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Fe doped Ni-Mn-Co-O ceramics with varying Fe content as negative temperature coefficient sensors

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ABSTRACT

Fe-doped Ni-Mn-Co-O (FNMC) ceramics with the formula, ($Fe_xNi_{0.3}Co_{0.9}Mn_{1.8-x}$, x=0.1, 0.3, 0.5, and 0.7)O_4 were synthesized using a spray drying process. Effect of Fe content on the phase evolution of FNMC compound during heat treatment was studied using X-ray diffraction. A single phase cubic spinel structure with improved crystallinity was observed when the Fe content increased over 0.5. Fe, Ni, Mn and Co ions were homogeneously distributed in the sintered the FNMC ceramics, implying no phase separation occurred during sintering. The valence state of each element was analyzed using X-ray photoelectron spectroscopy, which revealed that Ni, Co, and Fe might have a single valence state while Mn had mixed valence states in the FNMC spinel compounds. The temperature-dependent electrical resistance for the FNMC ceramics was measured. Room temperature resistance and the B-value substantially increased for the FNMC samples with Fe content higher than 0.5. The electrical properties of FNMC compounds can be optimized by controlling the Fe content, which is directly indicative of their potential role as negative temperature coefficient sensors.

1. Introduction

Spinel oxides with the chemical formula AB_2O_4 (A, B=Ni, Co, Mn, etc.) play an important role in electronics and in a variety of energy storage devices owing to their excellent electronic properties [1–4]. In particular, $(Ni_xCo_yMn_{3-x-y})O_4$ (NMC) compounds are intensively studied for application as a negative temperature coefficient (NTC) thermistor due to enhanced electrical hopping conduction within the cations with different valence states in tetrahedral A and octahedral B sites [5]. The hopping conduction occurs via thermally assisted lattice vibration, where the electrical conductivity reaches a maximum when the number of cations with 3^+ valence states equals the number of cations with 4^+ valence states [6–8]. The resistance of NMC compounds can be further controlled by introducing transition metals (Fe, Cu, Al, Zn, etc.) dopants into the spinel structure [9–11]. Among different dopants, the Fe dopant is widely used for controlling the resistance of NTC thermistors, since Fe ions can change cationic distribution and crystal structure of the spinel structure by randomly occupying tetrahedral or octahedral sites [12,13]. Consequently, Fe doping leads to variations in the distance and activation energy of hopping conduction.

The electrical performance and reliability of the NTC thermistor are influenced by multiple factors such as crystal structure, microstructure, cation valence states and elemental distribution. In this study, Fe-doped (Ni-Mn-Co)O_4 (FNMC) compounds with varying Fe content (0.1, 0.3, 0.5, and 0.7) are prepared via spray drying technique, which is a rapid, continuous, and single step powder synthesis technique [14,15]. The effect of Fe doping on the crystallographic evolution, microstructure, elemental distribution, cation valence states, and electrical properties was investigated using appropriate analytical techniques.

2. Experimental procedure

Oxide powders of Mn_3O_4 (99.9%, Junsei Chem. Japan), Co_3O_4 (99.9%, Junsei Chem. Japan), Fe_2O_3 (99.9%, Junsei Chem. Japan), and NiO (99.9%, Junsei Chem. Japan) were prepared with different stoichiometric amounts ($Fe_xNi_{0.3}Co_{0.9}Mn_{1.8-x}O_4$, x=0.1, 0.3, 0.5, and 0.7). Polyvinyl alcohol (PVA) solution as a binder was mixed with the oxide powders, and spray drying was used to prepare the spherical

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