

Synthesis and Characterization of TiO₂ Added-ZnFe₂O₄ Ceramics for NTC Thermistors

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Abstract. The effect of TiO₂ addition on the characteristics of ZnFe₂O₄ ceramics for NTC thermistors has been studied. The ceramics were produced by pressing a homogeneous mixture of ZnO, Fe₃O₄ and TiO₂ (0-0.75 w/o) powders in appropriate proportions to produce ZnFe₂O₄ based ceramics and sintering the pressed powder at 1200°C for 2 hours in furnace air. Electrical characterization was done by measuring electrical resistivity of the sintered ceramics at various temperatures from 25°C to 100°C. Microstructure and structural analyses were also carried out by using optical microscopy and x-ray diffraction (XRD), respectively. The XRD analyses showed that the ZnFe₂O₄ ceramics having crystal structure of cubic spinel have been well produced. The grain size of the ZnFe₂O₄ ceramics tends to intact by addition of TiO₂ up to 0.5 w/o and decreases abruptly at the TiO₂ concentration of 0.75 w/o. According to the electrical data, it was known that the TiO₂ addition increased the thermistor constant (B) and the room temperature electrical resistivity (ρ_{RT}). The value of B and ρ_{RT} of the produced ZnFe₂O₄ based-ceramics fitted those for market requirement. The best performance for thermistor with low room temperature resistivity was shown by the ceramic containing 0.25 w/o TiO₂.

Key words: Thermistor, NTC, ZnFe₂O₄, TiO₂.

I. INTRODUCTION

The need for NTC thermistor in the world is still increasing due to its potential use for many sectors such as biomedical, aerospace, instrumentation, communications, automotive and HVACR (Heating, Ventilation, Air conditioning and Refrigeration) [1,2]. This component can be applied as temperature measurement, circuit compensation, suppression of inrush-current, flow rate sensor and pressure sensor [3]. It is well known that most NTC thermistors are produced from spinel ceramics based on transition metal oxides forming general formula AB₂O₄ where A is metal ion in tetrahedral position and B is metal ion in octahedral position [2-10]. Many studies have been done to improve the characteristics of the spinel based-NTC thermistors [2,3,7]. However, the study on the effect of TiO₂ addition on the characteristics of ZnFe₂O₄ spinel ceramics for NTC thermistor has not been reported yet.

The ZnFe₂O₄ ceramic has capability of being NTC thermistors, potentially, due to its semi conductive property. However, its characteristics can be still improved by addition of additive or dopan. The additive of TiO₂ has a potential to improve the characteristics of the ZnFe₂O₄ ceramic. Since the TiO₂ added into the ZnFe₂O₄ ceramic, the following conditions may happen. First, the TiO₂ will dissolve in the ZnFe₂O₄ ceramic by substituting a part of Fe³⁺ ions and/or Zn²⁺ ions. The second, the TiO₂ will not dissolve but segregates at grain boundaries of the ZnFe₂O₄ ceramic.

Since the first condition happens, the ZnFe₂O₄ ceramic may have a lower electrical resistivity when the substitution of Fe³⁺ and /or Zn²⁺ creating free electron in the conduction band. For the second condition, the electrical resistivity may be higher because the segregated TiO₂ may change the microstructure. This works is to know the effect of TiO₂ addition on the characteristics especially the electrical characteristics of the ZnFe₂O₄ ceramic for NTC thermistor based on the above hypothesis.

II. METHODOLOGY

Powders of ZnO, Fe₃O₄ and TiO₂ were weighed in appropriate proportions to fabricate TiO₂ added-Zn₂Fe₂O₄ ceramics, where the TiO₂ were 0, 0.25, 0.50 and 0.75 w/o (weight %). The mixture of powders was calcined at 800°C for 2 hours. After that, the calcined powder was crushed and sieved with a siever of < 38 μ m. The sieved powder was then pressed with pressure of 3.9 ton/cm² into green pellets. The green pellets were sintered at 1200°C for 2 hours in furnace air.

The crystal structure of the sintered pellets was analyzed with x-ray diffraction (XRD) using K α radiation. The microstructure of the pellets was investigated by an optical microscope after grinding, polishing, and etching the pellets. The opposite-side surfaces of the sintered pellets were coated with Ag paste. After the paste was dried at room temperature, the Ag coated-pellets were heated at 500°C for 10 minutes. The resistivity of the pellets was measured at various temperatures from 25 to 100°C in steps of 5°C using a

digital multimeter and a laboratory made chamber equipped with a digital temperature controller. Thermistor constant (B) was derived from \ln resistivity vs $1/T$ curve where B is the gradient of the curve based on (1) [3,7]:

$$\rho = \rho_0 \cdot \exp(B/T) \quad (1)$$

where, ρ is the electrical resistivity, ρ_0 is a constant or the resistivity at T is infinite, B is the thermistor constant and T is the temperature in Kelvin.

Room temperature resistivity (ρ_{RT}) was determined as the electrical resistivity at room temperature (25°C) and sensitivity (α) was calculated using (2) [11].

$$\alpha = B/T^2 \quad (2)$$

where, α is the sensitivity, B is the thermistor constant and T is the temperature in Kelvin.

III. RESULTS

Fig.1, Fig.2, and Fig.3, show the XRD profile of $ZnFe_2O_4$ ceramic added with 0, 0.5 and 0.75 w/o TiO_2 , respectively. As shown in the figures, the profiles are similar. The XRD profiles show that the structure of the ceramics is cubic spinel after being compared to the XRD standard profile of $ZnFe_2O_4$ from JCPDS No. 22-1012). No peaks from second phases observed. It may be due to the small concentration of TiO_2 added which smaller than the precision limit of the x-ray diffractometer used. The added TiO_2 may be dissolved or not. This cannot be concluded from the XRD profiles in this works. The microstructure and electrical data may be used to evaluate whether the TiO_2 added was dissolved or not.

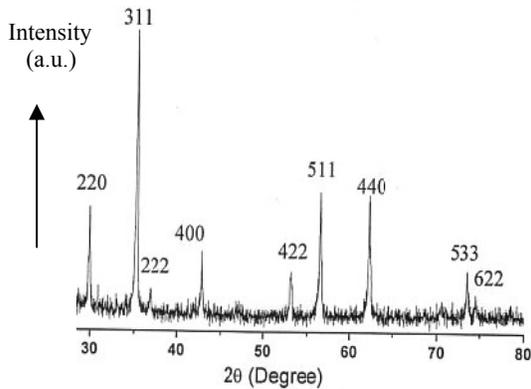


Fig. 1. XRD profile of $ZnFe_2O_4$ ceramic (0 w/o TiO_2).

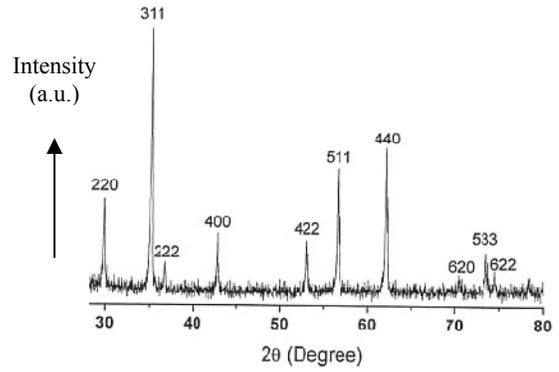


Fig. 2. XRD profile of 0.50 w/o TiO_2 added- $ZnFe_2O_4$ ceramic.

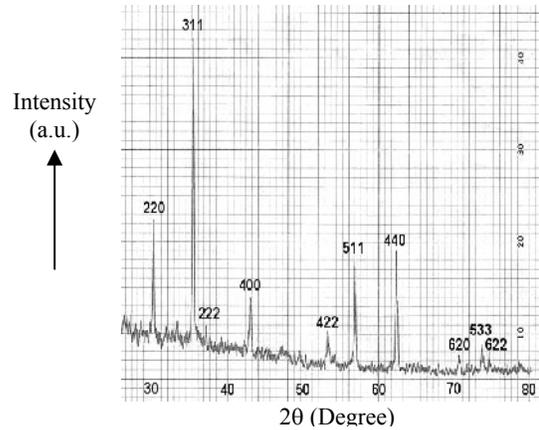


Fig. 3. XRD profile of 0.75 w/o TiO_2 added- $ZnFe_2O_4$ ceramic.

Microstructures of the $ZnFe_2O_4$ ceramic added with 0, 0.5 and 0.75 w/o TiO_2 , respectively, are represented in Fig.4, Fig.5 and Fig. 6 as the representative.

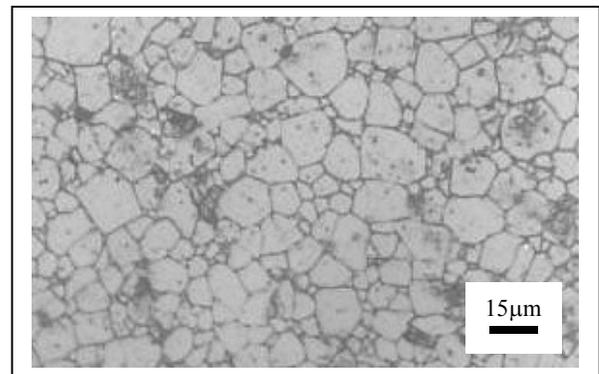


Fig. 4. Microstructure of the $ZnFe_2O_4$ ceramic (0 w/o TiO_2).

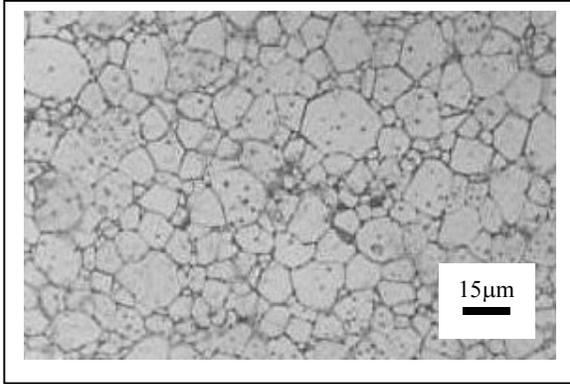


Fig. 5. Microstructure of the 0.50 w/o TiO₂ added-ZnFe₂O₄ ceramic.

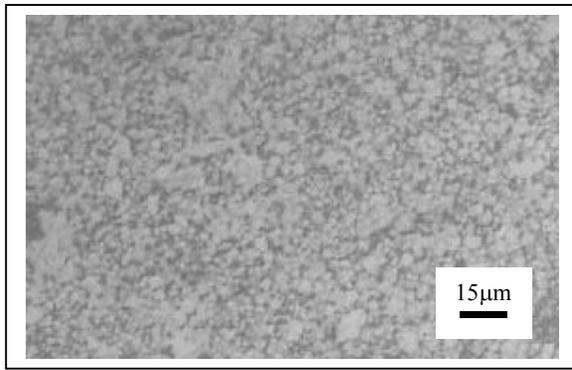


Fig. 6. Microstructure of the 0.75 w/o TiO₂ added-ZnFe₂O₄ ceramic.

From Fig. 4 and Fig. 5 the effect of TiO₂ addition on the microstructure change cannot be clearly seen significantly. No change of the grain size can be observed from samples added with 0 w/o TiO₂ to 0.5 w/o TiO₂ where the grain size of these samples are 10.2 μm (without TiO₂), 10.1 μm (with 0,25 w/o TiO₂) and 10.5 μm (with 0,5 w/o TiO₂), respectively. However, it is clearly shown from Fig. 6 that the addition of TiO₂ of 0.75 w/o decreases the grain size significantly (4.6 μm). The change of the grain size from the samples added with 0 to 0.5 w/o TiO₂ to that added with 0.75 w/o TiO₂ abruptly happens.

The electrical data of the TiO₂ added-ZnFe₂O₄ ceramics is shown in Fig.7 and Table 1. The electrical data of Fig. 7 shows that the ln resistivity increases linearly as the 1/T increasing, indicating that the electrical characteristics of the ceramics follows the NTC tendency expressed by (1).

As shown in Table 1, the addition of TiO₂ increases the room temperature resistivity (ρ_{RT}), thermistor constant (B) and sensitivity (α). However, the increase of the room temperature resistivity due to

0.25 w/o TiO₂ is not seen. For the application when the relatively low room temperature resistivity is needed, the addition of 0.25 w/o TiO₂ is very effective. This addition effectively increases the thermistor constant and sensitivity without increasing the room temperature resistivity. From the (B) value, the activation energy has been calculated by using (3) [3, 7] below:

$$E_a = B/k \quad (3)$$

where, E_a is the activation energy, B is the thermistor constant and k is the Boltzmann constant. The calculated activation energies are listed in Table 2. The small value of the activation energy exhibits the extrinsic property of the ceramics.

Compared to the B and E_a value for market requirement where B is 2000-7000°K and E_a is 0.1 - 1.5eV [7], the value of B and E_a of our ceramics is large enough and fits the requirement.

Table 1. Electrical characteristics of the TiO₂ added-ZnFe₂O₄ ceramics.

No.	Additive of TiO ₂ (w/o)	B (°K)	α (%/°K)	ρ _{RT} (Kohm-cm)
1.	0	2781	3.09	81
2.	0.25	3721	4.14	81
3.	0.50	4164	4.63	293
4.	0.75	4350	4.83	493

Market requirement ρ_{RT} = 10 ohm.cm-1Mohm.cm [4].

Table 2. The activation energy of the TiO₂ added-ZnFe₂O₄ ceramics.

No.	Additive of TiO ₂ (w/o)	E _a (eV)
1.	0	0.24
2.	0.25	0.32
3.	0.50	0.36
4.	0.75	0.38

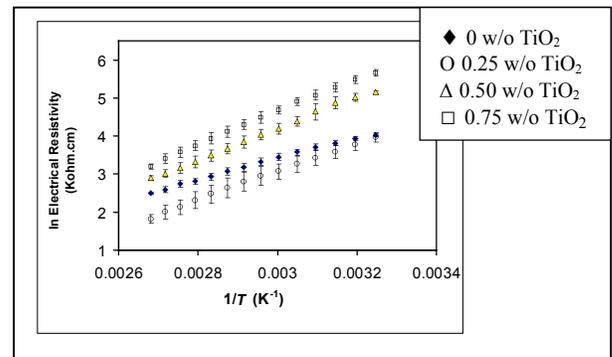


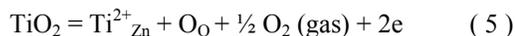
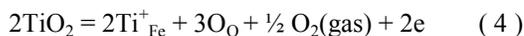
Fig.7. ln resistivity (ρ) vs 1/T of TiO₂ added-ZnFe₂O₄ ceramics.

IV. DISCUSSION

The XRD data show that the synthesis of ZnFe₂O₄ ceramics has been done well. The product crystallized in cubic spinel. No second phase observed either TiO₂ or other materials which formed from a reaction of the TiO₂ with ZnO or Fe₃O₄. There is a possibility that the added TiO₂ is dissolved partly in the matrix of ZnFe₂O₄ by either substituting Fe³⁺ and/or Zn²⁺ based on the ionic radius of Ti⁴⁺ (74.5 pm[12]), Zn²⁺ (88 pm[12]) and Fe³⁺ (69 pm [12]) which are not so different. The possibility of substitution of Fe³⁺ by Ti⁴⁺ seems larger than that of substitution of Zn²⁺ by Ti⁴⁺. However, this cannot be confirmed by the XRD data due to the lower concentration of the added TiO₂ than the precision limit of the X-ray diffractometer used.

The substitution of Fe³⁺ and Zn²⁺ ions by Ti⁴⁺ ions may create defect, theoretically, such as oxygen vacancy and cation vacancy which can influence the microstructure and electrical characteristics. The change of grain size by the addition of additive can be used to confirm whether the additive dissolves or not. The decrease of the grain size may be caused by the segregation of the added TiO₂. The segregated TiO₂ inhibits the grain growth during sintering. The inhibition of the grain growth is seen clearly in the sample added with 0.75 weight % TiO₂. This data confirms that at least a part of the added-TiO₂ is not dissolved in the ZnFe₂O₄ ceramics which could not be concluded from the XRD data. The relatively same grain size of the samples added with 0 to 0.5 w/o and the abrupt change of the grain size from the sample added with 0.5 w/o to that added with 0.75 w/o indicates that there may be a solubility limit of the dissolved TiO₂ which lies between 0.5w/o and 0.75 w/o.

The change of the electrical characteristics is controlled by the change of the microstructure due to the TiO₂ addition. Since the TiO₂ dissolved in ZnFe₂O₄ by substituting Zn and/or Fe following (4) and (5), the room temperature resistivity (ρ_{RT}) and thermistor constant (B) should decrease. The large (ρ_{RT}) and (B) of the sample added with 0.75 w/o TiO₂ and the small grains as shown in Fig. 6 indicate that a part of the added TiO₂ is not dissolved and tends to segregate at the grain boundaries.



where, $\text{Ti}_{\text{Fe}}^{4+} = \text{Ti}^{4+}$ ion occupies Fe sublattice, $\text{Ti}_{\text{Zn}}^{2+} = \text{Ti}^{4+}$ ion occupies Zn sublattice, $\text{O}_O = \text{Oxygen}$ ion occupies oxygen sublattice, $\text{O}_2(\text{gas}) = \text{Released oxygen gas}$ and $e = \text{Released electron}$.

The room temperature resistivity changes constantly following the increase of the concentration of

TiO₂, but the decrease of the grain size does not change linearly following the increase of the TiO₂ concentration. This means that a part of the added TiO₂ may be dissolved but did not create defect which behave as electron donor.

V. CONCLUSION

The grain size of the ZnFe₂O₄ ceramics tends to intact by addition of TiO₂ up to 0.5 w/o and decreases abruptly at the TiO₂ concentration of 0.75 w/o. The abruptly change is caused by the segregation of the added TiO₂ at grain boundaries which inhibited grain growth during sintering. A part of the added TiO₂ may be dissolved in ZnFe₂O₄ ceramics. The addition of TiO₂ increased the room temperature resistivity (ρ_{RT}) and the thermistor constant (B) of the ZnFe₂O₄ ceramics due to the segregated TiO₂ and defects that do not contribute in increasing electron conduction. The TiO₂ concentration of 0.25 w/o seems to be the best one in low room temperature resistivity application point of view for increasing the thermistor constant and sensitivity. The value of (ρ_{RT}) and (B) of the ZnFe₂O₄ ceramics made in this work fits the market requirement.

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