

Thesis Abstract

Multifunctional materials with novel magnetic and electric properties have attracted intense research interest due to prospects in technological applications as well as understanding of fundamental physics. Perovskite materials with ABO_3 structure belong to one of the most interesting and vastly studied families by virtue of their rich magnetic and electrical properties. In the present thesis, efforts have been made to investigate the magnetic, electrical, and structural properties of A and B-site doped perovskites.

In the beginning, a general introduction to basic concepts of various physical phenomena are discussed. This is followed by a brief description of the various experimental methods employed including sample synthesis and single crystal growth. Fe^{3+} and Mn^{3+} have the same ionic radii in oxygen octahedra. However, Mn^{3+} is Jahn–Teller active, and the magnetic ground states of $RFeO_3$ and $RMnO_3$ are completely different. The evolution of structural and electrical properties with doping of Mn^{3+} ion in $RFeO_3$ was investigated on a series of $NdFe_{1-x}Mn_xO_3$ ($0 \leq x \leq 1$) compounds. Despite similar ionic radii in Mn^{3+} and Fe^{3+} , a large variation in the lattice parameters and a crossover from dynamic to static Jahn–Teller distortion were discernible. The magnitude of Fe/Mn–O–Fe/Mn bond angle on ab plane and activation energy corresponding to transport and dielectric relaxation (deduced by assuming the small polaron hopping (SPH) model) vary with doping in a characteristic manner which was attributed to changes in magnetic interaction. Effects of size mismatch at B-site were investigated by doping Mn-site with Ni cations in Ho_2NiMnO_6 compound. This induces B-site ordering which leads to double perovskite structure and ferromagnetic ordering at $T_C = 86$ K. Ideal Curie–Weiss law fails to provide a reasonable fit in the paramagnetic region which follows a modified Curie–Weiss law. Such a deviation occurs due to presence of heavy rare earth element Ho. Griffiths phase pertaining to the Ni/Mn subsystem was ascertained. Two dielectric relaxations due to phononic and Maxwell–Wagner mechanisms were observed. The system has also been shown to be a potential magnetocaloric refrigerant.

A solid solution of $RFeO_3$ and $RMnO_3$ offer much prospects due to its vastly different magnetic properties. A single crystalline phase is essential for such studies, and we were successful in growing single crystals of $ErFe_{0.55}Mn_{0.45}O_3$ which order antiferromagnetically at 365 K with spin canting-induced weak ferromagnetic moment along c axis. Upon cooling, magnetization along c axis passes through zero at 266.4 K and becomes negative below this temperature and a spin reorientation occurs from $\Gamma_4(G_x, A_y, F_z)$ to $\Gamma_1(A_x, G_y, C_z)$ configuration in the temperature window of 255 to 258 K. Magnetic behavior is explained with spin configuration and interplay between net magnetization of individual Er and Fe/Mn sublattices which are oppositely coupled and have different temperature evolution. To observe the effect of A-site doping on $RFeO_3$ perovskites, $Ho_{0.5}Dy_{0.5}FeO_3$ single crystals were grown. Two spin reorientations of Fe magnetic sublattice were evident viz. $\Gamma_4(G_x, A_y, F_z) \rightarrow \Gamma_1(A_x, G_y, C_z) \rightarrow \Gamma_2(F_x, C_y, G_z)$ at temperatures of 49 and 26 K. As magnetic field along c axis increases, the sample resumes Γ_4 state in place of Γ_1 state. Along c axis, field- induced transition from Γ_1 to Γ_4 is feasible. Studies on hybrid organic-inorganic perovskite compounds have also been carried out on heterometallic $[(CH_3)_2NH_2]Mn_{0.5}Ni_{0.5}(HCOO)_3$ and $[(CH_3)_2NH_2]Co_{0.5}Ni_{0.5}(HCOO)_3$ which were found to crystallize in trigonal space group R-3c at room temperature and order antiferromagnetically with weak ferromagnetism induced by spin canting at 17 and 8 K, respectively. Hydrogen bond ordering leads to spontaneous polarization and structural transition occurs from R-3c to Cc through mixed phase. This is reflected in impedance data also. Highlights of major findings in different chapters and a general conclusion to this study are presented at the end.