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The effects of pH value on the characterization of CoMnNiO NTC thermistor nanopowders

Jian-wen Zhuang [a,*], Ai-min Chang [a], Zheng Jia [a], Shun-chang Zhuang [a], Dian-zeng Jia [b]

[a] Xinjiang Technical Institute of Physics and Chemistry, CAS, Urumqi 830011, China
[b] Department of Chemistry, Xinjiang University, 830046, China

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Abstract

The effects of pH value on the properties of CoMnNiO NTC thermistor nanopowders during coprecipitation process are studied. It showed that the particle size and the agglomeration increased with the increase of pH value. At pH 7 and 9, the wave-like grain structure has been observed in the microstructure of sintered samples by SEM, the reason for this phenomenon is that the tetragonal phase separated out of the cubic phase. At pH 8, the powders showed excellent sinterability with homogeneous and dense microstructure in the sintered samples. So the optimal pH value for the preparation of NTC thermistor nanopowders is 8.

Keywords: pH value; Coprecipitation; NTC thermistor; Nanopowders

1. Introduction

NTC thermistor materials are high performance ceramic materials applied to the manufacture of temperature sensors, its microstructure, and performance are greatly dependent on the preparation process, especially the preparation process of powders. The properties of powders has great affection to the materials' microstructure and also the densification of sintered samples, and then the characteristics of sensor elements, such as mechanics and electrical properties [1,2].

The preparation process has essential relation with the microstructure and properties of materials [3–5]. Especially the pH value has a significant influence on the characterization of nanopowders, there have been some report on other materials [6–8], but no research has been reported on the influence of pH value on NTC thermistor nanopowders. So in this paper, the effects of pH value on the properties of CoMnNiO NTC thermistor nanopowders have been studied.

2. Experimental procedures

The solution of 1.0 M concentration are prepared according to stoichiometric ratio using cobalt nitrate, manganese nitrate, and nickel nitrate (1:1:1, molar ratio) as precursors. By adding $NH_3{\cdot}H_2O$ and nitric acid to adjust the pH value. Under the conditions of pH 7, 7.5, 8, 8.5, and 9, reaction temperature was 45–50 °C, the mixing ion solutions were added slowly to the precipitation solvent with stirring. The sintered NTC ceramics are chipped into the small chips by the size of 0.3 mm × 0.5 mm × 0.5 mm for the measurement of electrical properties.

The chemical reagents were weighed by Sartorius balance, the pH value were measured by PHS-2C acidity meter (precision ≤ 0.01), the microstructure of the sintered sample are analyzed by AMRAY-1000B scanning electronic microscope, and the crystal structure are analyzed by Philips PH-1700 X-ray diffraction meter, by HW-1 (25 ± 0.005 °C), R3-II (50 ± 0.01 °C) thermoregulated oil bath and ORION-3530A data collecting system to measure the resistance versus temperature characteristics of the samples.

* Corresponding author. Tel.:+886-512-57218238; fax: +886-512-57218204.
E-mail address: zhuangjianwen@sohu.com (J.-w. Zhuang).

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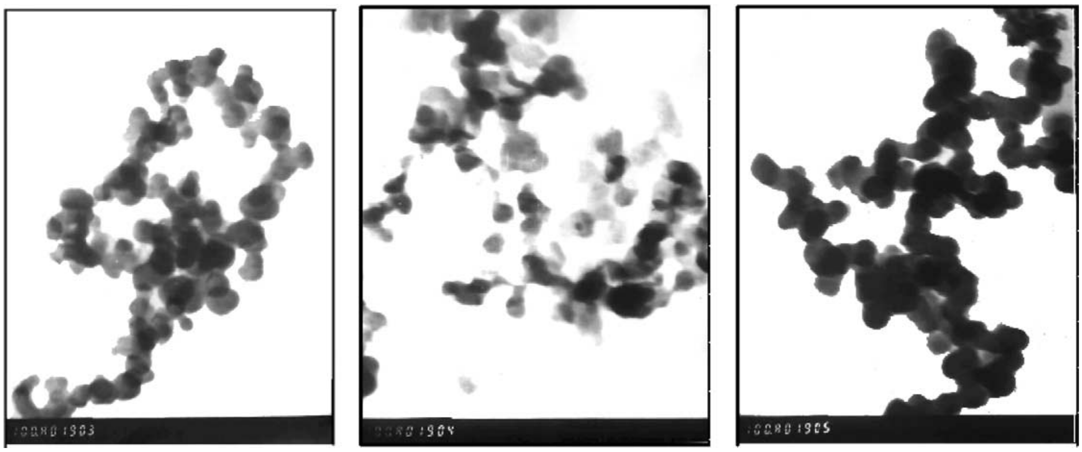

Fig. 1. The TEM photos of powders at pH 7, 8, and 9.

3. Results and discussions

3.1. Effect of pH value to the particle size of powders

By TEM observation shown in Fig. 1, the average grain size of powders versus pH 7, 8, and 9 is 27, 32, and 41 nm, respectively. The result shows that the grains grew coarser with the increase of pH value, and the agglomeration increased too.

According to the theory of colloid chemistry, when the colloid particle is charged, its electrical properties will change with the change of pH value. The effect of pH value can be explained by the diversity of sol and swelling effect. With the decrease of pH value, surface of colloid will bring positive charge, the effect of potential barrier will be enhanced. So the stability of the colloid will be improved with better diversity. After the colloid particle is charged, the osmotic pressure will increase, so will do the Donnan effect, and the extent of swelling increase and the particle size decrease.

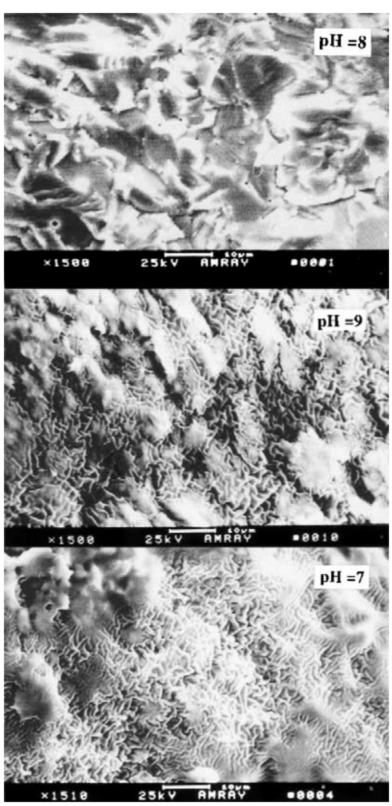

Fig. 2. SEM photos of sintered samples vs. pH 7, 8, and 9.

3.2. Effect of pH value to the microstructure and crystal structure of the samples

The sample prepared from the powders at different pH values were sintered at 1200 °C for 2 h. The SEM observa-

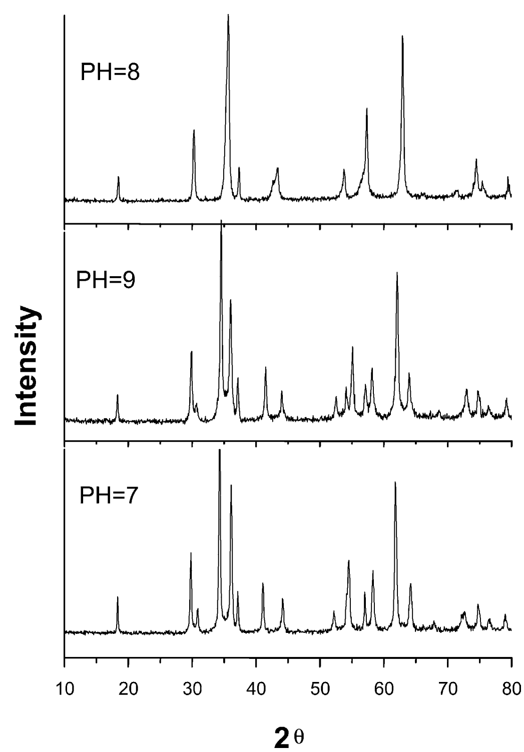

Fig. 3. XRD patterns of sintered samples vs. pH 7, 8, and 9.

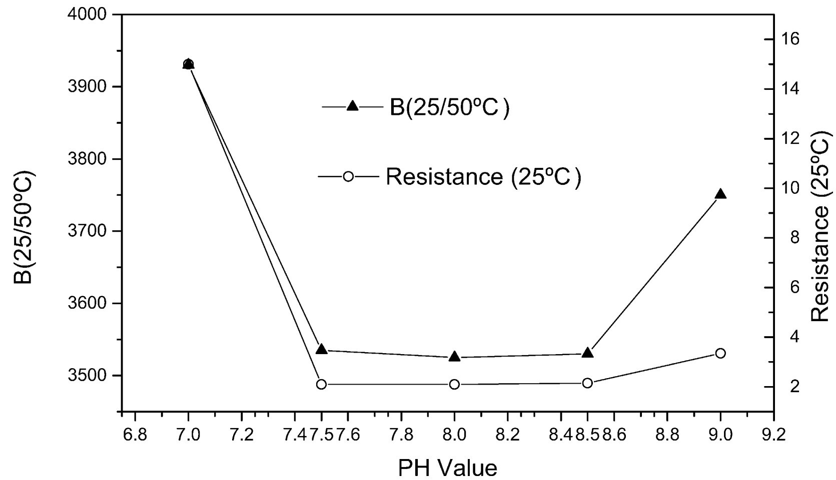

Fig. 4. The *B* constant and resistance of sintered sample vs. pH value.

tion of the sintered samples are shown in Fig. 2, it showed that when pH 7 and 9, there exist wave-like shape crystals in the sintered samples. The XRD patterns of the sintered samples are shown in Fig. 3, the results show that the main phase from different pH values are mainly cubic phase, with a small part of tetragonal phase. When the tetragonal phase are segregated from cubic phase solid solution (shown in Fig. 3), the wave-like crystal shape will appear in the SEM observation. When pH = 8, the microstructure is very homogeneous and dense with very small pores (shown in Fig. 2), and no wave-like crystal shape appeared. The powders derived from pH 8 also showed excellent sinterability.

3.3. *Effect of pH value to the electrical properties of NTC thermistors*

The resistance of a thermistor material is expressed by $R = R_0 \exp(B/T)$ where R_0 is the resistance at infinite temperature, T the sample temperature in Kelvin, and $B = Q/k$ is the energetic constant of the material in Kelvin, where Q is the site activation energy, k the Boltzmann constant.

The B constant and resistance of the samples at room temperature with pH value are shown in Fig. 4. With the increase of spinel phase (shown in Fig. 3), the conductivity of the sintered samples increased, while the materials constant, B constant decreased. At pH 8, the sample contained the highest content of spinel phase, and thus deserved the smallest B constant and smallest resistance of samples at room temperature ($B = 3515$, $R_{25} = 1.95\,\mathrm{k}\Omega$, shown in Fig. 4). At pH 7 and 9, the conductivity of the sintered samples decrease with the increase of tetragonal phase. At pH 7, the XRD analysis showed highest amount of tetragonal phase, and induced the largest B constant and also the largest resistance of sample at room temperature. ($B = 3930$, $R_{25} = 15\,\mathrm{k}\Omega$, shown in Fig. 4).

The result shows that when pH value is larger or smaller, the ratio of Mn^{3+} to Mn^{4+} will be indirectly affected by stoichiometric ratio deviation induced by the complexation of Co^{2+} and Ni^{2+}, thus the conductivity of the samples will be affected, and also the materials constant, B constant.

4. Conclusions

1. At the range of pH 7–9, the particle size and the agglomeration of the CoMnNiO NTC thermistor powders prepared by coprecipitation method increased with the increase of pH value.
2. At pH 7 and 9, the wave-like grain structure observed in the sintered samples are induced by the tetragonal phase separated out of the cubic phase.
3. At pH 8, the CoMnNiO thermistor nanopowders showed excellent sinterability with homogeneous and dense microstructure in the sintered samples.

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