Chapter 7

The important findings of the thesis were outlined below:

In this thesis, the effect of transition metals such as Fe/Cr and cation deficiency on structure, J-T distortion, photoluminescence and magnetic properties of $RMnO_3$(R=La,Gd) perovskite are discussed.

- The effect of Fe doping on the evolution of structure and rich sequence of magnetic transitions in $GdMnO_3$ perovskite synthesized through sol-gel technique are studied using XRD, Raman, XPS, magnetization and ac susceptibility measurements. Rietveld refinement of XRD revealed the O' type orthorhombic structure with contraction in 'a' and 'b' parameters and expansion in 'c' leading to decrease in lattice volume in $GdMn_{1-x}Fe_xO_3$ (x = 0, 0.1 and 0.2). The Jahn-Teller (J-T) distortion factor calculated using the bond lengths obtained from Rietveld refinement was found to reduce with an increase in Fe concentration. The lattice contraction was attributed to the presence of Mn^{4+} with oxygen vacancies confirmed through XPS analysis. The observed decrease in J-T distortion resulted from the asymmetric stretching bond located at 487 cm^{-1} in Raman spectra. Magnetic measurements showed increase in T_N from ~42 to ~84 K with an increase in Fe concentration 0 to 20 at%. The maximum magnetization measured at 70 kOe decreased with increasing Fe concentration whereas the coercivity enhanced by two-fold. The maximum magnetization diminished on account of Mn^{4+} ions, whereas enhancement in H_c was attributed to the increase in bond angle, Mn-O-Mn.

The interaction between Mn^{3+} and Mn^{4+} confirmed spin glass and/or cluster glass behavior in $GdMn_{1-x}Fe_xO_3$ perovskites.

- In this chapter, the evolution of structure and the rich sequence of magnetic transitions in $GdMnO_3$ nanoparticles are synthesized through sol-gel technique after increasing Fe concentration (x) from 0.3 to 0.5. Using XRD, Raman, XPS, PL, magnetization and ac susceptibility measurements, we studied the structural transformation from O' to O type orthorhombic structure along with the reduction in lattice volume. While decrease in lattice volume was contributed by the presence of Mn^{4+}, the structural transformation was attributed to reduction in J-T distortion factor calculated using the bond lengths obtained from Rietveld refinement. Raman spectra confirmed a significant reduction in J-T distortion factor due to decrease in the intensity of asymmetric stretching bonds at 487 and 610 cm^{-1}. Further, the emission peak at ~286 nm in PL spectra disappeared with reduction in J-T distortion factor. PL and XPS both confirmed the presence of Mn^{4+}. PL study demonstrated the emission spectra emerging due to allowed electronic transitions within Mn^{4+} energy bands. Magnetic measurements showed an anomalous increase in T_N to ~ 298 K almost room temperature when '*x*' reached 0.5. While T_N increased with Fe doping, T_{SR} decreased distinctly. The mixed valency of Mn was contributed towards SG behavior observed in both samples.
- We systematically examined the structural evolution and rich sequence of magnetic transitions in Cr doped $GdMnO_3$ synthesized using sol-gel technique. As Cr concentration increased from 0.1 to 0.4, we observed the structural transformation from *O'* to *O* type orthorhombic one along with the reduction in lattice volume. The

decrease in lattice volume was due to the smaller ionic radius of Cr^{3+} compared to Mn^{3+}. The structural transformation was manifested by the reduction in J-T distortion factor calculated using the bond length obtained from Rietveld refinement. Raman spectra supported the observed reduction in J-T distortion factor as reflected showing decrease in the intensity of asymmetric stretching bonds at 487 and 610 cm^{-1}. Further, the emission peak at ~286 nm in PL spectra disappeared indicating decrease in J-T distortion factor. PL study demonstrated the emission spectra related to Mn^{4+} energy levels which improved after incorporating 10 at% of Cr^{3+}. Magnetic measurements showed an increase in T_N from ~ 42 K for x=0 to ~ 130 K when x reached 0.4. Along with increase in T_N, magnetization reversal with spin reorientation and magnetic switching effect also observed as x reached 0.3. This type of material can be used in magnetic switching, magneto caloric and spintronics devices.

- In this work, we demonstrated that monoclinic phase of $La_{1-x}MnO_3$ (x=0 and 0.2) could be achieved within a range of x varying from 0 to 0.2 synthesized through simple, cost effective co-precipitation technique. Rietveld refinement of X-ray diffraction pattern at room temperature pointed towards monoclinic distortion causing buckling and tilting of MnO_6 octrahedra, evidenced from the Mn-O-Mn bond angle and Mn-O bond length. FESEM analysis combined with crystallite size calculated from XRD peak profile confirmed nanosize particle and polycrystalline in nature. While Curie temperature of the LaMnO1 and LaMnO2 are 124 K and 219 K respectively, the effective magnetic moment is high in the former sample than the later one due to the presence of more oxygen vacancies evidenced from XPS

analysis. The investigation of frequency dependent ac susceptibility after fitting with Neel–Arrhenius, Vogel–Fulcher and Power law while discarded the canonical spin-glass, cluster-glass and interacting superparamagnetism nature in, both samples, LaMnO2 showed conventional spin glass behavior with a higher relaxation time.

Although the effect of J-T active element and cation deficiency on structural transformation, optical and magnetic properties could show some important findings, there are still several open issues which need to be clarified with proper experimentations in future. Few important suggestions are appended below.

- Due to its optical property and existence of oxygen vacancies, these materials may be used in photocatalytic degradation of dyes.
- The study of structural, magnetic and optical properties of these materials will be studied in thin films.
- Dielectric properties of these samples may be studied to show the magneto-electric coupling.
- To vary the valancy of Mn by different dopant and by creation of oxygen vacancies, these materials may be used in supercapacitors.