UNIVERSITI TEKNOLOGI MARA

EFFECTS OF MANGANESE (Mn) DOPING AT B-SITE ON THE STRUCTURAL, OPTICAL, AND DIELECTRIC PROPERTIES OF La2CuTiO6, La2CuRuO6, AND La2NiRuO6 DOUBLE PEROVSKITES

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ABSTRACT

Double perovskites offer broad compositional flexibility and tunable structure, band gap, and dielectric response, making them attractive candidates for high-performance dielectric and energy storage applications. This thesis investigates the effects of B site manganese (Mn) doping modifies structure, band gap, and dielectric response in La2CuTiO6, La2CuRuO6, and La2NiRuO6 with a focus on capacitor energy storage. The gap addressed is the lack of a coherent cross system understanding that connects crystal structure and microstructure to frequency dependent dielectric behavior under identical processing. All compositions were synthesized by the same solid state route and characterized using one toolkit that includes Rietveld X–ray diffraction, Field emission scanning electron microscopy (FESEM) with energy dispersive X–ray (EDX) analysis, Fourier transform infrared spectroscopy (FTIR), UV–Vis diffuse reflectance, impedance and modulus spectroscopy. X–ray diffraction shows that La2CuTi1-*x*Mn*x*O6 remains single phase with orthorhombic P*nma* symmetry, La2NiRu1-*x*Mn*x*O6 remains single phase with monoclinic *P*21/*n* symmetry, and La2CuRu1-*x*Mn*x*O6 contains two closely related perovskite phases with a dominant *P*21/*n* symmetry. In La2CuTi1-*x*Mn*x*O6 and La2NiRu1-*x*Mn*x*O6, manganese increases the unit cell volume and shifts BO6 stretching modes, and elemental maps show uniform chemistry. For the La2CuRu1-*x*Mn*x*O6 series, which is two phases, a monotonic lattice trend and chemical uniformity cannot be stated from our data, so structure property discussion is made with reference to the dominant phase only. The optical band gap narrows with Mn doping, for example from 2.06 eV to 1.62 eV in La2CuTiO6 and to about 1.64 eV in La2CuRuO6 at $x = 0.10$, with a similar decrease in La2NiRuO6. Dielectric measurements from 1 kHz to 1 MHz link directly to these structural changes. Manganese mainly tunes the bulk pathway by lowering grain resistance and modestly adjusting grain capacitance at the best compositions, which shifts the dominant relaxation to higher frequency, increases the real permittivity, lowers the dielectric loss, and reduces the Nyquist arc diameter, consistent with faster intra grain transport. The optimal compositions identified are $x = 0.05$ for La2CuTiO6 and $x = 0.04$ for both La2CuRuO6 and La2NiRuO6, defining practical operating ranges for capacitors in the upper kHz to MHz region. The novelty of this work is a direct cross system comparison under identical processing with one analysis framework that delivers general design rules connecting crystal structure and local distortion to relaxation kinetics and dielectric loss. In summary, manganese doping preserves the host frameworks, moves dielectric relaxation to higher frequency, increases permittivity, and reduces loss at the stated compositions, thereby improving the suitability of these La based double perovskites for capacitor grade energy storage.

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Discovered in 1839 in the Ural Mountains of Russia, perovskite derives its name from the renowned Russian mineralogist Lev Perovski. Victor Goldschmidt further elucidated its crystal structure in 1926 while investigating tolerance factors in solid-state materials. Perovskite materials have sparked considerable interest across various scientific domains owing to their diverse compositions, easily achievable synthesis methods, and appealing characteristics. For instance, hybrid organic-inorganic perovskites have found widespread use in fields such as solar cells, light-emitting diodes, lasers, and photodetectors. Their extended charge diffusion lengths for both electrons and holes, as well as their high carrier mobility and adjustable bandgap (Eg), make them particularly desirable. Additionally, $AB0_3$ — type perovskite oxides have emerged as a focal point in modern industrial catalysis and thermoelectric applications due to their structural versatility, remarkable stability, and cost-effectiveness. In this arrangement, an A-site ion situated at the center of the lattice structure typically consists of an alkaline or rare earth element. Conversely, B-site ions positioned at the corners of the lattice may comprise transition metals, spanning from *3d to 5d* transition metals.

In recent times, double perovskite compounds have garnered increasing attention due to their intriguing properties and potential applications. These compounds, stemming from the basic perovskite structure ($AB0_3$), showcase a diverse range of characteristics and can incorporate various elements from the periodic table through cation substitution. The formation of double perovskite structures, designated as $A_2BB'0_6$, enhances flexibility, allowing for the inclusion of different transition metals and rare-earth or alkaline earth elements. Research spanning halides, nitrides, sulfides, and hydroxides has delved into different structural configurations, providing insights into their unique traits. With numerous options for cation combinations at A and B sites, the synthesis of double perovskite compounds offers a promising avenue for material exploration and advancement. Additionally, the intriguing flexibility of inorganic double perovskites has sparked attention in the realm of solar cells and light-emitting diodes, owing to their ability to tailor photoelectric properties to specific needs