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EFFECT OF Bi SUBSTITUTION ON STRUCTURAL, OPTICAL, MAGNETIC AND ELECTRICAL PROPERTIES OF $Nd_{1-x}Bi_xMnO_3$ AND $Nd_{0.75-x}Bi_xNa_{0.25}MnO_3$

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ABSTRACT

The samples of $Nd_{1-x}Bi_xMnO_3$ (x = 0, 0.25 and 0.50) and $Nd_{0.75-x}Bi_xNa_{0.25}MnO_3$ (x = 0, 0.05, 0.10 and 0.15) were synthesised using a conventional solid-state method to investigate the effect of Bi substitution on their structural, optical, magnetic, and electrical properties. The XRD analysis using the Rietveld refinement method has shown an increase in structural parameters and unit cell volume as Bi was substituted to both samples, indicating the possibility of substitution for the A-site. The FTIR analysis was carried out for all the samples and showed a significant band around 550 to 600 cm-1, corresponding to the vibration of Mn-O bonds. The SEM and EDX analysis were performed for all the samples, and the average grain size for all the samples was increased as Bi was substituted into the system. The morphologies of the samples also revealed that all the samples were agglomerated and non-spherical in shape. The EDX spectrum shows that all the elements existed in the samples. The UV-Vis measurement for all the samples has been analysed using two different methods: Kubelka-Munk and Tauc's plot. The value of bandgap obtained for both methods are comparable and decreased as the substitution of Bi in the samples increased from 3.44 eV to 1.85 eV for $Nd_{1-x}Bi_xMnO_3$ (x = 0, 0.25 and 0.50) and from 2.32 eV to 2.24 eV for $Nd_{0.75-x}Bi_xNa_{0.25}MnO_3$ (x = 0, 0.05, 0.10 and 0.15). The magnetic properties of the samples were analysed using AC susceptibility and showed a transition of antiferromagnetic (AFM) to paramagnetic (PM) for all the samples. The samples of $Nd_{1-x}Bi_xMnO_3$ (x = 0, 0.25 and 0.50) show a decrease in Neel temperature, T_N and Curie temperature, T_C, which indicates the weakening of the ferromagnetic behaviour due to double exchange interaction. On the other hand, the appearance of the charge ordering temperature, T_{CO}, was observed for the $Nd_{0.75-x}Bi_xNa_{0.25}MnO_3$ samples at ~ 176 K (x=0) and disappeared at further substitution. The Neel temperature, T_N for the samples at x=0 to x=0.15 were decreased from 188 K to 178 K. The electrical properties for the $Nd_{0.75-x}Bi_xNa_{0.25}MnO_3$ were determined using the resistivity measurement has shown that all the Bi-doped samples exhibit insulating behaviour for the entire temperature region. The insulator region was fitted using small polaron hopping (SPH) model, showing an increase in activation energy from 176 meV to 197.89 meV.

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CHAPTER ONE
INTRODUCTION

1.1 Research Background

Hole-doped perovskite manganite with general formula of $RE_{1-x}A_xMnO_3$ where RE represent the rare-earth elements such as Nd, La, and Pr while A represents the alkali element such as Ba^{2+}, Ca^{2+}, Sr^{2+} etc have been tremendously studied by researchers in the last few decades due to the fascinating basis in physics and their significance in the technological importance such as magnetic sensor, spintronic devices, and magnetic memory devices. Perovskite manganite also have shown many unique properties such as colossal magnetoresistance (CMR), metal-insulator (MI) transition and ferromagnetic-paramagnetic (FM-PM) transitions. Few theories have arisen due to these properties such as double-exchange (DE) interaction involving a simultaneous transfer of e_g electrons of Mn^{3+} and Mn^{4+} with oxygen as an intermediate ion. However, double exchange alone is not sufficient to provide information regarding the physical properties of manganite, so Jahn Teller (JT) interaction is needed to explain the behavior of the manganite in the paramagnetic-insulator (PMI) region. Other factors that influence the physical behaviour of manganite are phase separation (PS), charge ordering (CO), and super exchange interaction.

Initially, $NdMnO_3$ is an antiferromagnetic (AFM) insulator due to the absence of mixed valences state. The low temperature antiferromagnetic phase of $NdMnO_3$ is at $T_N \sim 78$ K is characterized by ferromagnetic alignment of the Mn moments in the ab plane. The 2-fold degenerated electron, e_g orbital breaks down and stabilizes the A-type antiferromagnetic Mn ordering (Massa et al., 2013). Chatterji et. al., confirmed that $NdMnO_3$ has an A-type AFM structure or known as layered AFM, where the ferromagnetic and antiferromagnetic plane were stacked together along the c axis manganite is quite interesting due to the magnetic transition from A-type to E-type AFM (zigzag arrangement of spins) that were caused by structural disorder leading to the reduction of Mn-O bond angles causing the multiferroicity (Udeshi et al., 2014). Other than that, Nd also has a moderate e_g electron bandwidth and ionic radius compared to La, which makes dopant tune its magnetic properties to a large extent. Nd-based system