Enhanced aging and thermal shock performance of $\text{Mn}_{1.95-x}\text{Co}_{0.21}\text{Ni}_{0.84}\text{Sr}_x\text{O}_4$ NTC ceramics

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Research Article

Keywords: Sr-doped Mn-Co-Ni-O materials, Negative temperature coefficient (NTC) ceramics, Electrical properties, Thermal shock cycling

Posted Date: April 22nd, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-23324/v1>

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Enhanced aging and thermal shock performance of $\text{Mn}_{1.95-x}\text{Co}_{0.21}\text{Ni}_{0.84}\text{Sr}_x\text{O}_4$ NTC ceramics

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Abstract

Herein, the $\text{Mn}_{1.95-x}\text{Co}_{0.21}\text{Ni}_{0.84}\text{Sr}_x\text{O}_4$ (MCNS) ($0 \leq x \leq 0.15$) negative temperature coefficient (NTC) materials are prepared by co-precipitation method. The replacement of Mn by Sr plays a critical role in controlling the lattice parameter, relative density, microstructure and electrical properties. The lattice parameter and relatively density increase with the increase of Sr content. Moreover, a small amount of Sr retards the grain growth and increases the bulk density. Moreover, the ρ_{25} , $B_{25/50}$, E_a and α values of MCNS ceramics are influenced by the Sr content and ranged from 1535.0-2024.1 $\Omega\cdot\text{cm}$, 3654-3709 K, 0.3149-0.3197 eV and 4.111-4.173%, respectively. The XPS results explain the transformation of MCNS ceramics from *n*- to *p*-type semiconductors. Moreover, the aging coefficient ($\Delta R/R$) of MCNS ceramics is found to be $< 0.2\%$, which indicates the stable distribution of cations in the spinel. Finally, the MCNS ceramics demonstrate excellent thermal durability with $< 1.3\%$ of resistance shift after 100 thermal shock cycles.

Keywords: Sr-doped Mn-Co-Ni-O materials; Negative temperature coefficient (NTC) ceramics; Electrical properties; Thermal shock cycling

1. Introduction

Negative temperature coefficient (NTC) ceramic thermistors based on mixed-valence transition manganites are being widely employed in temperature sensors, temperature controllers, time delay, voltage regulators and infrared detectors [1-5].

The electrical properties of spinel Mn_3O_4 , doped with different transition metals (Co, Ni, Zn, Fe, Cu) cations, are mainly influenced by the $\text{Mn}^{3+}/\text{Mn}^{4+}$ couple at B-sites and changed with dopant content [2, 4-6, 8]. Moreover, a ternary spinel compound, i.e., $(\text{Mn}_{3-x-y}\text{Co}_x\text{Ni}_y)\text{O}_4(\text{MCN})$, renders promising electrical properties due to simple fabrication and outstanding thermistors properties [9]. One should note that the electrical mechanism of MCN can be interpreted by small polaron hopping conduction [10]. Furthermore, the electrical properties of MCN can be tuned by doping small-sized transition metals, such as Fe, Zn and Cu, at B-sites [2, 8, 11, 12]. Hence, the substituent Sr, which is a divalent ion with a larger radius than Mn, facilitates the conversion of Mn^{3+} to Mn^{4+} and creates oxygen vacancies. Therefore, Sr-doping effectively modifies the electrical properties of ceramic thermistors by inhibiting the migration of cationic vacancies and improving the aging performance. Mohapatra et al. have synthesized Sr-substituted polycrystalline LiFe_5O_8 spinel by solid-state method, resulting in improved dielectric and magnetic properties [13]. Furthermore, Zhao et al. have prepared $\text{La}_{0.7}(\text{Ca}_{0.3-x}\text{Sr}_x)\text{MnO}_3$ ($0 \leq x \leq 0.3$) using the sol-gel method and improved the electrical and magnetic properties due to Sr-induced double-exchange interactions [14]. Wang et al. have fabricated Sr-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics by solid-state reaction method and suppressed the dielectric dispersion due to Sr-induced defect compensation [15]. Nevertheless, the NTC behavior of MCNS ceramics has rarely been reported [16].

Moreover, the industrial utilization of advanced ceramics requires long-time thermal durability under different conditions, such as constant and variable temperatures. Recently Yang et al. [17] have investigated the microstructural evolution and mechanical behavior of oxide/oxide ceramic matrix composites under cyclic thermal shocks, demonstrating an increase in microcracks density under thermal shock. Parvanian et al. [18] have characterized the pore structure of open-cell silicon carbide (SiC)-based foams and evaluated the mechanical performance before and after thermal shock testing. Liao et al. [19] have synthesized multi-walled carbon nanotubes (MWCNTs)-enhanced $\text{Si}_2\text{BC}_3\text{N}$ ceramics by spark plasma sintering and demonstrated improved thermal stress resistance due to the presence of MWCNTs. One should note that the formation of microcracks or pores under thermal shock greatly influences the electrical properties of NTC ceramic thermistors. However, the influence of cyclic thermal shocks on the stability of NTC ceramics has not been studied yet.

Herein, Sr-substituted MCN ceramics are synthesized by the co-precipitation method, and the structure, microstructure and electrical properties are systematically explored. In addition, thermal shock testing is utilized to qualify the thermal stability of ceramic materials.

2. Experimental section

The Sr-doped MCN oxide, with chemical composition of $\text{Mn}_{1.95-x}\text{Co}_{0.21}\text{Ni}_{0.84}\text{Sr}_x\text{O}_4$ ($x = 0, 0.05, 0.1$ and 0.15 , labeled as A0, A1, A2 and A3), was obtained by co-precipitation method. Briefly, the commercially available nickel acetate, cobalt acetate, manganese acetate and sodium hydrate were used as raw materials, whereas strontium acetate was used for Sr-doping. First, the stoichiometric mixture solution of nickel acetate, cobalt acetate, manganese acetate and sodium hydrate was prepared by using the deionized water. The sodium hydrate solution (2 M) was used, as a precipitation agent, into the above solution (1 M) at 50 °C under continuous stirring. The whole reaction was carried out for 10 h. Finally, the precipitate was filtered, washed and dried at 80 °C for 12 h. The precursor was

ball-milled for 12 h and calcined in a muffle furnace at 800 °C for 4 h. The calcined powder was ground in an agate mortar for 12 h and pressed into pellets with a diameter of 10 mm and thickness of 2 mm. The pellets were sintered at 1175 °C for 2 h. Finally, the silver paste was coated on both surfaces of the sintered pellets and heated at 850 °C for 20 min.

The A0, A1, A2 and A3 powders were analyzed by thermogravimetric and differential thermal analysis (TG/DTA, NETZSCH STA 449C) in the temperature range of 30 to 1200 °C in air. The temperature was increased at the heating rate of 10 °C/min. The crystalline structure was determined by X-ray diffraction (XRD, Bruker D8 Advance). The X-ray diffractometer is equipped with Cu K_α ($\lambda = 0.15418$ nm) radiations and a nickel filter. The XRD patterns were recorded in the angular range of 10° to 80° (2θ). The microstructure was observed by using a scanning electron microscope (SEM, ZEISS SUPRA55VP), equipped with energy dispersive spectroscopy (EDS) for elemental analysis. The valence state of cations was investigated by X-ray photoelectron spectroscopy (XPS, Thermo Scientific Escalab 250xi), equipped with Al K_α radiations. The resistance was measured in the temperature range of -30 °C to 70 °C by Agilent 34970A digital multimeter. The sample was immersed in absolute alcohol to minimize the temperature fluctuations ($< \pm 0.05$ °C). The aging performance was assessed at 125 °C in a temperature-controlled furnace. Briefly, the sample was subjected to 100 thermal shock cycles and the low and high temperatures were fixed at -30 °C and 70 °C, respectively. The dwelling time at each temperature was 10 minutes, whereas the dwelling time at ambient temperature was 15 minutes. The testing equipment and temperature-cycling profile are shown in Fig. 1.

Fig. 1. The (a) schematic illustration of the thermal shock equipment and (b) temperature-cycling profile.

3. Results and discussion

3.1. TG/DTA analysis

Fig. 2. TG/DTA curves of the A2 sample.

Fig. 2. presents the TG and DTA curves of the A2 hydroxide precursor in the temperature range of RT to 1200 °C. The DTA curve exhibits an endothermic peak at 125 °C, and an initial weight loss of 5.07 % in the temperature range of RT to 200 °C, which can be ascribed to the removal of water adsorbed by hydroxide and crystal lattice. In the temperature range of 200 °C to 800 °C, A2 ceramic rendered a weight loss of 15.44% due to the decomposition of precursor and formation of the MCN phase. Moreover, the exothermic peak in DTA curve indicates the decomposition of precursor. However, the further increase in temperature (>800 °C) resulted in a weight loss of 1.82% due to the reduction of Mn^{4+} into Mn^{3+} [11]. Also, a wide endothermic peak at ~1100 °C can be attributed to the stable formation of MCNS ceramics due to cation redistribution. Therefore, 800 °C is chosen as the calcination temperature.

3.2. Structure and density analysis

Fig. 3. XRD patterns of A2 ceramic at different temperatures.

The influence of calcination temperature on the phase composition of A2 precursor is shown in Fig. 3. Apparently, the calcination at 800 °C resulted in a mixture of cubic Fd3m spinel-type (JCPDS no. 01-1110) and hexagonal P63/mmc perovskite-type phases (JCPDS no. 72-0197). In the temperature range of 900 to 1175 °C, the A2 precursor exhibited a single-phase cubic spinel structure, which is characterized by distinct diffraction peaks at $2\theta = 18.3^\circ$ (111), 30.1° (220), 35.5° (311), 37.1° (222), 43.2° (400), 53.5° (422), 57.1° (511), 62.7° (440) and 74.1° (533). One should note that the solubility of Sr improved with increasing calcination temperature, resulting in the formation of a single-phase cubic

structure.

Fig. 4. XRD patterns and lattice parameters of A0, A1, A2 and A3 ceramics after sintering at 1175 °C.

The XRD patterns of single-phase MCNS ceramics, with different amounts of Sr-doping, are shown in Fig. 4, confirming that the cubic structure is maintained after Sr-doping. Moreover, the typical diffraction peak of MCNS ceramics shifted towards lower diffraction angles with increasing Sr concentration, which can be ascribed to the larger ionic radius Sr. However, the (311) peak of A3 ceramic shifted towards a higher diffraction angle due to concentration quenching [13, 14, 20]. The lattice parameter (a) is obtained from XRD patterns, as shown in Fig. 4b, which increased from 0.83821 nm to 0.83896 nm with increasing Sr content from 0 to 0.1, respectively. However, the lattice parameter decreased to 0.83833 nm at $x = 0.15$, indicating the solubility limit of Sr ($x = 0.1$). The X-ray density (ρ_x) can be calculated from the given relationship:

$$\rho_x = \frac{Z \cdot M}{N \cdot V} \quad (1)$$

where Z refers to the number of molecules per unit cell (herein, $Z = 8$), M represents the molecular weight, N denotes the Avogadro constant and V corresponds to the unit cell volume ($V = a^3$, cubic phase). The X-ray density of A0, A1, A2 and A3 ceramics was found to be 5.251, 5.276, 5.31 and 5.359 kg/m³, respectively. The difference in X-ray density can be explained by the difference in atomic weight of different ions ($M_{\text{Sr}} > M_{\text{Mn}}$).

Fig. 5. The bulk density and relative density of A0, A1, A2 and A3 NTC ceramics.

The relative density (ρ_{rel}) can be given as:

$$\rho_{\text{rel}} = \rho_b / \rho_x \quad (2)$$

where ρ_b refers to the bulk density, which is determined by the Archimedes method. The change in bulk density (ρ_b) with respect to Sr²⁺ content is illustrated in Fig. 5. Obviously, the bulk density of A0 to A3 ceramics linearly increased with increasing Sr concentration from 5.057 to 5.174 kg/m³,

respectively. Fig. 5 shows that the relative density of A0, A1 and A2 ceramics linearly increased from 96.3% to 96.8% with increasing Sr content from 0 to 0.1 et. %, respectively, and decreased to 96.4% at $x = 0.15$.

3.3. Surface analysis

Fig. 6. SEM images of the A2 ceramic after sintering at (a) 1150 °C and (b) 1175 °C, where the inset in (b) shows the corresponding cross-sectional SEM image. (c) SEI and EDS maps of different elements from A2 ceramic.

Fig. 6a and 6b show the SEM images of A2 ceramic after sintering at 1150 °C and 1175 °C, respectively. Herein, the density and grain size increased with increasing sintering temperature. Secondary electron image (SEI) and elemental mapping were utilized to determine the distribution of different elements, as shown in Fig. 6c. The element maps show that Mn, Co, Ni, Sr and O are homogeneously distributed in A2 ceramic after sintering at 1175 °C, which is selected as the sintering temperature in subsequent experiments.

Fig. 7. The surface morphology of (a) A0, (b) A1, (c) A2 and (d) A3 ceramics after sintering at 1175 °C.

Fig. 7 presents surface morphology of MCNS ceramics after sintering at 1175 °C, showing high density and regular morphology. Nonetheless, it can be seen that the grain size of ceramics decreased from 10-12 μm (A0) to 3-4 μm (A2) after Sr-doping, indicating that a small amount of Sr dopant hinders the grain growth during sintering due to the dragging effect [21]. On the other hand, the surplus Sr in A3 ceramic may cluster at the grain boundaries and improve the transport rate for grain coarsening [22]. Therefore, the A3 ceramic exhibited distinct grain boundaries with some undesirable pores. It is worth emphasizing that an optimal amount of dopant is required to achieve the desired

densification and avoid grain coarsening [23, 24].

3.4. Electrical characterization and XPS analysis

Fig. 8. The relationship between (a) resistivity (ρ) and absolute temperature (T), and (b) $\ln(\rho)$ and reciprocal of absolute temperature ($1000/T$) of A0, A1, A2 and A3 ceramics.

The relationship between resistivity and absolute temperature of MCNS ceramics is shown in Fig. 8(a). The resistivity of MCNS ceramics exponentially decreased with increasing temperature, which can be given by the Arrhenius equation:

$$\rho = \rho_0 \exp(B/T) = \rho_0 \exp(E_a / k_B T) \quad (3)$$

where ρ_0 represents the resistivity at an infinite temperature ($T \rightarrow \infty$), T corresponds to the absolute temperature, and B denotes the material constant, as given by Eq. (3), where E_a refers to the activation energy and k represents the Boltzmann constant. The $B_{25/50}$ constant can be given as:

$$B_{25/50} = \frac{\ln(R_{25} / R_{50})}{1/T_{25} - 1/T_{50}} \quad (4)$$

where R_{25} and R_{50} represent the resistance of ceramic at 25 °C and 50 °C, respectively.

Fig. 8(b) shows the relationship between $\ln(\rho)$ and reciprocal of absolute temperature ($1000/T$) of MCNS ceramics. The room temperature resistivity, thermal constant, activation energy and sensitivity of MCNS ceramics are summarized in Table 1.

Table 1: The room-temperature resistivity, B constant and activation energy of MCNS ceramics.

Ceramic sample	ρ_{25} ($\Omega \cdot \text{cm}$)	$B_{25/50}$ / K	E_a / eV	α (%)
A0	1707.9	3676	0.3168	4.136
A1	1590.3	3667	0.3160	4.111
A2	1535.0	3654	0.3149	4.125
A3	2053.6	3709	0.3197	4.173

As shown in Table 1, the ρ_{25} , $B_{25/50}$, E_a and α values of as-prepared MCNS ceramics are in the range of 1535.0-2053.6 $\Omega \cdot \text{cm}$, 3654-3709 K, 0.3149-0.3197 eV and 4.111-4.173 %, respectively, after sintering at 1175 °C. The resistivity initially decreased from 1707.9 $\Omega \cdot \text{cm}$ to 1535.0 $\Omega \cdot \text{cm}$ with increasing Sr content from 0 to 0.1, respectively, followed by an increase to 2053 $\Omega \cdot \text{cm}$ at $x = 0.15$. The linear relationship between $\ln(\rho)$ and $1000/T$ shows the characteristics of small-polaron hopping transport, which is often observed in Mn-based spinel structures (Fig. 8b). One should note that the MCNS spinel phase contains Mn element with different valence states, which facilitates electron

jumping between Mn^{3+} and Mn^{4+} ions at octahedral sites [2, 11]. As mentioned above, the NTC thermistor characteristics are described by the Nernst-Einstein relationship:

$$\sigma = \frac{N_{\text{oct}} e^2 d^2 \nu_0}{kT} NC(1-C) \exp\left(\frac{-E_a}{kT}\right) \quad (5)$$

where N_{oct} refers to the concentration of octahedral sites per cubic centimeter, d represents the jumping distance for charge carriers, ν_0 denotes the lattice vibrational frequency, which is associated with conduction, k refers the Boltzmann constant, e represents the electronic charge, N denotes the concentration of per formula unit of sites, which are available for the charge carriers, $NC(1-C)$ is related to the number of Mn^{3+} and Mn^{4+} cations at octahedral sites and E_a refers to the hopping energy. Furthermore, XPS analysis was carried out to quantify the $\text{Mn}^{3+}/\text{Mn}^{4+}$ couple and clarify the mechanism of resistivity variation.

Fig. 9. The high-resolution Mn $2p_{3/2}$ XPS spectra from a) A0, b) A1, c) A2 and d) A3 ceramics.

The high-resolution Mn $2p_{3/2}$ XPS spectra are analyzed to investigate the change in valence state of Mn due to Sr-doping. The experimental data were normalized by the least square procedure and peak intensities of Mn^{2+} (641.2eV), Mn^{3+} (642.4eV) and Mn^{4+} (643.8eV) were calculated [25, 26], as shown in Fig. 9. It can be concluded that the ratio of Mn^{2+} , Mn^{3+} and Mn^{4+} ions in different ceramics is equal to the ratio of peak areas, respectively. Hence, the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio in A0, A1, A2 and A3 ceramics was found to be 1.24, 1.66, 1.67 and 1.40, respectively (Table 2). The $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio initially increased with increasing Sr content, followed by a decrease at $x = 0.15$.

Table 2: The relative concentration of Mn ions and thermopowder Q values in different ceramics.

Ceramic sample	Mn^{2+} (%)	Mn^{3+} (%)	Mn^{4+} (%)	$\text{Mn}^{3+} / \text{Mn}^{4+}$	Q (μV)
A0	47.1	29.3	23.6	1.24	-0.69
A1	54.9	28.2	17.0	1.66	24.4
A2	54.8	28.2	16.9	1.67	25.0
A3	56.1	25.6	18.3	1.40	9.77

One should note that the carrier-type can be related to $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio through the thermopower Q value, which can be defined as: $Q = (k_B/e) \ln \left(\frac{1}{\beta} \left(\frac{[\text{Mn}^{3+}]}{[\text{Mn}^{4+}]} \right) \right)$, where k_B refers to the Boltzmann constant, e

represents the unit charge and $\beta = 5/4$ denotes the spin degeneracy factor. The A0, A1, A2 and A3 ceramics rendered a Q value of $-0.69 \mu\text{V}$, $24.4 \mu\text{V}$, $25.0 \mu\text{V}$ and $9.77 \mu\text{V}$, respectively, showing a transition from n - to p -type semiconducting behavior [10, 27].

One should note that Sr^{2+} can occupy the octahedral sites in MCNS because the interstitial occupancy is not allowed due to the large ionic size. To maintain the electrical neutrality, the incorporation of Sr leads to the following reaction [15, 22, 28,]:

Hence, Sr-doping facilitates the formation of oxygen vacancies. It has been reported that more oxygen vacancies exist in grains of 0.05% Sr sample than MCN. Moreover, the re-oxidation reaction eliminates oxygen vacancies and produces holes in the grain boundaries during the cooling process, as given below [29, 30]:

Then, the resulting holes combine with Mn^{3+} ($\text{Mn}^{3+} + h^* \rightarrow \text{Mn}^{4+}$) and influences the resistivity according to the Nernst-Einstein relationship. Hence, Sr-doping lowered the resistivity of Sr-doped MCN ceramics because the conduction is governed by hole carriers. These results are in good agreement with XPS analysis. Moreover, it can be seen that the electrons migrate through the shortest contact point between the particles. Therefore, the loose grain boundary increases the electron transportation distance between Mn^{3+} and Mn^{4+} ions. Consequently, the difference in hopping of carriers increases the resistivity and E_a , as shown by the A3 ceramic [31].

3.5. Aging performance and thermal shock cycling

Fig. 10. The relative resistance drift of MCNS ceramics at 125 °C of 1000 h.

Fig. 11. The relative resistance drift of MCNS ceramics under different numbers of thermal shock cycles.

Furthermore, the aging performance of MCNS ceramics, at 125 °C, has been assessed by resistance variation and results are shown in Fig. 10. We have observed that the variation of aging coefficient ($\Delta = \Delta R / R$) ranged from 0.16 to 1.31% during 1000 h. However, the relative resistance drift is found to be smaller in Sr-doped MCNS at $x = 0.1$. Fig. 11 shows the relative resistance variation of MCNS ceramics with different numbers of thermal shock cycles. The relative resistance shifts was found to be 1.3-8.9% after 100 thermal shock cycles. The resistance of MCNS ceramics significantly changed with increasing number of thermal shock cycles and attained an almost constant value after 50 cycles. Hence, a small amount of Sr-doping can significantly improve the aging and cyclic thermal performance of MCNS ceramics. One should note that the single-phase Sr-doped MCN ceramics do not exhibit aging. However, the large amount of dopant results in a deviation from the single-phase structure and compromises the aging performance [32]. Moreover, the cationic vacancies diffuse into B-sites within the grains and increase the resistance. The addition of Sr forms the oxygen vacancies and decreases the concentration of cationic vacancies at the grain boundaries. Consequently, the inhibition of cationic vacancies diffusion greatly improves aging performance [33, 34].

Fig. 12. XRD patterns of A0 ceramic during aging after (a) 0 h, (b) 1000 h, and (c) 100 thermal shock cycles, and A2 ceramic during aging after (d) 0 h, (e) 1000 h and (f) 100 thermal shock cycles.

XRD patterns of A0 ceramic have been recorded during aging after 0 h, 1000 h and 100 thermal shock cycles. The results revealed that the A0 ceramic maintained the spinel structure after aging for

1000 h (Fig. 12a and 12b), whereas the rock salt phase appeared after 100 thermal shock cycles due to the segregation of NiO phase (Fig. 12c). In the case of A2 ceramic, the cubic spinel structure is maintained after aging for 1000 h and 100 thermal shock cycles. However, the diffraction peak at $2\theta = 35.5^\circ$, corresponding to (311) planes of the spinel phase, has been shifted towards a higher diffraction angle after 100 thermal shock cycles, which can be ascribed to the concentration quenching.

Fig. 13. The microstructural evolution of A2 ceramic during aging after (a) 0 h, (b) 200 h and (c) 600 h, and thermal shock testing after (d) 30 cycles and (e) 50 cycles.

The A2 ceramic surface does not exhibit any obvious change after long time aging, as shown in Fig. 13b and 13c. Meanwhile, the SEM images of the A2 ceramic were taken after 30 and 50 thermal shock cycles (Fig. 13d and 13e). However, the pores started to appear after 30 cycles and increased after 50 cycles, as shown in Fig. 13d and 13e. Hence, the thermal shock testing resulted in pore formation and decreased the densification of A2 ceramic due to grain coarsening, which can be ascribed to the concentration quenching. Meanwhile, the grain size of A2 ceramic increased by the thermal shock cycling.

Fig. 14. The high-resolution Mn $2p_{3/2}$ XPS spectra from A2 ceramic during aging after (a) 200 h and (b) 600h, and thermal shock testing after (c) 30 cycles and (d) 50 cycles.

The high-resolution Mn $2p_{3/2}$ XPS spectra from A2 samples after aging and thermal shock testing are shown in Fig. 14. As mentioned earlier, the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio decreased to 1.45 and 1.42 after aging for 200 and 600 h, respectively. Similarly, the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio reduced to 1.14 and 1.11 after 30 and 50 thermal shock cycles, respectively. Based on Fig. 10 and Fig. 11, the large resistance shift between aging and thermal shock cycling can be interpreted as: (1) in the case of A0 ceramic under thermal shock cycling, the precipitation of low-conductivity NiO phase resulted in a significant increase in ceramic resistance (8.9%); (2) compared with the aging performance, the thermal shock testing of A2 ceramic resulted in pore formation due to grain coarsening and influenced the drift resistivity of ceramics; (3) the atmospheric oxygen sorption ($\text{O}_0^\times \rightarrow \frac{1}{2}\text{O}_2 + V_0^{**} + 2e^-$) increased with increasing pores and resulted in oxidation of Mn^{2+} to Mn^{3+} , rendering unstable configuration of cationic

distribution and resistance drift, as reported elsewhere [12, 35, 36]; and (4) the presence of a large number of pores at grain boundaries induced a high energy barrier and reduced the $\text{Mn}^{3+}/\text{Mn}^{4+}$ couples. Therefore, the XRD, SEM and XPS analysis explained the resistance shift under aging and thermal shock cycling.

4. Conclusions

In summary, Sr-doped Mn-Co-Ni ceramics have been successfully synthesized by using the co-precipitation method. The MCNS ceramics exhibited a single-phase cubic spinel structure after sintering. Furthermore, the addition of a small amount of Sr improved the density and decreased the resistivity, however, the excessive amount of Sr ($x > 0.1$) resulted in higher resistivity due to grain coarsening. Moreover, the Sr-doped MCNS ceramics demonstrated a transition from *n*- to *p*-type semiconducting behavior, which can be ascribed to Sr-doping. Furthermore, the aging and thermal shock rendered a similar effect on resistivity shift according to the Sr content. However, the thermal aging of MCNS ceramics exhibited a rapid resistance shift under thermal shock than the constant temperature. In addition, the thermal shock aging resulted in microstructural evolution from highly dense to porous structure under thermal shock testing. These results demonstrate that Sr-doping is an effective strategy to improve the thermal stability of MCNS ceramics.

Acknowledgments

This study was supported by Xinjiang Key Laboratory of Electronic Information Materials and Devices Foundation (Grant No. 2018D04006), Tianshan Cedar Project of Xinjiang Uygur Autonomous Region (Grant No. 2018XS09) and the National Natural Science Foundation of China (Grant No. 51872326).

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Figures

Figure 1

The (a) schematic illustration of the thermal shock equipment and (b) temperature-cycling profile.

Figure 2

TG/DTA curves of the A2 sample.

Figure 3

XRD patterns of A2 ceramic at different temperatures.

Figure 4

XRD patterns and lattice parameters of A0, A1, A2 and A3 ceramics after sintering at 1175 °C.

Figure 5

The bulk density and relative density of A0, A1, A2 and A3 NTC ceramics.

Figure 6

SEM images of the A2 ceramic after sintering at (a) 1150 °C and (b) 1175 °C, where the inset in (b) shows the corresponding cross-sectional SEM image. (c) SEI and EDS maps of different elements from A2 ceramic.

Figure 7

The surface morphology of (a) A0, (b) A1, (c) A2 and (d) A3 ceramics after sintering at 1175°C.

Figure 8

The relationship between (a) resistivity (ρ) and absolute temperature (T), and (b) $\ln(\rho)$ and reciprocal of absolute temperature ($1000/T$) of A0, A1, A2 and A3 ceramics.

Figure 9

The high-resolution Mn 2p_{3/2} XPS spectra from a) A0, b) A1, c) A2 and d) A3 ceramics.

Figure 10

The relative resistance drift of MCNS ceramics at 125 °C of 1000 h.

Figure 11

The relative resistance drift of MCNS ceramics under different numbers of thermal shock cycles.

Figure 12

XRD patterns of A0 ceramic during aging after (a) 0 h, (b) 1000 h, and (c) 100 thermal shock cycles, and A2 ceramic during aging after (d) 0 h, (e) 1000 h and (f) 100 thermal shock cycles.

Figure 13

The microstructural evolution of A2 ceramic during aging after (a) 0 h, (b) 200 h and (c) 600 h, and thermal shock testing after (d) 30 cycles and (e) 50 cycles.

Figure 14

The high-resolution Mn 2p_{3/2} XPS spectra from A2 ceramic during aging after (a) 200 h and (b) 600h, and thermal shock testing after (c) 30 cycles and (d) 50 cycles.