

PREFACE

Perovskites, rare earth manganites (RMnO_3 , R= rare earth) are well-studied material for their novel magnetic, electrical and magneto-resistive properties. The structural parameters of these compounds impart a significant role in their properties (Tiwari *et al* 2017). The basic building block of RMnO_3 perovskite structure is MnO_6 octahedra. For ideal perovskite structure, tolerance factor, $t=1$ whereas the stable perovskite structure occurs over the range of $0.89 < t < 1.02$. Tilting of MnO_6 octahedra cooperatively gives an enlarged orthorhombic unit cell when t lies between 0.75 and 0.9. Structural deformation of the perovskite lattice occurs mainly due to two types of distortions: one arises from tilting of MnO_6 octahedra and other is from the asymmetry in six Mn–O bond length surrounding Mn atom in MnO_6 octahedra. The latter one causes the lattice distortion termed as the Jahn-Teller (J-T) distortion. Like other perovskites, in manganites, their physical properties strongly depend on inherent structural imperfections. Several authors have demonstrated the constructive modifications in the structural and magnetic properties of RMnO_3 after doping either at R site or at Mn site. While divalent or monovalent dopant at R site modifies the octahedral distortion due to the mismatch in ionic radii of rare earth and dopants, the dopants substituting Mn site can modify its structure and properties if it is replaced by a non J-T active element.

Among rare earth manganites, GdMnO_3 with an orthorhombic (O') crystalline structure reveals canted AFM at ~ 23 K along with T_N at ~ 42 K [Das *et al*, 2013]. However, a stable structure along with enhanced physical properties of GdMnO_3 finds potential applications in e.g. spintronics and magnetic switching devices etc. Such modifications are strongly coupled with their intrinsic J-T distortion factor. In this context, Nandy *et al.* show

that monovalent dopant like Na in GdMnO_3 which reduces J-T distortion by increasing the tolerance factor from 0.8650 to 0.8782. This leads to an increase in Neel transition, T_N from ~ 42 to 51 K by increasing Mn-O-Mn bond angle from 146.1° to 149.5° [Nandy *et al* 2016]. Sarguna *et al.* report that yttrium (Y^{3+}) having ionic radius of 1.075 \AA smaller than gadolinium (Gd^{3+}), 1.107 \AA , decreases the bond angle Mn-O-Mn from 146.1° to 144.69° resulting in a decrease in T_N from 34 to 32 K. While 5% doping of Tm^{3+} (smaller ionic radius) effectively suppresses the AFM ordering, substituting Yb^{3+} , the magnetoelectric coupling is found to be enhanced [Sarguna *et al* 2014].

Structure stability with physical properties can also be tuned by creating the cation deficiency. LaMnO_3 parent compound exhibits AFM behavior below $T_N \sim 140$ K. Besides, one may find various ground states such as AFM, canted, spin-glass, ferromagnetic insulator or even a ferromagnetic metal with high T_C depending on the stoichiometric La or Mn. The role of La and Mn vacancies thus establish the existence of a pseudocubic crystallographic phase. When the number of vacancies at Mn sites reach 10%, ferromagnetism is destroyed. Ritter *et al.* report that La vacancy is accompanied with oxygen rich composition which shows three different crystal structures such orthorhombic with large J-T distortion, orthorhombic with small J-T distortion and rhombohedral structure. Many efforts have been made by various researchers to increase the T_C by synthesizing various dopants in LaMnO_3 nanostructured materials under different physical conditions like pressure, magnetic field and electric field. Therefore either substitution of various dopants or cation deficiency resulting non-stoichiometry in perovskites not only provides enough opportunities to control the structure, magnetic, magneto-electric and transport properties but also it is important for technological applications.

Important findings of the present work:

Our thorough investigations demonstrate detailed studies on the effect of dopant and cation deficiency in rare earth manganites. RMnO_3 (R=La,Gd) have revealed several key findings which we have reported and published in peer reviewed journals. Some of the important results are listed below:

1. The effect of Fe doping on the evolution of structure and rich sequence of magnetic transitions in GdMnO_3 nanoparticles synthesized through sol-gel technique have been studied using XRD, Raman, XPS, magnetization and ac susceptibility measurements. XRD reveals the formation of pure crystalline phase, orthorhombic structure with space group $Pbnm$ in $\text{GdMn}_{1-x}\text{Fe}_x\text{O}_3$ ($x= 0, 0.1$ and 0.2). The Rietveld refinement establishes the O' type orthorhombic structure with contraction in 'a' and 'b' parameters and expansion in 'c' leading to decrease in lattice volume. The Jahn-Teller (J-T) distortion factors are calculated using bond lengths obtained from Rietveld refinement which reduces with increase in Fe concentration. The lattice contraction is attributed to the presence of Mn^{4+} accompanied with an increase in oxygen vacancies. Decrease in J-T distortion is also confirmed from the asymmetric stretching bond located at 487 cm^{-1} in Raman spectra. Magnetic measurements show that T_N increases from ~ 42 to ~ 84 K with an increase in Fe concentration upto 20 at%. The maximum magnetization measured at 70 kOe are decreased whereas the coercivity is enhanced by two fold with increasing Fe concentration. The interaction between Mn^{3+} and Mn^{4+} confirm spin glass (SG) and/or cluster glass behavior in $\text{GdMn}_{1-x}\text{Fe}_x\text{O}_3$ compounds.

2. With increase in Fe concentration (x) from 0.3 to 0.5, along with the reduction in lattice volume, we observe structural transformation from O' to O type orthorhombic one. While decrease in lattice volume is contributed by the presence of Mn^{4+} , the structural transformation is attributed to reduction in J-T distortion factor calculated using the bond lengths obtained from Rietveld refinement. Raman spectra confirm a significant reduction in J-T distortion factor. Further, the reduction in J-T distortion factor is correlated with the disappearance of emission peak at ~ 286 nm in PL spectra. PL and XPS both confirm the presence of Mn^{4+} . PL analysis demonstrates the emission spectra emerging due to allowed electronic transitions within Mn^{4+} energy bands. Magnetic measurements show an anomalous increase in T_N from ~ 42 to ~ 298 K almost room temperature when x increases from 0 to 0.5. Interestingly, we have captured T_{SR} (spin reorientation temperature) at ~ 270 K for $x=0.3$, which has not been observed earlier. While T_N increases with Fe doping, T_{SR} decreases distinctly. The mixed valency of Mn is contributed towards SG behavior observed in both samples.
3. In Cr doped $GdMnO_3$, with increasing Cr concentration (x) from 0 to 0.4, along with the reduction in lattice volume, we observe a similar structural transformation from O' to O type orthorhombic one. The decrease in lattice volume from 231.22 to 228.20 after Cr doping is due to small ionic radius of Cr^{3+} (0.61\AA) than that of Mn^{3+} (0.64\AA). Raman spectra confirm a significant reduction in J-T distortion factor. Further, the emission peak at ~ 286 nm in PL spectra is disappeared with reduction in J-T distortion factor. PL study demonstrates the emission spectra emerging due to allowed electronic transitions within Mn^{4+} and Cr^{3+} energy bands. Magnetic measurements show the existence of compensation temperature (T_{Comp}) with spin reorientation (T_{SR}) in $x=0.3$

and 0.4. The magnetic switching is observed in both $x=0.3$ and 0.4 samples which are used in magnetic switching devices. SG behavior is observed in all samples.

4. $\text{La}_{1-x}\text{Mn}_x\text{O}_3$ is synthesized through simple, cost effective co-precipitation technique within a range of x varying from 0 to 0.2. Rietveld refinement of X-ray diffraction pattern at room temperature pointed towards monoclinic distortion causing buckling and tilting of MnO_6 octahedra, 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 the particles are of nanosize and polycrystalline in nature. While Curie temperature of the samples are obtained 124 K and 219 K for $x=0$ and 0.2, respectively. The effective magnetic moment is high in the former sample than the later LaMnO_3 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 canonical spin-glass, cluster-glass and interacting superparamagnetism nature are cancelled out, both samples show conventional spin glass behavior with a higher relaxation time in the oxygen rich sample.

This thesis is organized into VII chapters:

Chapter I: In this chapter a brief introduction and review of literatures of Rare earth manganites are discussed.

Chapter II: This chapter describes the synthesis technique for preparation of pure and Fe/Cr doped RMnO_3 ($R=\text{La},\text{Gd}$). A concise overview of the instruments is provided which are used for structural characterization of RMnO_3 ($R=\text{La},\text{Gd}$) through XRD, for particle

morphology SEM and PL for optical properties. XPS is used for elemental analysis and magnetic properties are studied using MPMS.

Chapter III: This chapter deals with the structural, J-T distortion and magnetic properties in GdMnO_3 after incorporating Fe upto 20 at%.

Chapter IV: In this chapter, we explain the O' to O orthorhombic structural transformation in GdMnO_3 compound after incorporating 50 at% of Fe. The detailed relation of photoluminescence properties, Raman and magnetic properties with J-T distortion is discussed in this chapter.

Chapter V In this chapter O' to O orthorhombic structural transformation is observed in GdMnO_3 compound after incorporating 40 at% of Cr. The magnetic switching behavior with spin reorientation observed after doping Cr is discovered. These compounds can be of potential application in magnetic switching devices.

Chapter VI The effect of cation deficiency on J-T distortion and magnetic transition in LaMnO_3 are discussed in this chapter.

Chapter VII This chapter summarizes the main findings of the present work. We present the future works to be done in this area.