

**UNIVERSITI TEKNOLOGI MARA**

**EFFECTS OF A-SITE AND B-SITE  
SUBSTITUTION ON THE  
STRUCTURAL, MAGNETIC AND  
ELECTRICAL PROPERTIES OF Bi-  
DOPED  $\text{La}_{0.7}\text{Pb}_{0.3-x}\text{Bi}_x\text{MnO}_3$  AND V-  
DOPED  $\text{La}_{0.7}\text{Pb}_{0.3}\text{Mn}_{1-y}\text{V}_y\text{O}_3$   
MANGANITES**

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## ABSTRACT

Substitution of paramagnetic metal cations onto the A-site and B-site appears to influence the lattice stability and electron conduction behaviour of perovskite-type compounds. The variation of structural, electrical, and magnetic behaviour in perovskite manganites  $\text{La}_{0.7}\text{Pb}_{0.3-x}\text{Bi}_x\text{MnO}_3$  ( $x = 0 - 0.04$ ) and  $\text{La}_{0.7}\text{Pb}_{0.3}\text{Mn}_{1-y}\text{V}_y\text{O}_3$  ( $y = 0 - 0.1$ ) was studied and reported in the present dissertation. Each compound was prepared according to the conventional solid-state synthesis method. All the samples crystallized in a rhombohedral structure with a space group of  $R-3c$ . A clear transition peak of the metal-insulator was observable in both samples, with variation in  $T_{\text{MI}}$  values. The  $T_{\text{MI}}$  values of  $\text{La}_{0.7}\text{Pb}_{0.3-x}\text{Bi}_x\text{MnO}_3$  ( $x = 0 - 0.04$ ) compound decrease from 292 K ( $x = 0$ ) to 256 K ( $x = 0.04$ ) while the  $\text{La}_{0.7}\text{Pb}_{0.3}\text{Mn}_{1-y}\text{V}_y\text{O}_3$  ( $y = 0 - 0.1$ )  $T_{\text{MI}}$ 's value also exhibits the same pattern, dropping from 292 K ( $y = 0$ ) to 250 K ( $y = 0.1$ ). The deterioration of the  $T_{\text{MI}}$  value was due to several factors, such as variations in cell parameters,  $\text{MnO}_6$  octahedral distortion, and the existence of hopping mechanism competition introduced by dopants (Bi and V) may affect the itinerant electron double-exchange (DE) behaviour, causing the  $T_{\text{MI}}$  value to shift away from room temperature (300 K). Further discussion on the electrical behaviour of the samples was elucidated via mathematical fittings to determine the most appropriate,  $e_g$  electron conductivity behaviour in the metallic region ( $30 \text{ K} < T < T_{\text{MI}}$ ) and insulating region ( $300 \text{ K} > T > T_{\text{MI}}$ ). All the samples exhibited a smooth magnetic phase transition curve from ferromagnetic (FM) to paramagnetic (PM) with different Curie temperature ( $T_{\text{C}}$ ) values. A declining pattern of  $T_{\text{C}}$  value can be observed in all the samples as the dopant (Bi and V, respectively) increases. An assumption can be constructed where the electron hopping between  $\text{Mn}^{3+} - \text{O}^{2-} - \text{Mn}^{4+}$  is suppressed due to the Mn - O bond angle and length alteration induced by the dopant element. Furthermore, substituting V at B-site of  $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$  may alter the  $\text{Mn}^{3+}/\text{Mn}^{4+}$  stoichiometry ratio, further disrupting the electron DE mechanism. In summary, the substitution of Bi at the A-site and V at the B-site of the  $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$  compound resulted in alterations to its structure, electrical properties, and magnetic characteristics.

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# CHAPTER 1

## INTRODUCTION

### 1.1 Research Background

A perovskite manganite is a compound with the generic formula  $RE_{1-x}AE_xMnO_3$ , where RE is a trivalent rare-earth metal ( $La^{3+}$ ,  $Pr^{3+}$ , and  $Nd^{3+}$ ) and AE represents alkaline earth ranging from monovalent to trivalent ( $K^+$ ,  $Na^+$ ,  $Sr^{2+}$ ,  $Ca^{2+}$ ,  $Pb^{2+}$ ,  $Bi^{3+}$  and  $Eu^{3+}$ ). The compound crystallises to form a perovskite structure named after the mineral  $CaTiO_3$ . Because of the distinct magnetic and electric effects that can occur within the compound depending on its composition, it may become a catalyst for new technologies such as sensors, magnetic memory components, coolants, data storage, and even as the electrolyte of a fuel cell (Xia et al., 2020). The study of perovskite manganites began around 1950. Jonker and Van Statten determined that doping different ratios of alkaline metal into  $LaMnO_3$  can modify the  $Mn^{4+}$  quantity within the compound and, as a result, unexpectedly changes its Curie temperature  $T_C$  (Jonker & Van Santen, 1950). Zener proposed that a double-exchange mechanism (DE) will occur because of  $Mn^{3+}-O^{2-}-Mn^{4+}$  interaction to explain the unusual finding by Jonker and Van Santen. The phenomenon will induce ferromagnetic effects and metallic behaviour in manganites (Zener, 1951). Further studies are required as DE mechanisms are inadequate to elucidate manganite's complex behaviour, such as insulation behaviour, the minimum resistivity occurrence at low temperatures, and magnetoresistance (MR) behaviour (Aritra Banerjee et al., 2002). The behaviour may be effectively explained only by considering other competing mechanisms, such as electron-phonon coupling, the Jahn-Teller (JT) effect related to  $Mn^{3+}$  ions, charged ordering (CO), phase separation (PS), and Griffith's phase theory (Ghorai et al., 2021; Lakhani et al., 2021). Previous studies on manganites also suggested that the alteration of average ionic radii at the A-site of manganite,  $\langle r_A \rangle$  due to the substitution of doping element at the A-site, can subsequently affect the tolerance factor,  $\tau$  may contribute to the changing of manganite's physical properties besides the differences of  $Mn^{3+}/Mn^{4+}$  ratio.