Closer observation revealed a decrease in the kagome layer distortion and increase of local disorder with nonmagnetic Zn in kagome layer leading to suppression of the electric polarization. On the other hand, the structural, dielectric and pyroelectric current studies on $DyBaCo_4O_7$ and $YBaCo_4O_7$ shows the absence of electric polarization. The absences of kagome layer distortion and charge ordering (Co^{3+}:Co^{2+} ; 1:3) seem to be important to establish multiferroic properties in $ABaCo_4O_7$ compounds.

Keywords: Geometric frustration, structural distortion, multiferroicity, ↑↑↓↓ magnetic ordering, neutron diffraction and multiglass.