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Fabrication, Characterization and Comparison of Nanocrystalline NiMn₂O₄ and NiZn_{0.2}Mn_{1.8}O₄ NTCR Ceramic Thermistor Powders

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ABSTRACT

Here, NiMn₂O₄ and NiZn_{0.2}Mn_{1.8}O₄ nanocrystalline ceramic powders are fabricated, characterized, and compared for thermistor applications. Solution route was used to synthesize the materials. The NiMn₂O₄ is a spinel single crystal material with the average crystallite size 26.82 nm and a particle size less than 1 μm and has uniform morphology. The EDS results confirmed the composition of NiMn₂O₄ that consisted of Ni, Mn, and O₂ only. The average crystallite size of NiZn_{0.2}Mn_{1.8}O₄ is 37.48 nm and the particle size is less than 0.5 μm. There has been observed some agglomeration formation due to high calcination temperature. The β-value of NiMn₂O₄ is larger than NiZn_{0.2}Mn_{1.8}O₄, hence thermistors constructed from NiMn₂O₄ are more stable and applicable as NTCR thermistor powder.

1. Introduction

Nowadays miniaturized materials for temperature measurement application attracts the scientists' attention because of (1) accurate and precise temperature measurement is required in medical and other areas. (2) as the size of the materials decreases, the size of the resulting device also decreases. (3) the temperature sensors are being built on a flexible substrate in the form thin film [1–4]. In miniaturized materials as the size of the materials decreases, the surface area to volume ratio of the materials increases. Hence, the physical and chemical properties of the materials will change. One important chemical property is the rate of interaction during a chemical reaction. Generally as the size of reactants decreases, the rate of chemical reaction increases. This phenomena also holds for physical properties. Another very important activity that attracts scientist attention is introducing impurities in semiconductor materials.

The process of introducing impurities in semiconductors is called doping. Generally, doping enhance the property of the materials by increasing the number of charge carriers and hence then increases the conductivity of the materials [5–7].

The most important temperature measuring devices are derived from thermistor materials. Some of the thermistor materials are transitional and non-transitional metal titanates and manganate. Typically NiMn₂O₄ and its derivatives are a low-temperature miniaturizable negative temperature coefficient resistance (NTCR) thermistor material [1,8,9].

NiMn₂O₄ ceramic thermistor material can be synthesized in the miniaturized form using different fabrication techniques. Some of the methods are solid state reaction followed by successive heat treatments and solution method [10–16]. Solid state reaction technique is a very simple and economical technique but it takes a long time, results in impure materials and it consumes huge energy. Solution route gives the pure product. Thermistor materials have so many applications in science, engineering and technology. Nowadays temperature sensors are embedded with almost every electrical, electronic, mechanical and electromechanical devices and systems as a life of those devices or systems. Some of the applications of thermistors include time delay and device protection, voltage regulation, speech volume limitation, testing equipment for ultrahigh frequency power, and detection of very small radiant power [17].

Thermistors may be classified as low temperature and high-temperature thermistors based on the capacity of measuring temperature

range. They can also be classified as a negative temperature coefficient resistance (NTCR) thermistors and positive temperature coefficients resistance (PTCR) thermistors depending on resistance temperature characteristics [18,19]. In NTCR thermistors as the temperature increases the resistance decreases but in the case of PTCR thermistors the opposite of this phenomenon holds true but thermistor are nonlinear devices.

The variation of conductivity in thermistors under the application of temperature is due to the existence of different oxidation states of one or more constituent elements in the compound. These different oxidation states enable the transfer of electric charge in the material.

In material science and technology, if materials are made in the form of composites of more than two elements, they will experience a different property that may, in turn, enhance or inhibit their role in specific applications. Hence in this work, we are going to present the fabrication, characterization, and comparison of NiMn₂O₄ and NiZn_{0.2}Mn_{1.8}O₄ miniaturized thermistor powders for NTCR thermistor applications. We have used the transitional metal acetates as a precursor material, distilled water as a solvent and oxalic acid as a catalyst. The miniaturized NiMn₂O₄ ceramic powder is prepared using this method for the first time and using moderately low temperature but NiZn_{0.2}Mn_{1.8}O₄ is the first of its kind miniaturized derivative of NiMn₂O₄. The structural, morphological and compositional characteristics of the materials are studied. The temperature versus resistance electrical characteristics are also studied. Finally, their β-coefficients of the two materials are calculated and compared.

2. Experimental Methods

2.1 Experiment for NiMn₂O₄ Ceramic Powder Fabrication

Nickel acetate tetrahydrate, manganese acetate tetrahydrate, distilled water, and oxalic acid are the chemicals used to fabricate NiMn₂O₄ nanocrystalline ceramic powder. Magnetic stirrer, Muffle furnace, FESEM/EDS, XRD, alumina crucibles and mortar, and pestle are equipment used in this experiment. The procedures of the experiment are given below in stepwise from step 1 to step 7 and some ideas are taken from this work [20].

Step 1: mixed 2 g of nickel acetate tetrahydrate with 3.94 g of manganese acetate tetrahydrate.

Step 2: dissolved the above mixture in 40 mL distilled water and kept on a hot plate with a magnetic stirrer at a temperature of 75 °C for an hour.

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Step 3: dissolved 0.38 g of oxalic acid in 6 mL of distilled water at room temperature in a separate beaker.

Step 4: mixed the oxalic acid solution drop by drop to the solution prepared in step 2 under vigorous stirring and keep the resulting mixture on a hot plate at the same temperature for 30-60 minutes.

Step 5: dried the resulting thick solution at 100 °C in a muffle furnace for some time.

Step 6: milled the resulting dried powder using mortar and pestle.

Step 7: calcined the resulting powder at 1000 °C for 3-4 hours.

2.2 Experiment for $\text{NiZn}_{0.2}\text{Mn}_{1.8}\text{O}_4$

In addition to the above-mentioned chemicals in preparation of NiMn_2O_4 and equipment used, zinc acetate tetrahydrate also used here. The detailed steps are given below from step 1 to step 7:

Step 1: mixed 1 g of nickel acetate tetrahydrate, 0.98 g of manganese acetate tetrahydrate and 0.14 g of zinc acetate tetrahydrate in a single beaker.

Step 2: dissolved the above mixture in 20 mL distilled water and keep on a hot plate with a magnetic stirrer at a temperature of 75 °C for an hour.

Step 3: dissolved 0.36 g of oxalic acid in 6 mL of distilled water at room temperature in a separate beaker.

Step 4: mixed the oxalic acid solution drop by drop to the solution prepared in step 2 under vigorous stirring and keep the resulting mixture on a hot plate at the same temperature for 30-60 minutes.

Step 5: dried the resulting thick solution at 100 °C in a muffle furnace.

Step 6: milled the resulting dried powder using mortar and pestle.

Step 7: calcined the resulting powder at 1000 °C for 3-4 hours.

2.3 Thermistor Samples Fabrication

In addition to the above thermistor nanocrystalline powders, we have used thermally conductor but electrical insulator 1 mm internal diameter and 1.5 mm external diameter cylindrical tube for pressing and keeping the thermistor powder, and folded and rolled aluminium foils pieces and wire for the electrodes. The detail processes to fabricate the thermistor samples are given in the following steps and also in Fig. 1.

- Take two 1 cm lengths and 1 mm inner diameter electrical insulator and thermally conductor cylindrical tubes
- Take aluminium electrodes and insert tightly to the cylindrical tubes in one side only for both tubes prepared in step i.
- Press tightly folded and rolled aluminium foils to the open sides of the cylindrical tubes prepared in step ii.
- Press 1.2 g of NiMn_2O_4 and $\text{NiZn}_{0.2}\text{Mn}_{1.8}\text{O}_4$ each into the respected cylindrical tubes in step iii.
- Insert rolled and folded aluminium foils tightly in the opened end of the tube in step vi.
- Insert tightly aluminium electrode into the cylindrical tubes in step v.

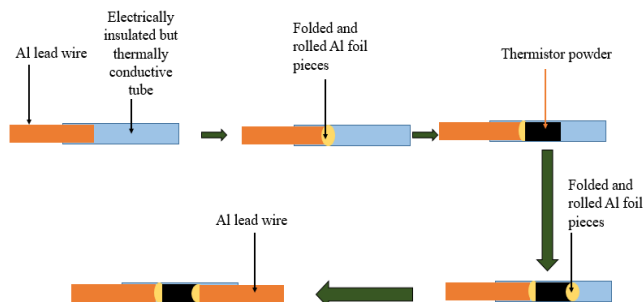


Fig. 1 overall detailed steps for the thermistor fabrication process

3. Results and Discussion

3.1 NiMn_2O_4 Ceramic Powder

3.1.1 FESEM/EDS Characterization

The analysis of the microstructure was carried out with FESEM which was bought from ZEISS Company. This microscopy device delivers high-resolution surface information and superior materials contrast in nano-range. The EDS which was used to find the material composition is integrated with FESEM. The FESEM results confirmed the formation of well-structured morphology as well as uniform structure as shown in Fig.

2. As anyone can observe from the Fig. 2 the particles are tetrahedral in morphology and are evenly sized. The particles are agglomerated at the surface. The agglomerates were probably due to the high calcination temperature, humidity and the magnetic property of the resulting materials. This device also showed that the size of the particle size of the resulting powder is lower than 1 μm . The EDS pattern showed that the resulting NiMn_2O_4 ceramic powder is really composed of Ni, Mn, and O₂ only in appropriate proportion as shown in Fig. 3.

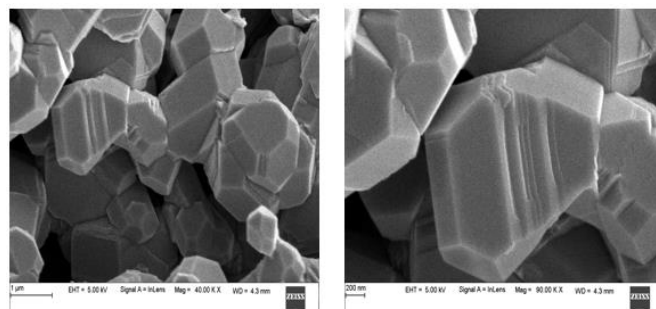


Fig. 2 FESEM micrograph of NiMn_2O_4 ceramic powder

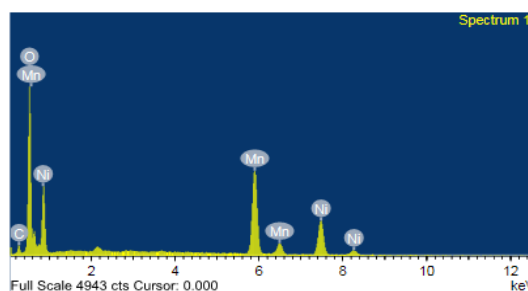


Fig. 3 EDS result of NiMn_2O_4 ceramic powder

3.1.2 XRD Characterization

Ka Diagrams were recorded in the step-scanning mode, with a 0.02° (2 θ) step scan and 2s per step counting time in the range 10° \leq 2 θ \leq 80°. There are 9 peaks observed in this measurement of which the maximum peak (2957.91 cps) is observed at 35.29° with 0.2492° FWHM whereas the smallest peak (196.89 cps) is observed at 18.06116° with 0.2106° FWHM as shown in Fig. 4 and Table 1. By using Debye-Scherrer equation [21], $D = K\lambda/\beta\cos\theta$, where β is the full-width half maximum in radian, θ is the scattering angle (Bragg's angle), λ is the X-ray wavelength of radiation with 1.54 Å, K is the correction factor and D is the crystallite size of material in nm [22], the average crystallite size was determined and found to be around 26.82 nm.

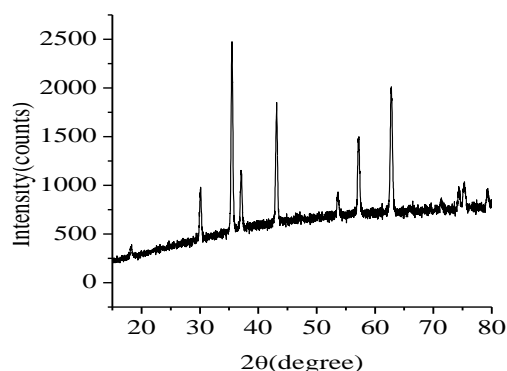


Fig. 4 XRD patterns of NiMn_2O_4 ceramic powder

Table 1 XRD peaks for NiMn_2O_4 ceramic powder

S. No.	2-theta (deg)	Height (cps)	FWHM (deg)
1	18.0616	196.89	0.2106
2	29.9047	785.49	0.2451
3	35.2922	2957.91	0.2492
4	36.9535	570.7	0.2559
5	42.9924	1260.96	0.2579
6	56.9338	1167.83	0.2646
7	62.5886	1635.18	0.2724
8	74.1891	240.21	0.34
9	75.1515	268.72	0.2723

3.2 NiZn_{0.2}Mn_{1.8}O₄ Ceramic Powder

3.2.1 FESEM/EDS Characterization Results

The FESEM results confirmed the formation of well-structured morphology as shown in Fig. 5. It can be observed that the particles are tetrahedral in morphology and are evenly sized. The particles are agglomerated at the surface. The agglomerates were purely due to the high calcination temperature, humidity and the magnetic properties of the resulting materials. This device also showed that the size of the particles in resulting powder is lower than 0.5 μm which is smaller than that of NiMn₂O₄. The EDS confirmed that the resulting NiZn_{0.2}Mn_{1.8}O₄ ceramic powder composed of Ni, Mn, Zn, and O₂ only in appropriate proportion as shown in Fig. 6.

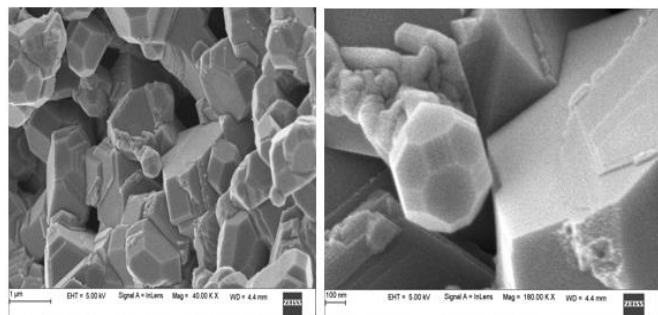


Fig. 5 FESEM micrograph for NiZn_{0.2}Mn_{1.8}O₄ ceramic powder

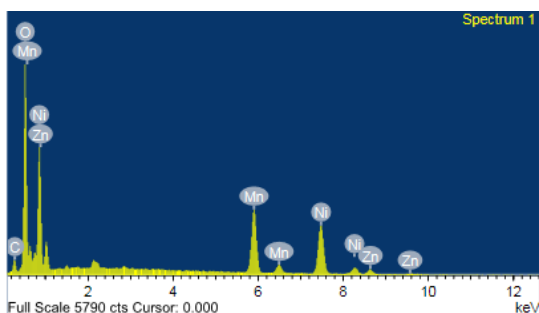


Fig. 6 EDS results of NiZn_{0.2}Mn_{1.8}O₄ ceramic powder

3.2.2 XRD Characterization Results

There are 9 peaks observed in this measurement of which the maximum peak (3477.4 cps) is observed at 35.29° with 0.2492° FWHM whereas the smallest peak (212.57) is observed at 18.06116° with 0.2106° FWHM.

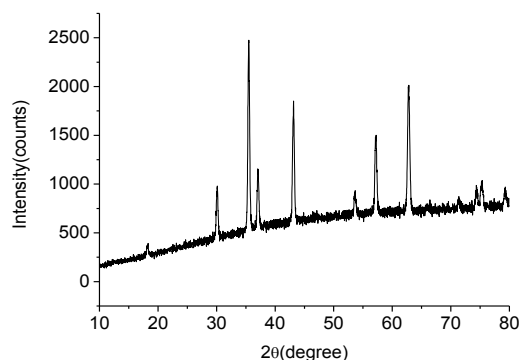


Fig. 7 XRD pattern for NiZn_{0.2}Mn_{1.8}O₄ ceramic powder

Table 2 XRD peaks for NiZn_{0.2}Mn_{1.8}O₄ ceramic powder

S.No.	2-theta (deg)	Height (cps)	FWHM (deg)
1	19.0616	197.89	0.3106
2	30.0753	898.98	0.3249
3	35.4579	3477.40	0.3137
4	37.0412	1070.01	0.3168
5	43.0967	2104.59	0.3311
6	53.642	446.93	0.2832
7	57.1062	1560.77	0.3191
8	62.7336	2416.97	0.3743
9	74.5286	212.57	1.4184

The numbers of peaks (Table 2) are equal for the two samples but the maximum peaks of the two samples are different and occurred almost at

the same angle. The smallest peaks are also different and observed at different angles. By using Debye-Scherrer equation the average crystallite size of the synthesized sample was determined and found to be about 37.48 nm.

The differences in XRD patterns are due to the existence of the Zn ions. These differences also confirmed that the single crystal structure of the two samples are also different.

3.2.3 Temperature vs. Resistance Characterization

Temperature versus electrical resistance characterization of the samples was done using LM35 IC temperature sensor interfaced with microcontroller and FTO coated glass electric heater. Electrical resistance versus temperature measurement was carried out in the temperature range 30 °C to 42 °C in 0.001 Ω resolution of resistance. From Fig. 8a, the value of the thermistor coefficient (β) for NiMn₂O₄ becomes 6320 K which is larger but 1039 K for NiZn_{0.2}Mn_{1.8}O₄ which is much smaller which can be calculated using the data obtained from Fig. 8b. The lower the β-coefficient means the lower the sensitivity of the thermistor with respect to the temperature. Therefore the doping of Zn in NiMn₂O₄ decreases the sensitivity of the resulting thermistor.

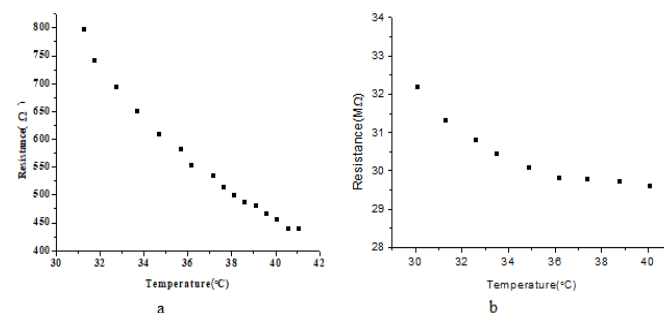


Fig. 8 Temperature versus resistance graph for (a. NiMn₂O₄ and b. NiZn_{0.2}Mn_{1.8}O₄)

4. Conclusion

In this work, NiMn₂O₄ and NiZn_{0.2}Mn_{1.8}O₄ ceramic NTCR thermistor powders have been synthesized, characterized, and compared. The XRD pattern and FESEM micrograph confirmed that the NiMn₂O₄ is a spinel single crystal material with the average particle size is less than 1 μm and has uniform morphology. The XRD pattern results with Debye Scherrer equation gave the average crystallite size which was calculated and found to be about 26.82 nm. The EDS results also confirmed the composition of NiMn₂O₄ which consisted of Ni, Mn, and O₂ only. The XRD pattern and FESEM micrograph of NiZn_{0.2}Mn_{1.8}O₄ also confirmed the existence of spinel single crystal structure with uniform morphology. EDS also confirmed the composition of NiZn_{0.2}Mn_{1.8}O₄ are Ni, Zn, Mn, and O₂. The average particle size of NiZn_{0.2}Mn_{1.8}O₄ is less than 0.5 μm and the average crystallite size was 37.48 nm. The β-value of NiMn₂O₄ (6320K) is larger than NiZn_{0.2}Mn_{1.8}O₄ (1039) and also its crystallite size is smaller, hence thermistors fabricated from NiMn₂O₄ are more stable and applicable as NTCR thermistor. In the future, further characterization of these powders and formation of the thermometer from these powders for different applications in different forms will be performed.

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