

**UNIVERSITI TEKNOLOGI MARA**

**INFLUENCE OF  $\text{Ca}^{2+}$  AND  $\text{Mg}^{2+}$   
DOPING IN  
 $\text{Sr}_{2-x}\text{Ca}_x\text{NiWO}_6$  AND  $\text{Sr}_2\text{Ni}_{1-x}\text{Mg}_x\text{WO}_6$   
DOUBLE PEROVSKITE ON THE  
STRUCTURAL, OPTICAL,  
MAGNETIC AND DIELECTRIC  
PROPERTIES**

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## ABSTRACT

Double perovskite compounds have drawn a lot of interest and are currently the subject of intensive research due to their intriguing structural, magnetic and electrical properties. Doping with cations of various sizes in the double perovskite compounds cause changes in the crystal structure which are connected with the magnetic and electrical properties. In this study, polycrystalline samples of  $\text{Sr}_{2-x}\text{Ca}_x\text{NiWO}_6$  ( $x=0.00, 0.02, 0.04, 0.06$ ) and  $\text{Sr}_2\text{Ni}_{1-x}\text{Mg}_x\text{WO}_6$  ( $x=0.00, 0.02, 0.04, 0.06$ ) were prepared through a solid state reaction method. The crystal structure, optical, magnetic and dielectric properties of the samples were studied using X-ray diffraction (XRD), scanning electron microscope (SEM), UV-Vis diffuse reflectance spectroscopy (UV-Vis), AC magnetic susceptibility (ACS) and electrochemical impedance spectroscopy (EIS) respectively. Rietveld analysis of XRD patterns for  $\text{Sr}_{2-x}\text{Ca}_x\text{NiWO}_6$  series confirmed that the samples crystallized in tetragonal structures with space group  $I4/m$ . The SEM images showed that the grain sizes of the samples decreased from  $2.51\ \mu\text{m}$  to  $1.65\ \mu\text{m}$  as the dopant increased up to  $x=0.06$ . The UV-Vis analysis revealed that the band gap energy of the samples decreased from  $3.17\ \text{eV}$  to  $3.11\ \text{eV}$  up to  $x=0.02$ . The expansion of the average bond angles of  $\langle\text{Ni-O-W}\rangle$  might increase the degree of overlap of Ni-O and W-O orbitals and cause the reduction in the band gap energy value. In addition, a following rising trend in the band gap energy value from  $3.12\ \text{eV}$  to  $3.13\ \text{eV}$  between  $x=0.04$  and  $x=0.06$  can be connected to the reduction in average particle size discovered through SEM analysis. The AC susceptibility measurement showed a magnetic transition from antiferromagnetic (AFM) to paramagnetic (PM) in the samples with the decrease of Neel temperature,  $T_N$  from  $33.49\ \text{K}$  to  $32.73\ \text{K}$ . The doping of smaller size  $\text{Ca}^{2+}$  ions decreased the stability of the compounds' structures by decreasing the tolerance factor from  $0.9820$  to  $0.9810$ . As a result, the tilting phenomenon of  $\text{NiO}_6$  and  $\text{WO}_6$  increased which caused a slightly increased in Ni-O and W-O bond length and suppressed the antiferromagnetic interaction between  $\text{Ni}^{2+}$  and  $\text{W}^{6+}$  ions. In addition, the dielectric constant increased from  $\sim 550$  to  $\sim 845$  which could be attributed to a drop in crystallite size from  $32.130\ \text{nm}$  to  $27.374\ \text{nm}$ . As the crystallite size decreased, the grain boundaries increased which impeding the hopping process between the different states and grains. The  $\text{Ca}^{2+}$  ions concentrate at the grain boundaries and increase the dielectric constant values. For  $\text{Sr}_2\text{Ni}_{1-x}\text{Mg}_x\text{WO}_6$  series, the Rietveld analysis of XRD patterns confirmed that the samples crystallized in tetragonal structures with space group of  $I4/m$ . The SEM morphologies indicated that the grain size of the samples increased from  $2.51\ \mu\text{m}$  to  $2.89\ \mu\text{m}$  upon  $\text{Mg}^{2+}$  doping. The UV-Vis analysis revealed that the band gap energy of the samples decreased from  $3.30\ \text{eV}$  to  $3.24\ \text{eV}$  when  $\text{Mg}^{2+}$  ions were substituted. This illustrated that increasing ionic radii reduced the electrons' excitation distance from valence band to conduction band. The magnetic properties of the compounds measured by AC magnetic susceptibility revealed that these compounds underwent antiferromagnetic to paramagnetic transition with the decreasing of  $T_N$  values. The increase of diamagnetic,  $\text{Mg}^{2+}$  ions composition from  $0.80\%$  to  $1.84\%$  at the  $\text{Ni}^{2+}$  site which can be observed from EDX analysis has reduced the super exchange interaction between the  $\text{Ni}^{2+}$  and  $\text{W}^{6+}$  ions. Apart from that, the dielectric constant increased from  $\sim 553$  to  $\sim 734$  upon  $\text{Mg}^{2+}$  ions doping which could be attributed to the increase in grain size. Larger grain size produced greater number of dipoles and hence increased the electrical dipole moment which consequently increased the polarization effect and enhance the dielectric constant values.

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# CHAPTER ONE

## INTRODUCTION

### 1.1 Research Background

In 1839, Gustav Rose, a German mineralogist was the first to discover the calcium titanate with a chemical formula of  $\text{CaTiO}_3$ . This material was considered as the origin of perovskite materials which were named after a Russian mineralogist, Lev Perovski. The name “perovskite” refers to a collection of materials with crystal structure that includes cuboid and diamond forms. Materials which have the same crystal structure with  $\text{CaTiO}_3$  are categorized as perovskite materials. Generally, perovskite materials have a general formula,  $\text{ABX}_3$  where A is referred as alkaline or rare earth elements, B are transition metals and X is an anion which is usually in oxide or halogen forms (Waththage et al., 2018) (Reshmi Varma, 2018). In this compound, A site cations occupy the space that formed between the adjacent  $\text{BX}_3$  octahedron meanwhile B elements are octahedrally coordinated to the X anions which form the basic building of the perovskite structure. In the  $\text{ABO}_3$  form, A elements are visualized as the largest atoms compared to the B elements.

Recently, double perovskite compounds which are derived from conventional perovskites,  $\text{ABO}_3$  (Halizan., 2021) gained a lot of attention for exhibiting a wide range of intriguing structural, magnetic and electrical properties (Wang et al., 2018) (Urusova et al., 2019) which making them highly desirable in development of various applications such as magnetic tunnel junction and low field magneto resistive sensors (Hussain, Khan, Rao, & Koo, 2019) (Rachedi et al., 2021) (Sahoo et al., 2019). Theoretically, double perovskites have a general formula  $\text{AA}'\text{BB}'\text{O}_6$  or  $\text{A}_2\text{BB}'\text{O}_6$  where A and A' = (Sr, Ca, Ba) are rare earth elements, B = (Fe, Co, Ni, Cr) and B' = (Mo, W, Re, U) are transition metal ions. Double perovskite structures are generated when one B' cation replaces exactly half of the B site cations and a rock salt ordering is achieved (Saha-Dasgupta, 2019). As illustrated schematically in Figure 1.1, the corner sharing of  $\text{BO}_6$  and  $\text{B}'\text{O}_6$  octahedra alternates along the three direction of the crystal where A site as the largest atom occupying the space between the octahedral (Burzo et al., 2015). Double perovskites materials have a very high flexibility in crystal structure and chemical composition (Yousef A Alsabah et al., 2017). Thus, it is possible for the