Preparation of chip type negative temperature coefficient thermistor

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Abstract. A thermistor is a class of resistor whose resistance varies with temperature. The two types of thermistors are Negative temperature coefficient (NTC) thermistor and Positive temperature coefficient (PTC) thermistor. NTC thermistors have a negative electrical resistance versus temperature (R/T) relationship. These thermistors are extremely versatile and accurate. This makes them best for a wide variety of applications that measure temperature. They find application in firebrand photographic processing, meteorological, geological, and oceanographic research equipment, as well as in consumer and household appliances. This paper presents the development of a chip-type Mn–Ni based negative temperature coefficient thermistor with varying CuO (Dopant) concentration. The changes in electrical properties are also reported. The expected results indicate an increase in resistivity, material constant and temperature coefficient of resistance \( \alpha \) with an increase in CuO concentration for all the compositions.

1. Introduction

The temperature of a process is an important measure to know as it indicates whether or not the process is in control. Thus, modern industrial applications demand a highly sensitive temperature sensor. Commonly used temperature sensors are thermocouples, resistance temperature detector, thermistors etc. A thermistor is a solid-state temperature sensing device whose electrical properties change at different ambient temperatures. The device is fabricated as a two-terminal solid-state transducer, where its resistivity is a direct function of temperature. They are made from various metal oxides or semiconductors (for example, arsenic diffusion into silicon), with metalized connecting leads onto a ceramic base (disc or bead). These thermally-sensitive materials are known to exhibit a large, precise and predictable decrease or increase in their resistivity over the operating temperature range. Based on temperature variation, they are classified into positive temperature coefficient (PTC) and the negative temperature coefficient (NTC) thermistor. NTC thermistors are resistors in which the resistance decreases with increasing temperature. They find use as resistive temperature sensors and current-limiting devices. NTC sensors find application in a range from \(-55^\circ\text{C}\) to \(200^\circ\text{C}\). The non-linear relationship between resistance and temperature exhibited by NTC resistors posed a significant challenge when using analogue circuits to measure temperature accurately. But the rapid development of digital circuits solved that problem and enabled the computation of precise values by interpolating lookup tables or by solving equations [1].

Mn-Ni based semiconducting materials commonly find use as negative temperature coefficient thermistor materials. Expanding applications and the rapid influx of sophisticated miniaturised devices
make high demand for good performance NTC thermistor devices [2]. The properties used to characterize NTC thermistor materials are room temperature resistivity and sensitivity index (thermistor constant) $\beta$

$$\beta = \frac{\ln \left( \frac{R_1}{R_2} \right)}{\frac{1}{T_1} - \frac{1}{T_2}}$$

$R_1$ – Resistance at temperature $T_1$

$R_2$ – Resistance at temperature $T_2$

Several studies have reported on the modification of nickel manganese-based NTC thermistor materials. Modification of thermistor characteristics is generally done by doping suitable ions or changing the process conditions like sintering temperature, rate of cooling, duration of sintering etc. Modifying and properly controlling these factors allow tuning the resistivity of the materials and also their material constant. [2]

This present study primarily focuses on the fabrication of chip-type NTC thermistor of varying CuO concentration and depicts the effect of CuO concentration on the electrical and microstructural characteristics.

2. Experimental Procedure

2.1. Materials
The raw materials used for the present study include MnCO$_3$, NiO, CuO, CoO and Li$_2$CO$_3$. A total of 8 samples were prepared from these raw materials by varying the CuO concentration and keeping other raw materials concentration constant. Table 1 shows the raw materials and the composition of each sample.

| Sample | MnCO$_3$ | NiO | CuO | CoO | Li$_2$CO$_3$ |
|--------|----------|-----|-----|-----|-------------|
| Sample 1 | 89 | 356 | 11 | 44 | 1.8 | 7.2 | 0.1 | 0.4 | 0.2 | 0.8 |
| Sample 2 | 89 | 356 | 11 | 44 | 1.5 | 6  | 0.1 | 0.4 | 0.2 | 0.8 |
| Sample 3 | 89 | 356 | 11 | 44 | 1.6 | 6.4 | 0.1 | 0.4 | 0.2 | 0.8 |
| Sample 4 | 89 | 356 | 11 | 44 | 1.7 | 6.8 | 0.1 | 0.4 | 0.2 | 0.8 |
| Sample 5 | 89 | 356 | 11 | 44 | 2.1 | 8.4 | 0.1 | 0.4 | 0.2 | 0.8 |
| Sample 6 | 89 | 356 | 11 | 44 | 2.2 | 8.8 | 0.1 | 0.4 | 0.2 | 0.8 |
| Sample 7 | 89 | 356 | 11 | 44 | 2.3 | 9.2 | 0.1 | 0.4 | 0.2 | 0.8 |
| Sample 8 | 89 | 356 | 11 | 44 | 2.4 | 9.6 | 0.1 | 0.4 | 0.2 | 0.8 |

2.2. Methodology
The flowchart for the manufacture of chip-type NTC thermistor is below:
The raw materials are transferred to a ball mixing jar with an equal amount of deionised water and twice the amount of zirconium balls. The ball mixer is operated for 30 minutes to form a homogenous mixture. Discharge from the ball mill is washed thoroughly and dried at a temperature of 90°C for 12 hours. The dried sample is ground to a fine powder using a mixer grinder, and then it is transferred to a prefiring equipment with ceramic temperature measuring ring. It is prefired at a temperature of 880°C for 2 hours 30 minutes. During prefiring, the colour of samples changed to black ash due to the conversion of manganese carbonate into manganese oxide. The prefired sample with an equal amount of deionised water
and twice the amount of zirconium balls are milled using a ball milling jar for 1 hour at 400 rpm. The mixture from the milling operation is washed and filtered using vacuum filtration and then dried for 12 hours at 90°C. The dried sample is then powdered and mixed with 2% PVA solution. It is again powdered and sieved using 150 mesh to form a uniform mixture.

The granulated powder is pressed into a cylindrical shape and sintered at high temperature (between 1000°C and 1400°C) for 24 hours to produce polycrystalline thermistor body. The cylinder is cut into wafers of small thickness and sintered at high temperature (between 1000°C and 1400°C) for 24 hours. Wafers are lapped using slurry to smoothen its surface, silver-plated, dried and silver fired. The silver-plated wafers are kept in the ageing chamber for one week and cut into chips of the desired length and separated using ultraviolet light. The separated chips are again placed in the ageing chamber for one week and tested and sorted out based on tolerance. A multimeter measures the thermistor resistance. The β value is estimated from the Steinhart and Harts equation.

\[
\beta = \ln\left(\frac{R_1}{R_2}\right)\frac{1}{T_1 - T_2}
\]

(2)

3. Result and discussion

Manganese Nickel based chip type negative temperature coefficient (NTC) thermistor was prepared using the above method.

3.1. Electrical properties

The typical electrical characteristics of NTC thermistors are resistance, resistance versus temperature (R-T) behavior, material constant or sensitivity index (β value) and the temperature coefficient of electrical resistance is measured using a multimeter. For an NTC thermistor as the temperature increases the resistance decreases. Figure 2 shows the variation of resistance with temperature for an NTC thermistor.

![Figure 2. Temperature versus resistance graph](image)

The manner in which resistance of a thermistor decreases is related to a constant known as β value. β value indicates the nature of the curve representing the relationship between resistance and temperature of an NTC thermistor. Calculating the β value is a vital step in the component selection process as it gives the characteristic at a given temperature versus the resistance for a specific application. β is measured in degree Kelvin (K).

The Steinhart and Hart equation calculates the material constant β value.

\[
\beta = \ln\left(\frac{R_1}{R_2}\right)\frac{1}{T_1 - T_2}
\]

(3)
The temperature coefficient of a thermistor indicates the rate of change of thermistor resistance per 1°C and is commonly expressed in %/°C. The following expression calculates the temperature coefficient of resistance (α):

\[ \alpha = -\frac{\beta}{T^2} \]  

For an NTC thermistor, the β-value is negative, which indicates that the thermistor resistance decreases with increasing temperature. The expected results shown in Table 2 shows the values of resistivity, material constant and temperature coefficient of resistance for all the eight samples.

| Samples | Expected Value | Resistivity at 298 K(Ωcm) Expected value | Temperature coefficient of resistance (% per K), Expected value |
|---------|----------------|----------------------------------------|------------------------------------------------------------|
| 1       | 3000-4000      | >3000                                  | -4.1 to -4.9                                               |
| 2       | 3000-4000      | 1550-1850                             | -4.1 to -4.9                                               |
| 3       | 3000-4000      | 1950-2500                             | -4.1 to -4.9                                               |
| 4       | 3000-4000      | 2500-3000                             | -4.1 to -4.9                                               |
| 5       | 3000-4000      | >3000                                  | -4.1 to -4.9                                               |
| 6       | 3000-4000      | >3000                                  | -4.1 to -4.9                                               |
| 7       | 3000-4000      | >3000                                  | -4.1 to -4.9                                               |
| 8       | 3000-4000      | >3000                                  | -4.1 to -4.9                                               |

4. Conclusion
Manganese Nickel based chip type negative temperature coefficient (NTC) thermistor of varying CuO concentration is prepared. A variation of dopant concentration is expected to cause substantial changes in the electrical properties of the sample. It was found that an increase in material constant (β-value) and temperature coefficient of resistance (α) with an increase in CuO concentration for all the eight samples. Thermistors are well known for their low-cost and small size. They are more sensitive than other temperature sensors. Their high sensitivity allows them to work well over a short temperature range. They are easy to use and provide a fast response. But they are non-linear and not robust.

NTC thermistors are widely used in industrial process controls, emission control and different temperature controls. These can also be used in automobile and truck tire curing as well as for monitoring and controlling engine temperatures. They are even used in missiles and aircraft. Other uses range from applications for sensor assemblies and industry to telecommunications, as well as many kinds of medical, laboratory and scientific instruments and testing.

Also, various characterisation techniques like scanning electron microscopy (SEM) analysis, X-ray photoelectron spectra (XPS) analysis and X-ray diffraction analysis can be used to evaluate the microstructural properties of these thermistors.

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