UNIVERSITI TEKNOLOGI MARA

EFFECTS OF K^+ AND Ni^{2+} SUBSTITUTION ON STRUCTURAL, MAGNETIC, ELECTRICAL TRANSPORT AND ELECTRONIC PROPERTIES OF CHARGE ORDERED MONOVALENT-DOPED $Pr_{0.75}Na_{0.25}MnO_3$ MANGANITES

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Thesis submitted in fulfillment
of the requirements for the degree of
Doctor of Philosophy in Science

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AUTHOR'S DECLARATION

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

I, hereby, acknowledge that I have been supplied with the Academic Rules and Regulations for Post Graduate, Universiti Teknologi MARA, regulating the conduct of my study and research.

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ABSTRACT

This study involves investigation on physical properties of charge ordered (CO) monovalent-doped orthorhombic $Pr_{0.75}Na_{0.25-x}K_xMnO_3$($x$=0–0.20) and $Pr_{0.75}Na_{0.25}$ $Mn_{1-x}Ni_xO_3$ (x=0–0.10) manganites and density functional theory (DFT) computations of electronic properties of insulating $Pr_{0.75}Na_{0.25}Mn_{1-x}Ni_xO_3$ (x = 0, 0.25 and 0.50) manganites using LDA+U method. The CO manganites were substituted with K^+ and Ni^{2+} at Na- and Mn-sites of the $Pr_{0.75}Na_{0.25}MnO_3$ respectively, to activate its electronic and magnetic properties. Both substitutions successfully suppressed the CO state and induced ferromagnetic to paramagnetic (FM-PM) transition, accompanied by metal to insulator (M-I) transition. The inducement of FMM-PMI transition for K^+-substitution increased Curie temperature (T_C) and M-I transition temperature (T_{MI}) which was attributed to the reduction in MnO_6 octahedral distortion which leads to the enhancement of double exchange (DE) interaction. Meanwhile, for Ni-substituted samples the induced FMM-PMI transition caused lowering of T_C and T_{MI} which were suggested due to enhanced antiferromagnetic superexchange interactions involving Mn^{3+}–O–Mn^{3+}, Mn^{4+}–O–Mn^{4+} and Ni^{2+}–O–Ni^{2+} which decreased the ferromagnetic superexchange interaction between Ni^{2+}–O–Mn^{4+} leading to reduction of DE interaction. DFT calculation of orthorhombic $Pr_{0.75}Na_{0.25}MnO_3$ with FM phase via LDA+U with U_{Mn} =2 eV showed better agreement with the experimental crystal volume and bandgap results. Meanwhile, DFT calculations on orthorhombic $Pr_{0.75}Na_{0.25}Mn_{1-x}Ni_xO_3$ (x = 0, 0.25 and 0.50) with AFM phase with U value for Mn *3d* set at 2 eV (x = 0) and 6 eV(x = 0.25, 0.50) while for both Pr *4f* and Ni *3d* the U values were set at 6 eV to compensate for the strong Coulomb repulsion of *3d* electrons for Ni. The calculated crystal volume structure and bandgap for Ni free and Ni-substituted (x = 0.25 and 0.50) samples showed better agreement with the experimental data for the selected U values. DOS calculations revealed that all the FM and AFM samples showed half-metallic (HM) character. Partial DOS results showed Mn, Ni and O atoms contributed more significantly to the electronic states at E_F for the spin down channel with higher degree of hybridization between the Mn *3d*/Ni *3d* and O *2p* electrons.

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