PREFACE

Perovskites with the general formula ABO_3 (A represents a rare earth ion, and B represents a transition metal) have been widely studied in the field of oxide material research. Among these perovskite oxides, rare earth orthochromites ($RCrO_3$) compounds, which possess a distorted perovskite structure, have attracted significant attention due to their distinct physical properties and potential applications. One notable characteristic of these compounds is their multiferroic properties, which means they exhibit both ferromagnetic and ferroelectric behavior. These orthochromites materials, are semiconducting in nature and have also attracted researchers for applications in photocatalysis and light harvesting. Due to high electronic conductivity at elevated temperatures of these materials, they may suitable for various applications such as electrodes in magneto-hydrodynamic generators or interconnectors in solid oxide fuel cells. Due to fascinating magnetic properties these compounds have drawn the attention of researchers, not only due to their fundamental aspects but also their potential for utilization in various applications such as spintronics, spin-resolving devices, and magnetic switching devices. Few exciting results are the occurrence of negative magnetization, also known as magnetization reversal, spin reorientation, exchange bias etc., in single phase materials. These observations have sparked considerable interest and curiosity within the scientific community. Magnetization reversal is one of the prominent characteristics of these materials, which refers to the ease with which the direction of magnetization can be switched. This property is highly desirable for magnetic storage and magnetic switches, creating potential opportunities for their application in these areas.

$CeCrO_3$, belonging to the $RCrO_3$ family, has been relatively less studied. $CeCrO_3$ exhibit a temperature dependent magnetization reversal and exchange bias phenomena, with a potential application in spintronics and thermally assisted random access memory devices. $CeCrO_3$ has the highest Néel temperature after $LaCrO_3$ among $RCrO_3$ compounds, which makes it desirable for applications near room temperature. Taheri et al. have reported a decrease in the Neel temperature (T_N) from 260 to 178 K by substituting rare earth Eu^{3+} ions for Ce^{3+} ions in $CeCrO_3$. There have been limited research conducted on the influence of rare earth and transition elements as dopants in $CeCrO_3$ and their impact on the unique magnetic transitions observed. There is no report on $CeCrO_3$. Therefore, the objective of this thesis is to provide a comprehensive study on Fe doped rare earth chromite materials, encompassing various aspects related to their structure, optical, and magnetic properties.

Chapter 1 accounts for the introduction and review of the literature. In the introduction, the structure of perovskite including distortion, and magnetism in perovskite, exchange interactions and exchange bias effect have been discussed. In literature review we have mentioned the captivating characteristics of $RCrO_3$ materials in particular $CeCrO_3$, including negative magnetization, exchange bias, and magnetization switching. Finally, the chapter concludes by elucidating the reason behind the selection of rare earth chromites.

Chapter 2 addresses the synthesis technique employed for the preparation of pure and Fe-doped $CeCrO_3$. A brief overview of the instruments used for characterization, such as X-ray diffractometer (XRD) for structural analysis, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) for particle morphology and size analysis, UV-Visible spectroscopy for band gap, and X-ray photo electron spectroscopy (XPS) for

elemental analysis, are provided. The magnetic properties of $CeCr_{1-x}Fe_xO_3$ are studied using magnetic property measurement system (MPMS). Additionally, temperature dependent magnetic structure analysis is conducted through time-of-flight neutron diffraction.

The structural and optical properties of $CeCr_{1-x}Fe_xO_3$ ($x = 0$ and 0.05) is discussed in **Chapter 3** by using XRD, Raman spectroscopy and UV-visible spectroscopy. Structural analysis revealed an expansion of lattice parameters and volume upon the substitution of Fe. The structural analysis combined with Raman spectroscopy indicates an increased distortion in the orthorhombic structure. Moreover, the optical band gap analysis shows a decrease in the band gap from 2.9 to 2.6 eV with the incorporation of Fe. Further, magnetic transitions and magnetization switching behavior is discussed using MPMS. The introduction of Fe results in a decrease in the Néel temperature from 260 to 253 K. Further, the T_{SR} and T_{comp} increases from 15 to 30 K and from 61 to 110 K, respectively. A new compensation T_{comp2} at 13 K is observed below T_{SR} when x increased to 0.05. A stable field induced bipolar magnetization switching behavior is demonstrated, which has been reported for the first time.

In **Chapter 4,** we present the structural and magnetic transition with bipolar magnetization switching of $CeCr_{1-x}Fe_xO_3$($x = 0.06$ and 0.1) using XRD, Raman and magnetic measurement. While the structural analysis shows an increase in lattice parameter, the magnetic measurement demonstrates decrease in Néel transition temperature from ~260 K to 245 K after the substitution of Fe up to $x = 0.1$. The negative magnetization persists upto $x = 0.07$ and above this concentration magnetization becomes positive. The spin reorientation temperature (T_{SR}) increases from 30 to 44 K as x increases from 0.06 to 0.1. Notably, a stable

bipolar switching of magnetization by varying the external field is also demonstrated for x = 0.06, which possesses the highest compensation among all the compounds.

Objective of **Chapter 5** is to study the impact of Fe concentration from x = 0.2 to 0.5 on structure, band gap and magnetic properties. Structural analysis demonstrates an increase in lattice parameter and volume with increase in x from 0.2 to 0.5 while the band gap decreases from 2.48 to 1 eV. Further magnetization vs. temperature measurement reveals two spin reorientations T_{SR1} (62 K) and T_{SR2} (37 K) at x = 0.2. With increase in x from 0.2 to 0.5 both spin reorientation temperatures T_{SR1} and T_{SR2} are found to increase from 62 K to 138 K and 37 K to 83 K, respectively. In addition, coercivity initially increases up to T_{SR1} and then decreases with increasing temperature for x = 0.2 to 0.5.

In **Chapter 6,** we present the magnetic structure analysis using time of flight neutron diffraction and various magnetic measurement. Temperature dependent nuclear structure analysis from time of flight neutron diffraction demonstrates no structural changes within the temperature range 6-300 K. Magnetic structure analysis shows possibility of multiple magnetic structures (Γ_4, Γ_2 and Γ_1) in the temperature range of 6-300 K. The reversible to irreversible changes observed from temperature dependent M_{FCC} and M_{FCW} around T_{SR} clearly indicates the transformation of magnetic structure. Furthermore, the magnetization vs. magnetic field (M vs. H) measurements at 215 K while demonstrate a small coercivity representing the Γ_4 magnetic structure, an increased coercivity below T_{SR} predicts the presence of the Γ_2 spin structure. Besides, we have noticed a temperature driven sign reversal of exchange bias in $CeCrO_3$.

Finally, in **Chapter 7** we outline the key findings of the present thesis work and suggest the future work to be done in this area.

A list of journals and books used to bind up the thesis has been given at the end as references.