Proceedings

The 3rd Conference on Nanostructures

NS2010

March 10-12, 2010
Kish Island, I. R. Iran
Synthesis and structure of spinel-type oxides in Mn-Co and Ni ternary system nanopowders at low temperature

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Abstract: NiCo,Mn$_{2-x}$O$_4$ (x= 0, 0.4, 0.8, 1.2, 1.6) thermistors nanopowders have been synthesized by the auto-combustion method at low temperatures. The size and morphology of the calcinated powders have been investigated using XRD and TEM techniques. The average particle size was estimated to be about 65 nm in diameters with the cubic phase. The formation of spinel structure of powders has been studied by Fourier transform infrared (FTIR) spectroscopy.

Keywords: NTC thermistors; Nanopowder; Spinel structure.

Introduction

Spinel materials based on transition metals such as Ni, Co and Mn are widely used as negative temperature coefficient (NTC) thermistors [1], which are employed in manufacturing temperature measurement devices as sensors. NTC thermistors have spinel structure with general formula of AB$_2$O$_4$, where A and B are related to tetrahedral and octahedral lattice sites, respectively. The typical spinel structure is shown in Fig. 1.

High quality of the powders is a very important factor to the sensitivity of the thermistors. There are several methods for synthesis of powders such as the traditional solid solution [2], ethylene glycol – metal nitrate polymerized complex process [3], co-precipitation with different precipitators [4] and gel auto – combustion process of nitrate–citrate gels. The results show that the sol-gel combined with the combustion process leads to obtain homogeneous, fine and highly reactive powders in a shorter time and at lower temperatures than the traditional process.

In this work, we synthesized the NiCo,Mn$_{2-x}$O$_4$ nanopowders via the gel auto – combustion process. The average nanopowder size was determined via x-ray diffraction (XRD) and TEM image. The Fourier transform infrared (FTIR) was employed to confirmed the formation of spinel structure.

Experimental

The molar ratio of each composition was chosen based on the formula of NiCo,Mn$_{2-x}$O$_4$ (x=0.0, 0.4, 0.8, 1.2, 1.6). The materials used in this experiment were nickel nitrate [Ni(NO$_3$)$_2$.6H$_2$O], manganese nitrate [Mn(NO$_3$)$_2$.4H$_2$O], cobalt nitrate [Co(NO$_3$)$_2$.6H$_2$O], (Merck, Germany). By aqueous solutions of each single cation were prepared dissolving each of the raw materials in distilled water. The sol was prepared by mixing the solutions of each cation and then adding the aqueous solution of citric acid to the sol under continuous stirring at 40-50°C and maintaining the pH of 7 by using ammonium hydroxide. The sol was heated at 70-80°C to evaporate all the water and to obtain the gel. The nanopowder was produced by addition of nitric acid to the gel, in order to being ignited. The resultant powder was calcinated at temperatures of 400°C and 800°C.

The flow chart for synthesis of NTC nanopowders is shown in Fig. 2.
size is given in Table 1. Also we determined particle size by using transmission electron microscopy (TEM LEO 912B-Germany). The typical TEM image of the particles size for the composition of NiCo$_{1.2}$Mn$_{0.8}$O$_4$ calcinated at 800°C and the histogram of particle size are shown in Fig. 4. The geometric figure of particles is polygon. The average particle size is obtained from TEM image is about 65nm. Since the size of the particles obtained from Scherrer equation is bigger than that of observed in the TEM image, therefore we can deduce that the Scherrer equation gives an approximate value for the particle size.

FTIR Spectrum

FTIR spectroscopy was used (Shimadzu-4300) to monitor the organic groups and study the spinel structure. Fig. 5 shows the FTIR spectra of the NTC powders in the range of 400-4000 cm$^{-1}$ calculated at temperature of 800°C for different compounds. In this frequency interval, two broad bands are observed for each spectrum from 400-700 cm$^{-1}$ which are related to metal-oxygen bonds (M-O), where M=Ni, Co, Mn. The results are in good agreement with the data published previously [3]. There are two absorption bands at wavenumbers of about 1480 and 1590 cm$^{-1}$, due to C=O stretching variations between metal cations and citric acid. The other three peaks are observed at about 2360, 2900 and 3400 cm$^{-1}$ that belong to variations of CO$_2$, C-H and O-H respectively [7].
Table 1. NTC nanopowder characteristics prepared by gel auto-combustion, calcinated at 800°C.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Temperature (°C)</th>
<th>Structure</th>
<th>Lattice constant (nm)</th>
<th>Space group</th>
<th>Particle size measuring method</th>
<th>2θ (deg)</th>
<th>Average particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCo$_{1.2}$Mn$_0.8$O$_4$</td>
<td>800</td>
<td>Cubic</td>
<td>0.8232</td>
<td>Fd-3m (No. 227)</td>
<td>TEM image Scherrer equation</td>
<td>36.12</td>
<td>65</td>
</tr>
</tbody>
</table>

Fig. 5. FTIR spectra of the NTC nanopowders for different compounds calcinated at 800°C

Conclusions

Mn, Co and Ni ternary oxides nanopowders having spinel structure, which can be used as NTC thermistors, were prepared by gel auto-combustion method. XRD results show that spinel structure is formed at 800°C. This is also confirmed by FTIR spectra. Average particle size which was determined using both TEM image and Scherrer equation is about 50-80 nm. Spinel bands start forming at 400°C, and by rising temperature to 800°C, the percent of spinel bands formation increase and seems to complete at 800°C.

References


