

**UNIVERSITI TEKNOLOGI MARA**

**REVIEW OF STRUCTURAL AND ELECTRICAL  
PROPERTIES IN SUBSTITUTED CHARGE ORDERED  
MONOVALENT AND DIVALENT-DOPED  
MANGANITES**

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### **Author's Declaration**

I declare that the work in this thesis was completed in accordance with the regulations of Universiti Teknologi MARA. Unless otherwise indicated or acknowledged as referenced work, it is original and results of my own work. This thesis has not been submitted for any degree or qualification to any other academic or non-academic institution.

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# **Review of Structural and Electrical Properties in Substituted Charge Ordered Monovalent and Divalent-Doped Manganites**

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## **Abstract**

Rare earth doping causes a change in the valence states of manganese, which plays a key role in the transport characteristics, hence rare earth-doped perovskite manganite oxides have substantially more diversified electrical properties than their parent perovskite manganite oxides. Thus, this paper reviews on the effect of substitution at A and B-sites on electrical properties in monovalent-doped and divalent-doped charge ordered manganites. This paper provides an overview of the state of the art in fabrication, structural characterization, electrical properties, and applications of charge ordered manganites. Our review first begins with a brief introduction of the research history and significant discoveries in charge ordered manganites. The second part summarizes the various approaches for fabricating charge ordered manganites. The structural characterization of the A and B-sites substitution in monovalent and divalent charge ordered manganites are reviewed in detail in the third part. Following that, in the fourth part, the electrical properties of the A and B-sites substitution in monovalent and divalent charge ordered manganites are thoroughly reviewed. Charge ordered manganites' potential applications in the fields of magnetic memory devices, magnetic sensors and spintronic devices are highlighted in the following parts. Finally, this review concludes with some perspectives and challenges for charge ordered manganites future researchers in the final part.

***Keywords:*** *Rare earth-doped perovskite manganite, Charge ordered, Electrical properties, Manganites, Structural characterization, Potential applications*

## **Introduction**

Perovskites compounds have attracted much interest recently due to a variety of features that are crucial to apply in the modern electronic devices such as memory disc, smart devices, magneto resistive transducers, magnetic sensors, as well as computer memory systems (Ouni et al., 2019) and suitable for the fabrication of a new-generation of spintronic-based magnetic sensor elements (Arifin et al., 2018). Due to their electrical, magnetocaloric and magnetic properties as well as the discovery of colossal magnetoresistance (CMR) (Elyana et al., 2018), rare-earth perovskite manganites with the compositional formula,  $R_{1-x}A_xMnO_3$  where R is a trivalent rare earth element (R = La, Nd, Sm, Pr) and A is divalent alkaline earth ion (A = Ba, Sr, Ca) have attracted considerable interest among researchers (Arifin et al., 2018). In addition, it also attracted interest because of the simultaneous occurrence of transition from ferromagnetic (FM) to paramagnetic (PM) behavior at Curie temperature ( $T_C$ ) and metal-insulator transition at metal-insulator temperature ( $T_{MI}$ ) (Asmira et al., 2018). Moreover, research on these rare-earth manganites has found that the CMR effect is related to manganese-based perovskite oxides where the drastic change of their electrical resistivity behavior in presence of magnetic field (Krichene et al., 2015) and can be interrelated to antiferromagnetic (AFM) super-exchange, Jahn-Teller (JT) effect, charge ordering state (Razali et al., 2018), metal-insulator transition ( $T_{MI}$ ) (Jethva et al., 2017) and lattice distortion. Numerous studies of mixed-valence manganites have revealed that the magnetic and electrical properties are mostly determined by the struggle between various interactions (charge, spin, orbital). Several intrinsic characteristics, including as the  $Mn^{3+}/Mn^{4+}$  ratio, substitution level, cation disorder, oxygen stoichiometry, grain boundary engineering, and particle size, are extremely sensitive to these interactions (Ouni et al., 2019).

The charge ordered (CO) in manganites have considerably unique interest due to its insulating and AFM behavior, which are susceptible to external perturbations such as magnetic fields, doping levels, and changes in the  $Mn^{3+}/Mn^{4+}$  ratio. CO in manganite generally involves spatial ordering of  $Mn^{3+}$  and  $Mn^{4+}$  ions. Because of the strong Coulomb interaction between electrons of neighboring  $Mn^{3+}$  and JT distortion which lowers the energy of  $e_g$  electrons, the  $e_g$  electrons are localized. CO also involves AFM ordering between Mn ions in  $Mn^{3+}-O-Mn^{3+}$  and  $Mn^{4+}-O-Mn^{4+}$  arrangements, in addition to the localization of  $e_g$  electrons of  $Mn^{3+}$  ions arranged in an ordered pattern in the  $MnO_2$  planes (Asmira et al., 2018). The pose stable CO state with AFM arrangement of Mn ions spins has been discovered in divalent half-doped perovskite type manganites  $R_{0.5}A_{0.5}MnO_3$ . The existence of CO state has been linked to the presence of an equal ratio of  $Mn^{3+}$  and  $Mn^{4+}$ , where the ions align themselves in an ordered pattern as in divalent doped