

Preparation and properties of spinel-type Zn-Co-Mn oxide negative temperature coefficient ceramic thermistors

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The effects of the addition of Co ions on the structural and electrical properties of $\text{Zn}_{1.10}\text{Co}_x\text{Mn}_{1.90-x}\text{O}_4$ NTC thermistor composition has been studied. All specimens exhibited a very dense microstructure without any porosities, and the average grain size decreased from 5.21 μm to 4.86 μm with an increase in Co content x from 0 to 0.25. All specimens exhibited the sintered density characteristic of at least approximately 96% of the theoretical values and displayed a good NTCR characteristic of less than $-4.7\%/^\circ\text{C}$. The electrical resistance at room temperature of the $\text{Zn}_{1.10}\text{Co}_{0.25}\text{Mn}_{1.65}\text{O}_4$ specimen is 7.2 k Ω . The $\text{Zn}_{1.10}\text{Co}_{0.15}\text{Mn}_{1.75}\text{O}_4$ specimen exhibited a minimum activation energy of 0.373 eV.

Key words: Temperature sensors, Zn-Co-Mn oxide, Structural properties, Electrical properties.

Introduction

Generally, materials produced from the transition metal manganite ($\text{M}_x\text{Mn}_{3-x}\text{O}_4$) are being used in various temperature sensors, such as in thermistor applications and infrared-detecting bolometers, which make use of the sensitivity of the electrical resistance change as a function of temperature [1, 2]. The electrical conductivity of these materials is due to the phonon-assisted hopping conduction between Mn^{3+} and Mn^{4+} ions in the octahedral sites of the spinel structure [3].

Zinc manganite ($\text{Zn}_x\text{Mn}_{3-x}\text{O}_4$) materials are known to be suitable for high-temperature applications due to their excellent thermal stability characteristics. Many studies on the crystal structure of the composition change and electrical properties of the phase change have been performed [4, 5]. However, zinc manganite ceramics have application limits as temperature sensors due to their very large electrical resistance characteristics at room temperature. In this study, $\text{Zn}_{1.10}\text{Co}_x\text{Mn}_{1.90-x}\text{O}_4$ materials were taken as the base composition and Mn was substituted using Co. The structural and electrical properties based on the Co amount were observed and their application in NTC thermistors was investigated.

Experimental

$\text{Zn}_{1.10}\text{Co}_x\text{Mn}_{1.90-x}\text{O}_4$ ($x = 0 \sim 0.25$) specimens were fabricated using the mixed-oxide method. The starting

materials ZnO (99%), Mn_2O_3 (99%) and Co_3O_4 (99%) were accurately weighed and ball-milled using ethyl alcohol as the solvent and yttria-stabilized zirconia balls as the grinding media for 24 hrs. The mixed powder was calcined at 900 $^\circ\text{C}$ for 2 hrs. The calcined powders were blended with an organic binder (PVA), and sieved through a 200-mesh screen. Disk-shaped powder compacts of diameter 12 mm were formed by uniaxial pressing at 1000psi. The green powder compacts were sintered at 1200 $^\circ\text{C}$ for 12hrs in air.

The microstructure and morphology of sintered ceramics were analyzed using X-ray diffraction (XRD) and field-emission scanning electron microscopy (FE-SEM). To measure the electrical properties, Ag paste was spread on both sides of the sintered specimens using a screen printing method and heated at 600 $^\circ\text{C}$ for 10 min to allow metallization. Electrical resistance was measured using an electrometer from -10 $^\circ\text{C}$ to 60 $^\circ\text{C}$.

Results and discussion

Fig. 1 shows the XRD patterns of $\text{Zn}_{1.10}\text{Co}_x\text{Mn}_{1.90-x}\text{O}_4$ specimens with varying amounts of Co. X-ray diffraction peak intensities decreased and full width at half maximum (FWHM) increased with an increase in Co content x . We believe that these properties are due to the tetragonal distortion from the cooperative Jahn-Teller effect [6] and the second phases with partial compositional fluctuation due to decomposition of the Zn ions located in tetrahedral and octahedral sites of the spinel structure with the increase in Co content [7].

Fig. 2 shows the surface FE-SEM micrographs of $\text{Zn}_{1.10}\text{Co}_x\text{Mn}_{1.90-x}\text{O}_4$ specimens with varying amounts of Co. All specimens exhibited a very dense microstructure

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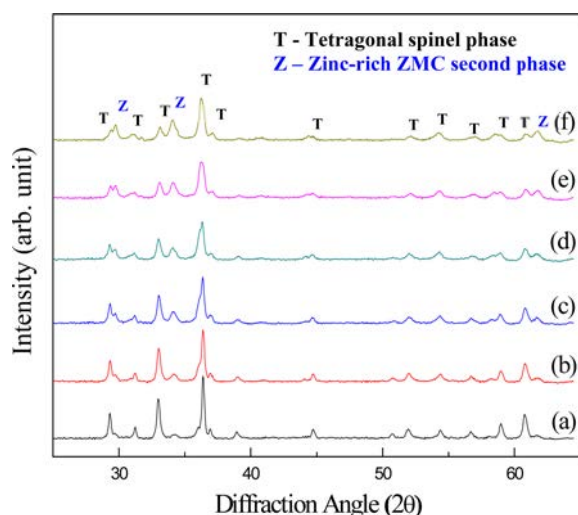


Fig. 1. XRD patterns of $\text{Zn}_{1.10}\text{Co}_x\text{Mn}_{1.90-x}\text{O}_4$ specimens; (a) $x = 0$, (b) $x = 0.05$, (c) $x = 0.10$, (d) $x = 0.15$, (e) $x = 0.20$ and (f) $x = 0.25$.

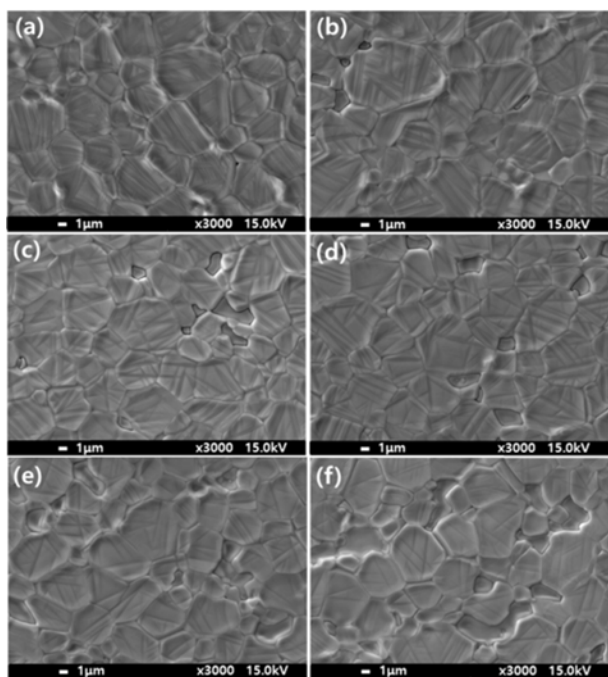


Fig. 2. FE-SEM images of $\text{Zn}_{1.10}\text{Co}_x\text{Mn}_{1.90-x}\text{O}_4$ specimens; (a) $x = 0$, (b) $x = 0.05$, (c) $x = 0.10$, (d) $x = 0.15$, (e) $x = 0.20$ and (f) $x = 0.25$.

without any porosities, and the average grain size decreased slightly from $5.21\ \mu\text{m}$ to $4.86\ \mu\text{m}$ with an increase in Co content x from 0 to 0.25. For $x \geq 0.05$, second phases were observed in grain boundary layers, and their distribution increased with the increasing Co content.

The EDS (energy dispersive spectroscopy) layer image scans for Zn, Co, Mn and O ions of $\text{Zn}_{1.10}\text{Co}_x\text{Mn}_{1.90-x}\text{O}_4$ specimens are shown in Fig. 3. The second phase distributed in the grain boundaries of Fig. 2 was identified as Zn-rich Zn-Co-Mn-O composition phases. As discussed in the XRD analysis of Fig. 1,

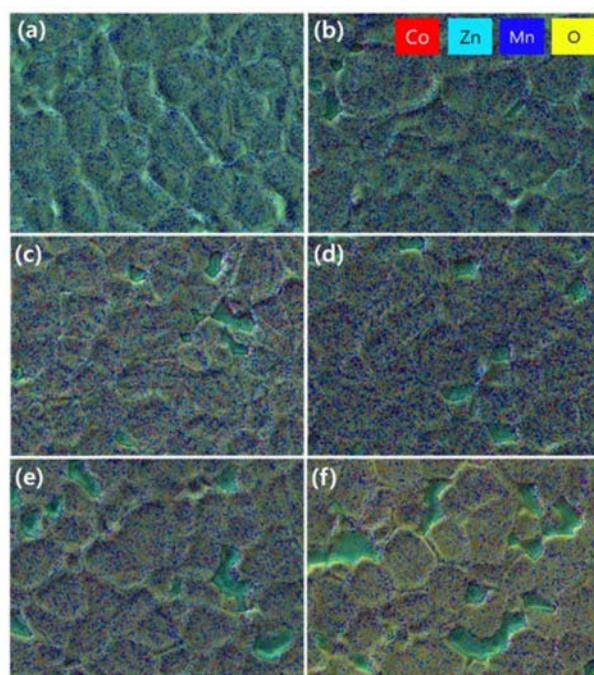


Fig. 3. EDS images of $\text{Zn}_{1.10}\text{Co}_x\text{Mn}_{1.90-x}\text{O}_4$ specimens; (a) $x = 0$, (b) $x = 0.05$, (c) $x = 0.10$, (d) $x = 0.15$, (e) $x = 0.20$ and (f) $x = 0.25$.

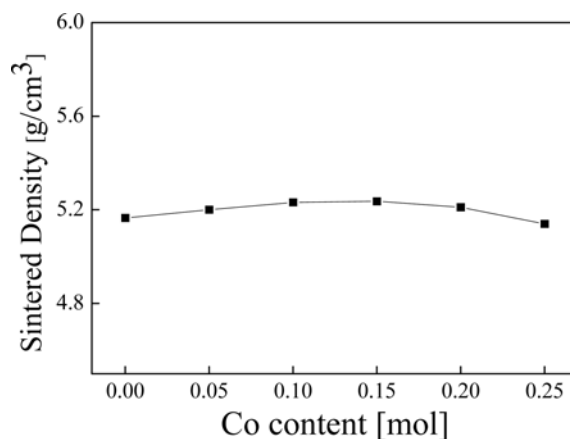


Fig. 4. Sintered density of $\text{Zn}_{1.10}\text{Co}_x\text{Mn}_{1.90-x}\text{O}_4$ specimens with variation of Co content.

with an increase in the composition ratio of Co ions, Zn ions in the spinel structure decomposed and Zn-rich second phases formed in the grain boundary layer. Fig. 4 shows the sintered density of $\text{Zn}_{1.10}\text{Co}_x\text{Mn}_{1.90-x}\text{O}_4$ specimens with varying amounts of Co. All specimens exhibited the good sintered density characteristic of at least approximately 96% of the theoretical values.

Fig. 5 shows the relationship between electrical resistance and temperature for $\text{Zn}_{1.10}\text{Co}_x\text{Mn}_{1.90-x}\text{O}_4$ specimens. All specimens exhibited the typical negative temperature coefficient of resistance (NTCR) characteristics where the resistance exponentially decreased with an increase in temperature. Resistance at room temperature decreased with an increase in Co content x , and exhibited a minimum

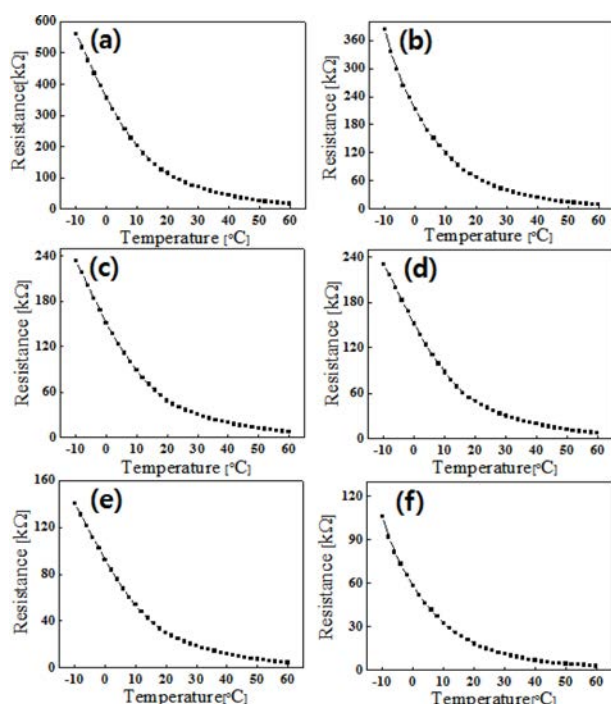


Fig. 5. Temperature-resistance of $\text{Zn}_{1.10}\text{Co}_x\text{Mn}_{1.90-x}\text{O}_4$ specimens; (a) $x = 0$, (b) $x = 0.05$, (c) $x = 0.10$, (d) $x = 0.15$, (e) $x = 0.20$ and (f) $x = 0.25$.

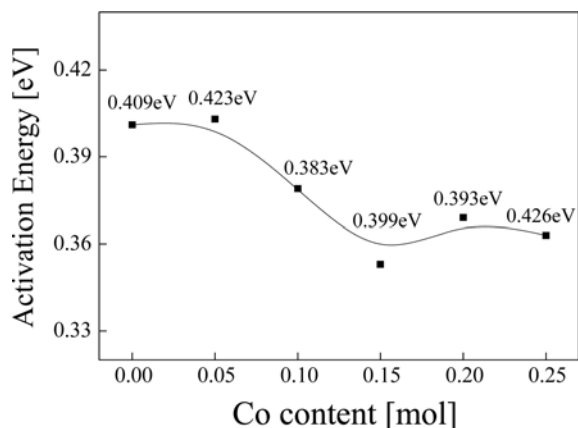


Fig. 6. Activation energy of $\text{Zn}_{1.10}\text{Co}_x\text{Mn}_{1.90-x}\text{O}_4$ specimens with variation of Co content.

value of 7.2 kΩ at $x = 0.25$. In general, for compositions of $x \leq 1.00$, $\text{Zn}_x\text{Mn}_{3-x}\text{O}_4$ ceramics have a single phase with a tetragonal structure, where Zn^{2+} and Mn^{3+} ions occupy the tetrahedral and octahedral sites in the spinel structure, respectively. However, for compositions of $1.00 \leq x \leq 1.10$, some Zn^{2+} ions probably occupy octahedral sites and Mn^{3+} ions are oxidized to Mn^{4+} ions in order to maintain the electrical charge neutrality. As a result, electrical conduction increases due to hopping conduction between Mn^{3+} and Mn^{4+} ions in the octahedral sites. For $\text{Zn}_{1.10}\text{Co}_x\text{Mn}_{1.90-x}\text{O}_4$ specimens, with an increase in Co content x , Co^{2+} and Co^{3+} ions can also occupy octahedral sites and contribute to the electrical conductivity along with the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ion

pairs [8, 9]. All specimens showed very good TCR characteristics of less than $-4.7\%/^\circ\text{C}$ and dependence on the composition ratio of Co was not observed.

Fig. 6 shows the activation energy for the hopping process of $\text{Zn}_{1.10}\text{Co}_x\text{Mn}_{1.90-x}\text{O}_4$ specimens with varying amounts of Co. The activation energy decreased from 0.418 eV to 0.373 eV with an increase in Co content x from 0 to 0.15, and it tends to be saturated for compositions of $x \geq 0.15$. As the Co content increases, Co^{2+} and Co^{3+} ions in the octahedral sites of the spinel structure increased. This gives rise to an increase in the ratio of $\text{Mn}^{4+}/\text{Mn}^{3+}$ ions in octahedral sites, which are responsible for hopping, resulting in an decrease in activation energy. However, for $x \geq 0.15$ compositions, we believe that the electrical conductance effects between the second phase in the grain boundaries and the formation of $\text{Mn}^{4+}/\text{Mn}^{3+}$ ions cancel each other out, so the activation energy becomes saturated [10].

Conclusions

Structural and electrical properties of $\text{Zn}_{1.10}\text{Co}_x\text{Mn}_{1.90-x}\text{O}_4$ ceramics with varying Co content were investigated for application in NTC thermistors. As the Co amount increases, tetragonal distortion due to the cooperative Jahn-Teller effect increased, and average grain size decreased slightly. For $x \geq 0.05$, Zn-rich Zn-Co-Mn-O second phases were observed in grain boundary layers. With an increase in Co content, Co^{2+} and Co^{3+} ions can also occupy octahedral sites in the spinel structure and these ions give rise to an increase in the ratio of $\text{Mn}^{4+}/\text{Mn}^{3+}$ ions in the same sites, which are responsible for hopping, resulting in a decrease in electrical resistance. However, the second phase in the grain boundaries may form a potential barrier, which also affects the electrical conduction characteristics.

Acknowledgment

This work was supported by the Industrial Strategic Technology Development Program (No. 10045177, Development of Resistive Ceramic Thin Film using Solution Process and Low Temperature Thin Film vacuum Getter).

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