Effect of Thermal Processes on the Electrical and Optical Properties of Fe$_2$TiO$_5$ Ceramics

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Abstract. Pseudobrookite (Fe$_2$TiO$_5$) is one of the Fe-Ti oxides that have been commonly studied. It is the most stable phase among the Fe-titanates. The multiferroic properties of Fe$_2$TiO$_5$ make the material can be used as a potential candidate for new applications due to the combination of semiconducting, magnetic, dielectric, and optical properties. In this research, Fe$_2$TiO$_5$ ceramics were synthesized using mechanical milling method for 7 h with various temperatures of 1100 $^\circ$C, 1200 $^\circ$C, and 1300 $^\circ$C. Scanning electron microscopy (SEM) observation and x-ray diffraction (XRD) measurements were performed to analyze the microstructures and crystal structures of the Fe$_2$TiO$_5$ ceramics. In order to investigate the band gap of the Fe$_2$TiO$_5$, the UV-Vis Diffuse Reflectance measurements were conducted. It has been found that the Fe$_2$TiO$_5$ ceramic can be applied as a promising candidate for semiconducting devices in which the electrical conductivity and the band gap of the Fe$_2$TiO$_5$ ceramic were $1.73 \times 10^{-7}$ $\Omega^{-1}.cm^{-1}$ and 1.71 eV, respectively.

1. Introduction
Iron titanate (Fe-Ti) oxides have four stable phases, namely ilmenite (FeTiO$_3$), pseudobrookite (Fe$_2$TiO$_5$), pseudorutile (Fe$_2$Ti$_3$O$_9$), and ulvospinle (Fe$_2$TiO$_4$). Among those Fe-Ti oxides, Fe$_2$TiO$_5$ is the most stable phase and has been intensively studied due to the multi-functional behaviors in one material. Fe$_2$TiO$_5$ particles have been successfully synthesized by solid state reaction [1], sonochemical [2], sol-gel [3, 4], precipitation [5], and mechanical alloying methods [6]. Fe$_2$TiO$_5$ phase also can be prepared from the mixture of Fe$_3$O$_4$/Fe$_2$O$_3$ and TiO$_2$ at a high temperature of 1423 K [7]. Recently, the synthesis of porous Fe$_2$TiO$_5$ microparticulate through a hydrothermal route might improve the electrochemical properties [8] and as a candidate for Li-ion battery anode material [9].

Fe$_2$TiO$_5$ nanopowders have been found to behave as ferrimagnetic and paramagnetic from the vibrating sample magnetometer (VSM) observation at room temperature [10]. The electronic structures and the optical properties, have been theoretically studied based on the LSDA and LSDA+U calculations. As a result, it has been found that the band gap of Fe$_2$TiO$_5$ was about 1.81 eV [11]. This result showed that Fe$_2$TiO$_5$ is an n-type semiconducting oxide.

The purpose of this work was to investigate the effect of the thermal process on the electrical and optical properties of the synthesized Fe$_2$TiO$_5$ ceramics through the combination of coprecipitation method to obtain Fe$_3$O$_4$ as one of the raw materials and mechanical alloying method to get the Fe$_2$TiO$_5$
ceramics. The temperature variation of heat treatment was conducted to understand the phase formation of Fe$_2$TiO$_3$ affecting the electrical and optical properties of the samples.

2. Experimental Method

FeCl$_2$·4H$_2$O was used as a raw material to synthesize Fe$_3$O$_4$ by coprecipitation method. FeCl$_2$·4H$_2$O was dissolved in distilled water, then mixed and stirred with HCl solution at room temperature. The NH$_4$OH solution was added into the dissolved FeCl$_2$ solution at a temperature of 70 °C to obtain the black precipitate of Fe$_3$O$_4$. This precipitate was then washed with distilled water until reaching the pH value of 7.0 and then dried to obtain Fe$_3$O$_4$ powders. In order to obtain the Fe$_2$O$_3$ powders, the Fe$_3$O$_4$ powders were heated at 900 °C for 5 h.

Fe$_2$TiO$_5$ ceramics were prepared by the mechanical alloying technique with Fe$_2$O$_3$ and TiO$_2$ as the starting materials. The composition ratio of Fe$_2$O$_3$ : TiO$_2$ = 3 : 2 was used according to the phase diagram in Ref. [12]. In this technique, the milling process was conducted for 7 h at the rate of 300 rpm and BPR of 15:1. The milled powders were then heated at various temperatures of 1100 °C, 1200 °C, and 1300 °C for 2 h to obtain Fe$_2$TiO$_5$ ceramic powders.

The prepared Fe$_2$TiO$_5$ powders were first characterized by X-ray diffractometry (XRD) to identify the phase formation in the samples. Scanning Electron Microscope (SEM) measurement with FEI Inspect S50 was performed to observe the particle morphology. The electrical conductivity measurement was conducted by IV meter connected to LabView development system to study the electrical properties of the samples. The Ultraviolet-Visible Spectrophotometer (UV-Vis) measurement using Shimadzu 2450 with double beam system and diffuse reflectance spectroscopic (DRS) was performed to investigate the optical properties of the Fe$_2$TiO$_5$ ceramics.

3. Results and Discussion

Figure 1 shows the XRD patterns for Fe$_2$TiO$_5$ powders after milling process and various heating temperatures of 1100 °C, 1200 °C, and 1300 °C for 2 h. The XRD data show that there is not any impurity detected in all samples after the heating process, suggesting a single phase of Fe$_2$TiO$_5$ has been formed by only performing heat treatment at 1100 °C. This temperature is within the temperature range in which the interdiffusion took place [13]. It can also be seen that the degree of crystallinity of Fe$_2$TiO$_5$ powders increased along with the increasing heating temperature, indicating the increase in particle size as well as the crystalline size of Fe$_2$TiO$_5$ powders. The particle morphology after milling process and various heat treatments can be seen in Figure 2. It is confirmed that the higher temperature results in the larger particle size due to a higher diffusion rate among atoms in the crystals which are comparable with the results of research conducted by Wiendartun et al. [14].

![Figure 1. XRD patterns of the milled Fe$_2$TiO$_5$ powders and the milled powders after heat treatment with various temperatures of 1100 °C, 1200 °C, and 1300 °C for 2 h](image-url)
Figure 2. Particle morphologies observed by SEM for the milled Fe$_2$TiO$_5$ powders after heat treatment at the temperatures of (a) 1100 °C, (b) 1200 °C, and (c) 1300 °C for 2 h.

Table 1 shows the average value of electrical conductivity of all prepared samples at room temperature. It can be seen that there was a slight increase of conductivity value, which was in the order of $10^{-7}$ together with the increasing temperature of heat treatment. This was probably due to the effect of a large particle size implying a less number of grain boundaries. It is well known that grain boundaries may act as the second resistance beside the first resistance from the grain itself in the ceramic materials. Higher conductivity value can be achieved by decreasing the number of grain boundaries in the ceramics.

Table 1. The electrical conductivity of Fe$_2$TiO$_5$ powders with different temperatures of heat treatment.

| Temperature (°C) | Resistivity (ρ) (x10$^6$ Ω.cm) | Conductivity (σ) (x10$^{-7}$ Ω$^{-1}$.cm$^{-1}$) |
|------------------|---------------------------------|-----------------------------------------------|
| 1100 °C          | 6.84                            | 1.46                                          |
| 1200 °C          | 4.63                            | 2.16                                          |
| 1300 °C          | 4.18                            | 2.39                                          |

UV-Vis measurements can be used to obtain the value of gap energy of a semiconducting material. In this report, each of Fe$_2$TiO$_5$ ceramic prepared by mechanical alloying technique shows semiconducting behavior since the conductivity value is in the order of $10^{-7}$. Figure 3 shows the UV-Vis absorption spectra for the milled Fe$_2$TiO$_5$ before and after heat treatment at the temperatures of 1100 °C, 1200 °C, and 1300 °C for 2 h. By analyzing these data using $E = \frac{hc}{\lambda}$, the band gap energies of these samples can be obtained and summarized in Table 2. It is found that the band gap energy of the prepared Fe$_2$TiO$_5$ samples has a smaller value compared to the previous result [11]. It is probably due to the formation of localized bands near conduction band. A smaller band gap is important in the photocatalytic reaction. With the small value of band gap, the sample would be more responsive to visible light [15]. It has been indicated that the photocatalytic activity of the addition of electronic stated within the gap [16]. From Table 2, it seems that the change of the band gap value was relatively small along with the increasing temperature. Accordingly, the band gap value has been found to be almost independent of the variation of heat treatment process.

Table 2. Band gap values of Fe$_2$TiO$_5$ powders with different temperatures of heat treatment.

| Sample     | Band Gap (eV) | $\lambda$ (cut-off wavelength) |
|------------|---------------|-------------------------------|
| 1100 °C    | 1.71          | 723                           |
| 1200 °C    | 1.73          | 710                           |
| 1300 °C    | 1.77          | 701                           |
| Fe$_2$TiO$_5$ (*) | 1.81         | -                             |

The (*) is the result of the former paper [11] written together as a comparison with the present data.
5. Boundaries. Based on the analysis of UV-Vis spectra, it has been revealed that the prepared Fe$_2$TiO$_5$ ceramics have a semiconducting behavior with the band gap energy of around 1.71 eV. It has been found that the thermal process played a minor role in the change of bandgap energy in Fe$_2$TiO$_5$ ceramics.

4. Conclusion

The effect of the thermal process on the electrical and optical properties of Fe$_2$TiO$_5$ ceramics has been investigated. For this purpose, the Fe$_2$TiO$_5$ ceramics have been successfully synthesized by a combination of coprecipitation and mechanical alloying methods continued by the temperature variation of heat treatment at 1100 °C, 1200 °C, and 1300 °C. It has been found that the electrical conductivity of the Fe$_2$TiO$_5$ ceramics slightly increased with the increasing temperature due to the increasing crystallinity and decreasing number of grain boundaries. Based on the analysis of UV-Vis spectra, it has been revealed that the prepared Fe$_2$TiO$_5$ ceramics have a semiconducting behavior with the band gap energy of around 1.71 eV. It has been found that the thermal process played a minor role in the change of bandgap energy in Fe$_2$TiO$_5$ ceramics.

5. References

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