The Effect of MnO_2 Content and Sintering Atmosphere on The Electrical Properties of Iron Titanium Oxide NTC Thermistors using Yarosite

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Abstract. The effect of MnO_2 content and sintering atmosphere on the characteristics of Fe_2TiO_5 ceramics for Negative Thermal Coefficient (NTC) thermistors by using Fe_2O_3 derived from yarosite has been studied. The ceramics were produced by pressing a homogeneous mixture of Fe_2O_3, TiO_2 and MnO_2 (0-2.0 w/o) powders in appropriate proportions to produce Fe_2TiO_5 based ceramics and sintering the pressed powder at 1100-1200^{o}C for 3 hours in air, O_2 and N_2 gas. Electrical characterization was done by measuring electrical resistivity of the sintered ceramics at various temperatures from 30^{o}C to 200^{o}C. Microstructure and structural analyses were also carried out by using an scanning electron microscope (SEM) and x-ray diffraction (XRD). The XRD data showed that the pellets crystallize in orthorhombic. The presence of second phase could not be identified from the XRD analyses. The SEM images showed that the grain size of pellet ceramics increase with increasing of MnO_2 addition, and the grains size of the ceramic sintered in oxygen gas is smaller than sintered in nitrogen gas. Electrical data showed that the value of room temperature resistance (R_{RT}) tend to decrease with respect to the increasing of MnO_2 addition and the pellet ceramics sintered in oxygen gas had the largest thermistor constant (B), activation energy (E_a), sensitivity (α) and room temperature resistance (R_{RT}), compared to the sintered in nitrogen gas. From the electrical characteristics data, it was known that the electrical characteristics of the Fe_2TiO_5 pellet ceramics followed the NTC characteristic. The fabricated Fe_2TiO_5 ceramics have thermistor constants (B = 2207-7145K). This can be applied as temperature sensor, and will fulfill the market requirement.

1. Introduction

Negative Temperature Coefficient (NTC) thermistor has been widely used around the world today, due to its capability used in various fields of electronics, such as thermometer, electric current limiter, water flow sensor, and pressure sensor [1-2]. The NTC thermistor is generally made of ceramic having structure of spinel of AB_2O_4 where A is the ion occupies tetrahedral position and B is the ion occupies octahedral position [3-4]. Fe_2TiO_5 ceramic is one of some ceramics that can be applied for NTC thermistor. The thermistor may be produced in the form of disk/pellet and thick film. Fe_2TiO_5 is one of semiconductor ceramics used as based material for main components fabrication of NTC thermistor as temperature sensor. The composition of mineral Fe_2TiO_5 is belong to pseudobrokyte group where the general formula of this compound is X_2YO_5 with octahedral in both side, X and Y [5]. The

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Fe_2TiO_5 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 and sintering atmosphere condition. Since the MnO_2 added into the Fe_2TiO_5 ceramic, the following conditions may happen. First, the MnO_2 will dissolve in the Fe_2TiO_5 ceramic by substituting a part of Fe^{3+} ions and/or Ti^{4+} ions. The second, the MnO_2 does not dissolve but segregates at grain boundaries of the Fe_2TiO_5 ceramic. Since the first condition happens, the Fe_2TiO_5 ceramic may have a lower electrical resistivity when the substitution of Fe^{3+} and /or Ti^{4+} creating free electron in the conduction band. For the second condition, the electrical resistivity may be higher because the segregated MnO_2 may change the microstructure. Thermistor constant *B* is a quantity which determine typical characteristic of thermistor corresponding to electrical resistance changes with temperature. The larger thermistor constant lead to better thermistor quality. The addition of MnO_2 dopant into the Fe_2TiO_5 ceramic with sintering atmosphere variation may increase the thermistor constant which then improves the performance of the thermistor. Here, the effect of MnO_2 content and sintering conditions on the electrical properties of iron titanium oxide ceramic using yarosite as raw material for NTC thermistor based on the above hypothesis were studied. In addition, the possibility of local material utilization was also studied in order to step up the added value of the local material especially the material contains Fe_2O_3.

2. Material and Method

Fe_2TiO_5 thermistor ceramic was prepared by using powder of Fe_3O_3 derived from a yarosite mineral deposit and TiO_2. The extraction was done by using a precipitation process. The Fe2O3 was chemically analyzed to know the composition. The chemical composition of the yarosite powder was depicted in Table 1 [3, 6]. Powders of Fe_2O_3, TiO_2 and MnO_2 were weighed in appropriate proportions to fabricate MnO_2 added-Fe_2TiO_5 ceramics, where the MnO_2 were 0, 0.5, 1.0, 1.5 and 2.0 w/o (weight %), was calcinated at 700^{o}C for 2 hour. In order to form pellets, pressed powder, the homogeneous mixture of Fe_2O_3 and TiO_2 was pressed at 4.10^7 kg/m^2. The raw pellets were sintered at a temperature of 1200°C for 3 hours in air atmosphere and 2.0 w/o MnO_2 dopant was sintered at 1100^{o}C for 3 hours in oxygen (O_2) and nitrogen gas (N_2). Sintering in N_2 was intended to determine the resistivity of the pellets can be decreased.

Table 1. Chemical composition of Fe_2O_3 powder derived from yarosite

No	Compound	Concentration (%)
1	Fe_2O_3	93.80
2	SiO_2	1.02
3	MgO	0.09
4	CaO	0.19
5	TiO_2	1.15
6	MnO	0.12
7	Na_2O	0.59
8	K_2O	0.50

The crystal structure of the sintered pellets was analyzed with x-ray diffraction (XRD) using Kα radiation at 40 kV in voltage and 25 mA in current. The microstructure of fractured pellets was investigated by a Scanning Electron Microscope (SEM). 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 600^{o}C for 10 minutes. The resistance of the pellets was measured at various temperatures from 30 to 200^{o}C in steps of 10^{o}C using a digital multimeter. Thermistor constant (B) was derived from Ln resistivity versus 1/*T* curve where B is the gradient of the curve based on (1) [6-7] :

$$R = R_{o.} \, exp\ (B/T) \quad (1)$$

Where, R is the electrical resistance, R_o is a constant or the resistant at the infinite temperature, B is the thermistor constant and *T* is the temperature in Kelvin and k is the Boltzmann constant. Room temperature resistance (R_{RT}) was determined as the electrical resistance at room temperature (25^{o}C).

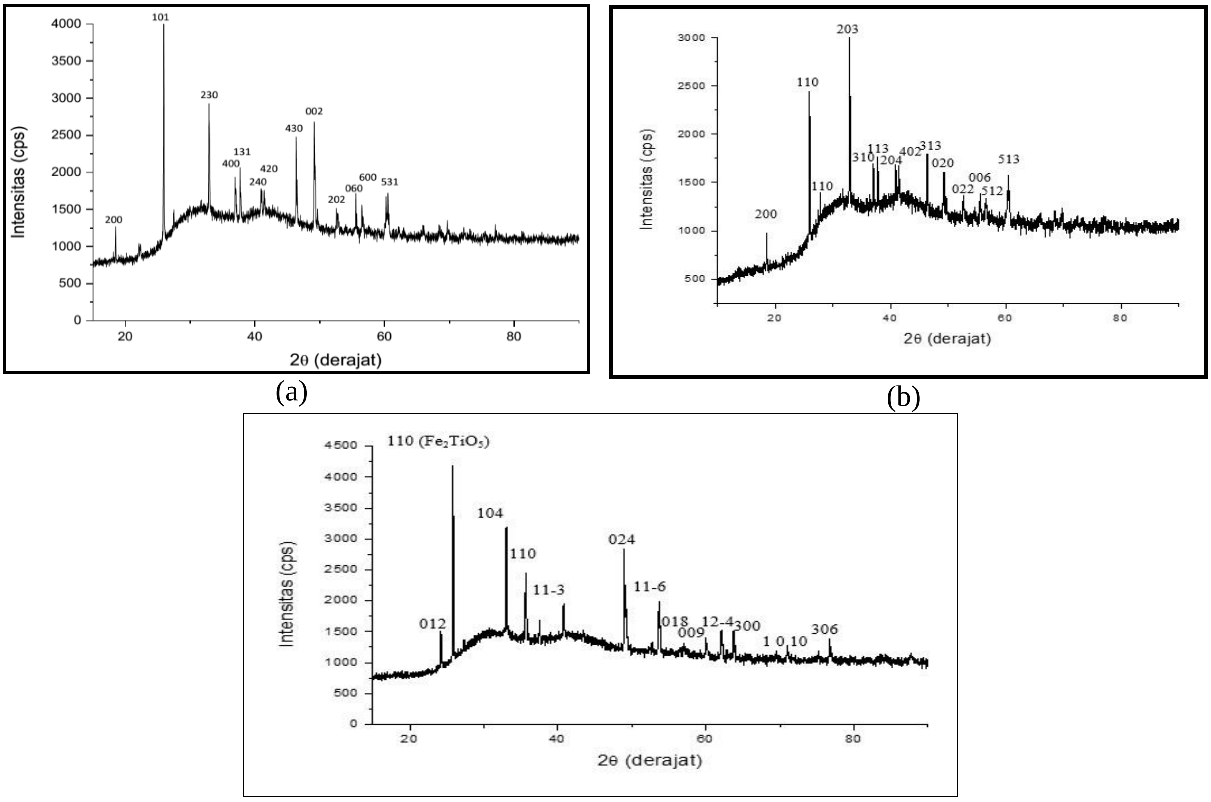
From the value of B, the activation energy (E_a) and sensitivity (α) were calculated using equation 2 and 3 [8-9].

$$E_a = B.k \quad (2)$$

$$\alpha = B/T^2 \quad (3)$$

3. Result and Discussion

The XRD profile of Fe_2TiO_5 without doping MnO_2, sintered at 1200^{o}C for 3 hours in air atmosphere is shown in Figure1A and XRD profiles of 2.0 % mole MnO_2 doped Fe_2TiO_5 pellet ceramics sintered at 1100^{o}C for 3 hours with sintering atmosphere of Oxygen and Nitrogen gas respectively are shown in Figure 1b and Figure 1c.



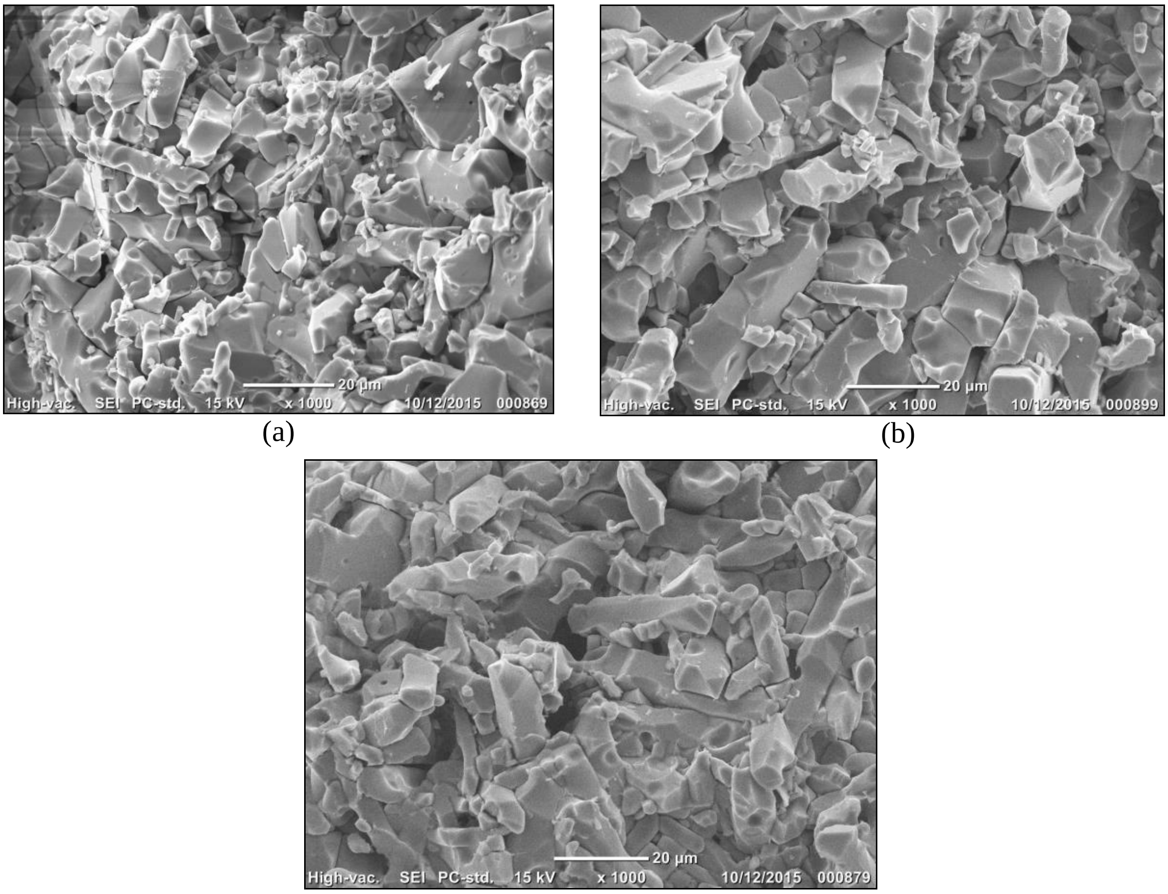
(a) (b)

(c)

Figure 1. XRD profile of the (a) 0.0 w/o MnO_2 added- Fe_2TiO_5 Ceramic sintered at 1200^{o}C for 3 hours in air, (b) 2.0 % mole MnO_2 doped Fe_2TiO_5 ceramic sintered in Nitrogen gasand (c) Oxygen gas.

As shown in the figure 1 the profiles are generally similar. The XRD profiles show that the structure of the pellet ceramics is orthorhombic after being compared to the XRD analyses program: X Powder aplication vers.2004.04.46 Pro. No peaks from second phases observed. It may be due to the small concentration of impurities which is smaller than the precision limit of the x-ray diffractometer used. The XRD data of Figure1 indicates that the synthesis of the Fe_2TiO_5 pellets has been well prepared from Fe_2O_3 (Yarosite) and TiO_2 powder with MnO_2 content and sintering atmosphere condition.

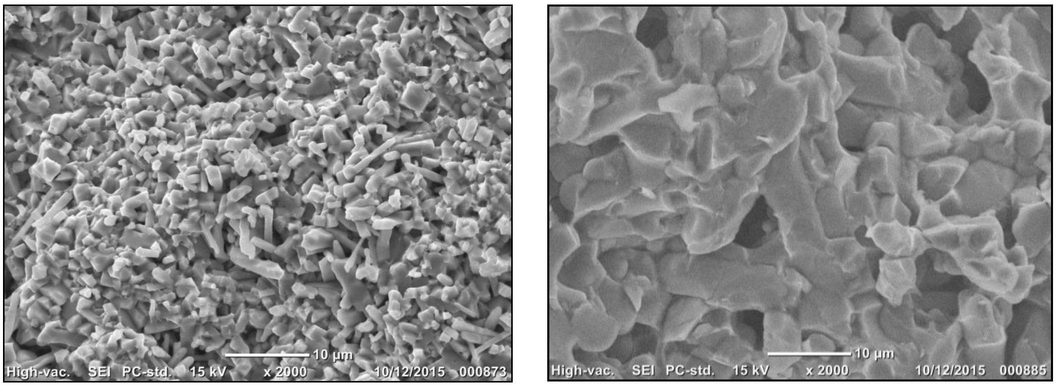
Microstructures of the Fe_2TiO_5 ceramic added with 0, 1.5 and 2.0 w/o MnO_2 respectively, sintered at 1200°C in air are represented in Figure2. Microstructures of the Fe_2TiO_5 pellet ceramic 2.0 % mole MnO_2 doped Fe_2TiO_5 pellet ceramics using Fe_3O_3 from yarosite sintered at 1100°C for 3 hours with sintering atmosphere of oxygen and nitrogen gas respectively, are showed in figure 2.



(a) (b)

(c)

Figure 2. Microstructure of the Fe_2TiO_5 Ceramics sintered at 1200°C/3h/Air Doped -0.0 w/0 (A), 1.5 w/o (B) and 2.0 w/o MnO_2(C).

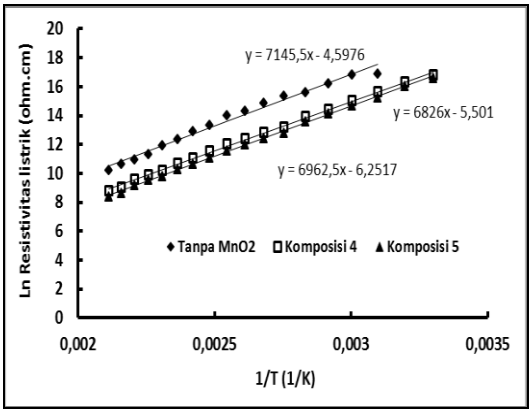


(a) (b)

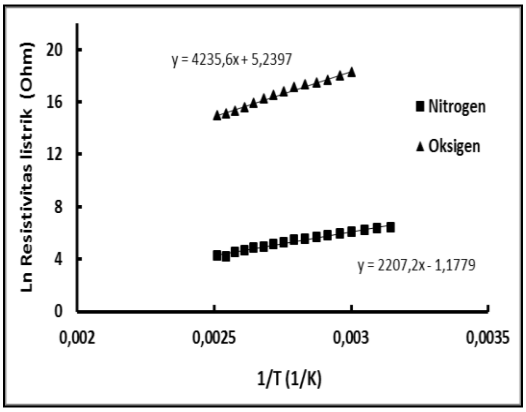
Figure 3. Microstructure of the Fe_2TiO_5 Ceramics sintered at 1100°C/3h in (a) Oxygen and (b) Nitrogen gas.

The samples could be well synthesized with air, nitrogen and oxygen gas sintering atmospheres. All of the pellets are characterized in porous structure with different grain size depending on the MnO_2 addition and sintering atmosphere condition. From Figure 2, it is seen that grains of the ceramic tend to become larger as the increase of MnO_2 addition. The increase of the grain size may be caused by the segregation of the added MnO_2. The segregated MnO_2 inhibits the grain growth during sintering [10-11] The grain size calculated by using of the intercept method is found to be 11.10 μm, 11.50 μm and 11.67 μm, respectively. From Figure 3, it is seen that the grain size of the ceramic sintered in oxygen gas is much smaller than that of the ceramic sintered in nitrogen gas. This situation can be explained as follow, a relatively poor oxygen for sample sintered in nitrogen gas, make the ceramic could not be well synthesized. Some of Fe_2O_3 and TiO_2 segregated at grain boundaries and inhibited grain growth, producing small grains. The grain size calculated by using of the intercept method is found to be 2.84μm and 8.08 μm for sintered in oxygen and nitrogen gas atmospheres, respectively. Sintering gas atmosphere also influence of the electrical properties of the pellets Fe_2TiO_5. In an atmosphere in which oxygen-rich grain growth does not work properly causing small grain size. In the otherwise, in an nitrogen gas atmosphere grains growth better [12-13].

The electrical data of the MnO_2 added-Fe_2TiO_5 ceramics and sintering atmosphere variation are shown in Figure 4 and Table 2-3. The electrical data of Figure 4 show that the Ln resistance increases linearly as the $1/T$ increases, indicating that the electrical characteristics of the ceramics follows the NTC tendency expressed by equation (1). As shown in Table 1, the increase of the MnO_2 added-Fe_2TiO_5 ceramics tend to decreases the thermistor constant (B), activation energy (E_a), sensitivity (α) and room temperature resistance (R_{RT}). As shown in Table 2, electricity resistance and thermistor constant of Fe_2TiO_5 ceramic in oxygen gas is larger than in nitrogen gas. The ceramics sintered in oxygen gas have relatively smaller oxygen vacancy and means smaller number of electron, so the resistance of this ceramic is larger. The small value of the activation energy exhibits the extrinsic property of the ceramics. The value of B and E_a of our ceramics is large enough and fits the requirement [14-15].



(a)



(b)

Figure 4. The relation between Ln resistance (R) vs $1/T$ of (a) MnO_2 added-Fe_2TiO_5 ceramics and (b) Oxygen-Nitrogen gas sintering atmospheres

Table 2. Electrical characteristics of the MnO_2 added-Fe_2TiO_5 ceramics 1200^{o}C/3h/air

Content of MnO_2 (w/o)	B(K)	E_a(eV)	α(%/K)	R_{RT}(MΩ)
0	7145	0.62	8.0	261.14
1.5	6826	0.59	7.7	36.21
2.0	6962	0.60	7.8	27.02

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Table 3. Electrical characteristics of the Fe_2TiO_5 doped 2.0 % MnO_2 Sintered at 1100°C for 3hrs with sintering conditions.

Atmosphere	B (K)	E_a (eV)	A (%/K)	R_{RT} (MΩ)
O_2 gas	4235	0.36	4.8	280.79
N_2 Gas	2207	0.19	2.5	5.07

4. Conclusion

Fe_2TiO_5 pellet ceramics using Fe_2O_3 from yarosite have been well produced with MnO_2 content and sintering atmosphere conditions. All of the pellets crystallize in orthorhombic structure. The grain size of the Fe_2TiO_5 ceramics tends to be larger by addition of MnO_2. The electrical characteristics of the Fe_2TiO_5 base ceramics followed the NTC characteristic. The value of B and R_{RT} of the produced Fe_2TiO_5 ceramics namely B = 2207-7145 K and R_{RT} = 5.07-280.79 MΩ, fitted market requirement and the Fe_2TiO_5 ceramic can be applied as NTC thermistor.

5. References

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