

Abstract

Substituted perovskite-type manganese oxides with the general formula $\text{La}_{1-x}D_x\text{MnO}_3$ ($D =$ divalent alkaline-earth ion) have been studied since 1950. The antiferromagnetic LaMnO_3 becomes ferromagnetic by this type of substitution due to a concomitant change in the valency of manganese; from trivalent to tetravalent. The recent interest in these oxides stem from the observation of huge change in the electrical resistance, under a magnetic field, known as Colossal Magnetoresistance (CMR), in 1994. In the La-site substituted compounds, the interesting magnetic and electrical properties are derived from the difference in the spin-states of Mn ions when compared to that in LaMnO_3 . Therefore, it can be expected that the effects derived from La-site substitution can be mimicked, to some extent, by the substitution of Mn, represented as $\text{LaMn}_{1-x}M_x\text{O}_3$ ($M = \text{Cr, Co, Ni, etc.}$). This latter class of compounds, which are equally important, but relatively underexplored is studied, in the present work. Similarly, a sub-class of Mn-site substituted compounds, called *double perovskites*, of the type $RE_2\text{MnMO}_6$ ($RE =$ lanthanide ion), which can show a number of interesting properties like ordering of ions in specific lattice sites, charge disproportionation, etc., are also explored.

The major challenge in the study of $\text{LaMn}_{1-x}M_x\text{O}_3$ is the difficulty in underpinning the spin-states of the Mn-site ions, as evident from the contradicting reports in the literature. This ambiguity may be an intrinsic property of the compounds or can be due to inadequate processing or investigation. To understand and explain the observed properties – especially magnetic properties – of the Mn-site substituted manganate compositions, a meticulous and detailed investigation from the point of view of processing-structure-property correlation study is required. The thesis deals with these studies and is divided into six chapters.

A general introduction to the subject and a review of the previous studies on

Mn-site substitution of the perovskite-type manganates are treated in the first chapter. The finding that majority of the reports in the literature on these systems are contradictory, is illustrated.

Details of the methods of synthesis of the compounds studied in the present work and the principles of techniques and devices used for structural, electronic, and static/dynamic magnetic property studies are discussed in the second chapter.

Structural and magnetic properties of the $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ compositions are presented in three sections of the third chapter; i) the double perovskite composition, $\text{La}_2\text{MnCoO}_6$ and its new ferromagnetic phases, which are synthesized in pure forms, for the first time, during this work, ii) the compositions in the region $0 < x < 0.5$, which showed an unprecedented magnetic behaviour, namely a ‘melt-down’ of ferromagnetic transition temperatures of all compositions to 150 K after annealing at higher temperatures, iii) the Co-rich region $0.5 < x < 1.0$, where all compositions are proved to be lacking long-range ferromagnetic order.

The fourth chapter describes detailed studies on two different ferromagnetic phases of $\text{La}_2\text{MnNiO}_6$, synthesized in single phase forms, by a low-temperature method, during this work. The origin of the mixed phase behaviour of $\text{La}_2\text{MnNiO}_6$, synthesized by the conventional solid-state method, is explained.

Structural and magnetic studies on $\text{La}_2\text{MnCo}_{1-x}\text{M}_x\text{O}_6$ ($M = \text{Ni, Fe, and Al}$) series are described in the fifth chapter. Interesting modifications in the magnetic properties of $\text{La}_2\text{MnCoO}_6$ are obtained on substitution, viz. Ni, reinforces the ferromagnetism of $\text{La}_2\text{MnCoO}_6$, Fe induces broadening of the magnetic transition, and Al results in a shift of the magnetic transition to lower temperatures.

The sixth chapter deals with the possible ferromagnetic phases of the rare-earth double perovskites RE_2MnMO_6 ($\text{RE} = \text{rare-earth ion, } M = \text{Co or Ni}$). The effect of ionic-size of RE^{+3} on the strength of the ferromagnetic exchanges in these substituted manganates is analyzed.