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# Crystal structures and electrical properties of cobalt manganese spinel oxides

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## ABSTRACT

Crystal structures and hopping motions of cobalt manganese spinel oxides across a wide composition range ( $\text{Co}_x\text{Mn}_{3-x}\text{O}_4$  (CMO),  $0.9 \leq x \leq 2.7$ ) are investigated in order to clarify the corresponding mechanisms of electrical behaviors as negative temperature coefficient thermistors. Based on the diffraction measurements, a tetragonal to cubic spinel transition are observed mostly with increasing Co content. Hopping distance for a series of CMO are calculated by the variable range hopping mechanism, which is changed as a function of composition, resulting to the observed unique electrical properties. According to the electrical and structural analysis, the electrical properties of CMO compounds with different Co contents majorly determined by tetragonal to cubic phase transition, cation distribution, and hopping distance. In addition, the formation of secondary phase (i.e., CoO) and another CMO phase may also significantly affect the electrical properties.

## 1. Introduction

Spinel type structures with a chemical formula of  $\text{AB}_2\text{O}_4$  have attracted great attention in the field of electronics, catalysis, magnetism, and energy storage devices [1–5]. In general, for an  $\text{AB}_2\text{O}_4$  spinel material, oxygen anions are close-packed with face-centered cubic configuration with 1/8 of the tetrahedral sites occupied by cation A and 1/2 of the octahedral sites occupied by cation B. Many types of cations can be inserted into the spinel framework by chemical modification. The tetrahedral and/or octahedral sites of spinel crystal structure can tolerate various atoms with different ionic radii and valence states, resulting in a large amount of oxide compounds with interesting properties [6]. Recently, cobalt manganese based spinel oxides,  $(\text{Co}_x\text{Mn}_{3-x})\text{O}_4$  (CMO), have been reported to have non-linear resistivity variation with temperature, suggesting the application for negative temperature coefficient (NTC) thermistors in microelectronic systems [1,7–9]. In addition, these CMO materials have other features such as element abundance, low cost, and low toxicity.

CMO oxides are normally synthesized by a conventional solid-state

method, which requires elevated temperatures and prolonged heat treatments. However, the produced powders often have irregular shapes, large particle sizes, phase separation, and microstructure inhomogeneity, seriously impeding their properties [10–12]. To avoid such problems, gel combustion synthesis was adopted in this study. Gel combustion is a simple and cost-effective method, and is suitable for preparing oxide nanopowders with a wide composition range [7,9]. Following gel combustion, spark plasma sintering (SPS) was conducted on the nanopowders to obtain the sintered pellets. Compared to conventional sintering procedures, SPS offers lower thermal input, shorter sintering time, and higher densification. The CMO pellets over a wide composition range ( $0.9 \leq x \leq 2.7$ ) were obtained using this method.

It is known that the Co/Mn ratio (composition) of CMOs can significantly affect the crystallographic structure as well as the electrical properties [2,13,14]. However, a systematic structural characterization of CMO across a wide compositional range is lacking in literature. A fundamental understanding of the responsible mechanism for the change of electrical properties as a function of composition is neither entirely clear. In this study, we performed electrical analysis and

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