Improving the stability of Fe$_{0.8}$Mn$_{1.54}$Ni$_{0.66}$O$_4$ NTC thermistor with nano-powders and N$_2$ annealing

Nam Chol Yu$^{1,}$*$^1$, Il Man Pak$^2$, Son Guk Pak$^3$ and Jin Sim Kim$^4$

$^1$ School of Science and Engineering, Kim Chaek University of Technology, 60-Kyogu, Yonggwang Street, Pyongyang, DPR, Republic of Korea
$^2$ Institute of Material Analysis, Kim Chaek University of Technology, 60-Kyogu, Yonggwang Street, Pyongyang, DPR, Republic of Korea
$^3$ Institute of Semiconductor, Kim Chaek University of Technology, 60-Kyogu, Yonggwang Street, Pyongyang, DPR, Republic of Korea
$^4$ Institute of Internet, Kim Chaek University of Technology, 60-Kyogu, Yonggwang Street, Pyongyang, DPR, Republic of Korea

$^*$ Author to whom any correspondence should be addressed.

E-mail: ync781213@star-co.net.kp

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Abstract

Fe$_{0.8}$Mn$_{1.54}$Ni$_{0.66}$O$_4$ nano-ceramics have been successfully prepared by sol-gel auto combustion. The microstructure and phase of these samples were observed by using SEM and XRD. The diameters of Fe$_{0.8}$Mn$_{1.54}$Ni$_{0.66}$O$_4$ ceramic particles pre-fired at 800 °C range from 52 to 83 nm. The powder sintered at above 1050 °C has the compact and uniform spinel structure. We have investigated the electrical characteristics of these thermistors at different sintering temperatures and concluded that the sample sintered at 1200 °C is sufficient to form the appropriate spinel phase. Moreover, the thermistor annealed for 72 h at 450 °C in N$_2$ atmosphere has the drift rate of <0.7%.

1. Introduction

NTC (Negative Temperature Coefficient) thermistors are widely used in industrial applications such as temperature measurement, control and compensation. One important problem in using of NTC thermistor is to overcome the aging phenomenon [1, 2]. Their electrical properties change with time particularly when the temperature increases and it is the main reason why they are unable to use at temperatures above 150 °C. Aging of electrical properties attributes to non-equilibrium states that exist inherently in semiconducting NTC ceramics [3].

In order to solve this problem, the previous authors doped the oxides of transition metals such as Zn, Co, Cr and Zr to nickel manganite materials and improved their aging characteristics and stability [4–12]. In addition, some authors employed various new powder preparation methods thereby changing parameters of both electrode coating and heat treatment after sintering [13–15].

Z B Wang and his colleagues reported that the improved aging behavior of the N$_2$-annealed thermistor is explained by the reduction of the concentration of the cation vacancy upon annealing under lower oxygen partial pressure and the suppression of cation redistribution [16]. However, they did not determine the reasonable temperature and time in N$_2$ annealing for high reliable NTC thermistor.

Wenwen Kong explained about the influence of oxygen atmosphere annealing on the thermal stability of Mn$_{1.2}$Co$_{0.5}$Ni$_{0.3}$O$_{4+δ}$ ceramic films fabricated by RF magnetron sputtering [17].

The sol-gel auto combustion method is an advanced process that is widely used in the nanopowder synthesis of Mn–Co–Ni–O NTC thermistor and several ferrite materials [18–27]. But, I could not find a report about the preparation of Fe$_{0.8}$Mn$_{1.54}$Ni$_{0.66}$O$_4$ nano-ceramics by sol-gel auto combustion.

So, the aim of this paper is to research the electrical properties of Fe$_{0.8}$Mn$_{1.54}$Ni$_{0.66}$O$_4$ nanoceramic material prepared by a more convenient sol-gel auto combustion method and determine the reasonable temperature and time in N$_2$ annealing.
2. Experimental procedure

The analytical grade Fe(NO$_3$)$_3$·6H$_2$O, Ni(NO$_3$)$_2$·6H$_2$O, Mn(NO$_3$)$_2$·6H$_2$O were mixed in molar ratio of Fe$_{0.8}$Mn$_{1.54}$Ni$_{0.66}$O$_4$ and dissolved in deionized water. This solution, citric acid and ethylene glycol were mixed in molar ratio of 1:2:4.4. A small amount of ammonium hydroxide was carefully added into the solution to change the pH value to 7. The solution was heated at 80 °C and stirred by using a magnetic stirrer continuously. Because of evaporation, the viscous solution was turned into a dried gel. When the gel was ignited in the air, it burnt in a self-propagating combustion way and it turned to loose powder.

The prepared mixture powder was pre-sintered at 800 °C for 2 h and ball-milled for 36 h in ethyl alcohol slurry and dried at 80 °C. Pellets of diameter 4 mm, thickness 2 mm were shaped from the powder under 30 MPa pressure with 5 wt% PVA binder. These pellets were classified into 4 batches and each of them was sintered at 1 050, 1 150, 1 200 and 1 250 °C for 2 h in the air, respectively. For metallization, these sintered pellets were coated with Ag paste on their both faces.

In order to determine the annealing temperature and time in the N$_2$ atmosphere, the N$_2$ gas was flowed with the rate of 4 l min$^{-1}$ into the quartz tube furnace (diameter 50 mm, length 400 mm). The specimens of 16 batches were in this furnace and maintained respectably at 350, 450, 550 and 650 °C for 24, 72, 96 and 144 h.

The precursor powder was analyzed using x-ray diffraction (D8-Advance diffractometer) for phase identification. The particle morphology in the pre-sintered powder and sintered pellets were observed with a Scanning Electron Microscope (Quantum 200). The electrical resistance was measured with a digital multimeter (DT9208A) at 25 °C and 50 °C, respectively.

The B value was calculated by the following equation:

$$B = 3853.89 \times \ln \left( \frac{R_{25}}{R_{50}} \right)$$

where $R_{25}$ and $R_{50}$ are the resistance measured at 25 °C and 50 °C.

Then the specimens were cooled to 25 °C. Their electrical parameters were measured and compared with the parameters before annealing.

3. Results and discussions

3.1. Phase formation and microstructure

From x-ray diffraction analysis, we find that the spinel phase was formed in the powders pre-fired at 800 °C.

Figure 3 is SEM photograph of specimen pre-sintered at 800 °C. As seen in this figure, the diameter of power particles ranges from 52 to 83nm. The relative densities of all the specimens were calculated at different sintering temperatures (figure 1).

From figure 1, we find that the relative density gets saturated when sintered at 1 200 °C and a high sintering temperature is necessary for densification of ceramics.

The actual density and the calculated density of sample are 3.965 g cm$^{-3}$ and 4.495 g cm$^{-3}$ respectively when sintered at 1 200 °C.
The SEM photograph of the specimen sintered at 1050 °C shows that the specimen is comparatively compact and its particles are dispersed uniformly and are fine without any big particle (figure 4).

The specimens sintered at 1200 °C and 1250 °C were denser than at 1050 °C. (figure 5 and figure 6) and there are no too big particles. However, it is difficult to get the homogeneous system of ceramic material because the activation energy is too high above 1200 °C (figure 6).

The XRD patterns for the powder after firing at 800 °C and specimen sintered at 1200 °C are shown in figures 2 and 7. We can identify from the above XRD patterns that the synthesized powder is a single cubic spinel phase. It can be seen that the amorphous gel is transformed directly into a single spinel phase after firing at 800 °C.

There are some unessential phases in figure 2. However, no other phases were formed after sintering at 1200 °C in figure 7.

3.2. Electrical properties

Figure 8 represents the resistivity at 25 °C and the B values of all the specimens.
For the Fe–Mn–Ni–O$_4$ ceramics, higher sintering temperatures than 1250 °C lead to NiO separation according to

$$\text{FeMnNiO}_4 \rightarrow a\text{NiO} + \frac{a}{6}\text{O}_2 + \frac{3-a}{3}\text{Fe}_{\frac{3-a}{2}}\text{Mn}_{\frac{3}{2-a}}\text{Ni}_{3\left(1-a\right)}\text{O}_4$$  \hspace{1cm} (2)

where $a$ is the number of moles of the separated NiO phase.

The resistivity of the sintered sample at 1250 °C is suddenly increased because the amount of the insulated NiO phase increases at this temperature.

### 3.3. Observation of the aging phenomenon

The analytical result of the resistivity and B values above shows that the specimen sintered at 1200 °C is suitable for the manufacture of temperature sensors.

Therefore, we observe in detail the aging phenomenon of the specimen sintered at 1200 °C.
The main problems are to analyze the effects of N₂ annealing temperature and time on the thermistor prepared by sol-gel auto combustion and to determine the reasonable annealing temperature and time. The drift rate \( \eta \) is calculated according to
\[
\eta = \left( \frac{R_1 - R_0}{R_0} \right) \times 100(\%)
\]
where \( R_0 \) is the resistance at 25 °C before annealing and \( R_1 \) is the resistance at 25 °C after annealing. Figure 8 represents the drift rate of the samples.

From figure 9, we find that the sample annealed at 450 °C for 72 h has the drift rate of 0.7%. When the annealing temperature is above 550 °C, the drift rate rather decreases, but the specimens show a partial change in mechanical characteristics of the ceramics due to the sudden temperature stress. From this results, it is found that the annealing in N₂ atmosphere is reasonable at 450 ~ 500 °C for 72 h.

Finally, we tested to compare the drift rate of two kind of thermistor prepared with nano-powder and micro-powder. The testing results are shown that the stability of samples prepared with nano-powder is superior to the samples prepared with micro-powder. The drift rate of the samples prepared with micro-powder is 0.9%–1.4%, but one of the samples prepared with nano-powder is <0.7%.
4. Conclusions

The nano-ceramics Fe-Ni manganite powders were prepared via a sol-gel auto-combustion process. The nitrite-citrate gels can burn in a self-propagating combustion process in air to transform into single phase. Nano-ceramics manganite particles with spinel crystal structure. The fine-grained Fe_{0.8}Mn_{1.54}Ni_{0.66}O_{4} ceramics with homogeneous microstructure were prepared at a lower temperature. During the sintering at high temperature, a small amount of NiO phase was formed due to the decomposition of spinel. The obtained ceramics have high activation energy.

We have investigated the electrical characteristics of these thermistors at different temperatures and concluded that the sample sintered at 1 200 °C is sufficient to form the appropriate spinel phases. Moreover, it is observed that the thermistor heat-treated for 72 h at 450 ~ 550 °C in N_{2}, has the drift rate of <0.7%. These samples will be used for several NTC thermistor applications.

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ORCID iDs

Nam Chol Yu @ https://orcid.org/0000-0003-2323-8188

References

[1] Wood S D, Mangum B W, Filliben J J and Tillett S B 1978 An investigation of the stability of thermistors J. Res. Natl. Bur. Stand. B 3 247–63
[2] Green W A, Metzmacher G, Zaspalis V, Huppertz P and Schuurman S 2001 Aging of NTC ceramics in the system Mn–Ni–Fe–O J. Eur. Ceram. Soc. 21 1793–6 PII: S0955 –2219(01)00117-0
[3] Hosseini M 2000 The effect of cation composition on the electrical properties and aging of Mn–Co–Ni thermistors Ceram. Int. 26 245–9 PII: S0272-8849(99)00049-8
[4] Varghese J M, Seema A and Dayas K R 2008 Microstructural, electrical and reliability aspects of chromium doped Ni–Mn–Fe–O NTC thermistor materials Mat. Sci. Eng. B 149 47–52
[5] Muralidharan M N, Rohini P R, Sunny E K, Dayas K R and Seema A 2012 Effect of Cu and Fe addition on electrical properties of Ni–Mn–Co–O NTC thermistor compositions Ceram. Int. 38 6481–6
[6] Li D F, Zhao S X, Xiong K, Bao H Q and Nan C W 2014 Aging improvement in Cu-containing NTC ceramics prepared by co-precipitation method J. Allo. Comp. 582 283–8
[7] Ren W, Zhu N N, Li L, Feng H J and Shang S G 2019 Improvement of ageing issue in Zn0.4Fe2.5Co2Mn0.5O8 thermistor films J. Eur. Ceram. Soc. 39 4189–93
[8] Guan F, Lin X J, Dai H, Wang J R and Huang S F 2019 LaMn1-xTixO3-NiMn2O4 (0 < x < 0.7): a composite NTC ceramic with controllable electrical property and high stability J. Eur. Ceram. Soc. 39 2692–6
[9] Sun X, Leng S, Zhang H, He Z and Li Z 2018 Electrical properties and temperature sensitivity of Li/Mg modified Ni0.7Zn0.3O based ceramics J. Allo. Comp. 763 975–82
[10] He L, Ling Z Y, Wu M Y, Zhang G and Ling D X 2017 Thermal and humidity sensing behaviors of Mn0.85Co0.3Ni0.5O4 thin films: effects of adjusting the surface morphology App. Surf. Sci. 410 201–5
[11] Yang T, Zhang B, Zhao Q, Luo P and Chang A 2016 New high temperature NTC thermistors based on the MgAl1-xCrx2O4 ceramics J. Allo. Comp. 685 287–93
[12] Zhang B, Zhao Q, Chang A, Wu Y and Li H 2016 Spark plasma sintering of MgAl2O4-LaCr0.5Mn0.5O3 composite thermistor ceramics and a comparison; investigation with conventional sintering J. Allo. Comp. 675 381–6
[13] He L, Ling Z Y, Wu M Y, Zhang G and Zhang S Q 2015 Annealing temperature-dependent microstructure and electrical properties of Mn-based thin film thermistors with a sandwich structure Ceram. Int. 41 10142–7
[14] Zhang H, Chang A, Guan F, Zhao L and Huang X 2014 The optimal synthesis condition by sol-gel method and electrical properties of Mn1.5-xCo1.5Ni0.5xO4 ceramics Ceram. Int. 40 7865–72
[15] Liang S, Yang J, Yi X, Zhang X and Bai Y 2011 An efficient way to improve the electrical stability of Ni0.6Si0.2Al0.6Mn1.6O4 NTC thermistor Ceram. Int. 37 2537–41
[16] Wang Z B, Zhao C H, Yang P H, Chen C S and Wannubst I 2006 Effect of annealing in O2 or N2 on the aging of Fe0.5Mn1.6O4 Ni0.66O4 NTC-ceramics Solid State Ionics 177 2191–4
[17] Kong W, Wang J, Yao J and Chiang A 2018 Influence of oxygen atmosphere annealing on the thermal stability of Mn2Col.5Ni0.5O4±6 ceramic films fabricated by RF magnetron sputtering Ceram. Int. 44 1455–60
[18] Deepak P P, Parakkaran M, Ranjith K R, Muralidharan M N and Ansaii S 2018 Optimization studies on nanocrystalline NTC thermistor compositions by a self-propagated high temperature synthesis route Ceram. Int. 44 1360–6
[19] Wang Q 2018 Ceram. Int. 09 177
[20] Hrort N E 2014 Microstructure of single-phase cobalt and manganese oxide spinel Mn3-xCoO4 ceramics J. Euro. Ceram. Soc. 34 317–26
[21] Savir S M, Tadir M, Jagliriz V, Vojicsalvijevik Z and Brankovir G 2014 Structural, electrical and magnetic properties of nickel manganite obtained by a complex polymerization method Ceram. Int. 40A 15515–21
[22] Wang W, Liu X, Gao F and Tian C 2007 Synthesis of nanocrystalline Ni1-Co0.2Mn1.8O4 powders for NTC thermistor by a gel auto-combustion process Ceram. Int. 33 459–62
[23] Duran P, Taitaj I, Rubio F, Moure C and Pera O 2005 Synthesis and sintering behavior of spinel-type CoNiMn2-xO4 (0.2 < x < 1.2) prepared by the ethylene glycol-metal nitrate polymerized complex process Ceram. Int. 31 599–610
[24] Yue Z X, Shan J H, Qi X W, Wang X H and Li L T 2003 Synthesis of nanocrystalline manganite powder via a gel auto-combustion process for NTC thermistor applications Materials Science and Engineering B 99 217–20
[25] Velinov N, Petrova T, Tsonecheva T, Genova I, Koleva K, Kovacheva D and Mitov I 2016 Auto-combustion synthesis, M ossbauer study and catalytic properties of copper–manganese ferrites Hyperfine Interact. 24 237–48
[26] Kanagas S, Ariz S B A, Hashim M, Ismail I, Tamselvels S, Altheen N B R M, Swamy M K and Rao B P C 2016 Synthesis, characterization and in vitro evaluation of manganese ferrite (MnFe2O4) nanoparticles for their biocompatibility with murine breast cancer cells (4T1) Molecules 21 312–37
[27] Cannas C, Musinu A, Piccaluga G, Fioriani D, Peddis D, Rasmussen H K and Morup S 2006 Magnetic properties of cobalt ferrite–silica nanocomposites prepared by a sol-gel auto-combustion synthesis technique The J. Chem. Phy. 125 164714–26