Effect of sintering temperature on crystal structure and grain size of Manganese Ores from West Sumatera

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Abstract. The effect of sintering temperature on crystal structure and grain size of manganese seed originating from West Sumatera has been investigated using X-ray Diffractometer (XRD). This investigation is important in relation to the emergence of new phases of economic value at a certain temperature. The sintering temperature variations used are 600°C, 700°C, 800°C, 900°C, and 1000°C, respectively. The result of manganese ore investigation is known that sintering temperature variation, there is no change of structure from phases found in manganese ore which are equally tetragonal but there is change of grain size from the existing phases. For bixbyite and rhodonite phases, the grain size decreases with increasing sintering temperature. As for rhodonite and hausmannite phases, the grain size tends to increase with increasing sintering temperature.

1. Introduction
Manganese (Mn) is one of the most important raw materials for iron and steel production. Manganese is used in steel alloys to enhance beneficial characteristics such as strength, hardness and durability [1]. Manganese is an element that must always exist in steel in small quantities and as a deterrent to oxidation, thus every chemical process and metallurgical process can take place well. The addition of manganese elements in the alloy steel adds strength and heat resistance as well as a cleaner and shiny appearance.

Manganese ore contains high value oxide compounds such as pyrolusite, bixbyite, psilomelane, hausmannite, rhodokrosit and rhodonite [2] with varying concentrations in each region. The presence of manganese phase oxide content present in manganese ore causes manganese ore to have the potential to be developed as industrial materials. Currently, pyrolusite is the main ingredient for the dry battery industry. Bixbyite can also be used as a dry battery material that produces good performance and with long durability [3] [4]. In addition, hausmannite is widely used in industry as a catalyst, magnetism, electrochemistry, or for air decontamination [5].

Because of the magnitude of the benefits of manganese oxide in the form of pyrolusite, bixbyite, and hausmannite, then made various attempts to get it. One way is to sintering at a certain temperature so that there is a change of structure and phase transformasi. The bixbyite and hausmannite phases can be obtained by heating from the pyrolusite phase. This phase change may occur due to the heating temperature. Pyrolusite phase can be bixbyite phase at sintering temperature above 400°C. The bixbyite phase can be a hausmannite phase at 400°C sintering temperature. The difference in sintering temperature in the formation of pyrolusite to bixbyite, influenced by other content contained in pyrolusite. Just as it contains small amounts of Si, Al, Ca, P, K. Ba, Ag, and other elements. The same
phases in each region have different compositions. The difference of oxide content in manganese ore and phase formed due to geological order and phases process in every region.

From these reviews, it can be concluded that new phases of manganese oxide can be obtained by sintering at different temperatures and are influenced by the characteristics of the area in which the manganese ore is found. In this paper, we focus on the effect of the sintering temperature on crystal structure and crystallite size of the emerging phases. On the other hand, knowledge of crystal structure and crystallite size is helpful in understanding the surface and bulk characteristic of manganese oxide for the benefit of the application of manganese.

2. Research Method

2.1. Preparation of manganese Powder

The sample of this research used manganese ore material obtained from West Sumatera, Indonesia. The cleansed manganese ore was crushed to obtain finer and homogeneous grains. The scour process is done for 3.5 hours. Furthermore, the crushed manganese ore sieved with an automatic sieve of 0.075 mm aims to have the same grain size. Samples were then disinterring by using furnaces at temperatures of 600°C, 700°C, 800°C, 900°C, and 1000°C, with a duration of 3 hour detention.

2.2. Physical Measurements

Manganese ore samples after disinterring were then analyzed by crystal structure and grain size using XRD Cement (CuKα 1.5606 Å, 40 mA, 45 kV). Measurements were made from 10° to 90° with step size 0.010. The process of identifying phase and structure were obtained from search match using high score plus program. The grain size was calculated using the Scherrer formula, \( D = \frac{0.9 \lambda}{\beta \cos \theta} \), where \( \lambda \) was the wavelength of X-ray radiation, \( \beta \) was the full width at half maximum (FWHM) of the peaks at the diffracting angle \( \theta \) [6][7].

3. Results and discussion

3.1. Crystal Structure

Figure 1 shows the diffraction pattern of the sintered manganese sample at a temperature of 600°C. The type of manganese oxide phase contained in the sintered sample at a temperature of 600° C is the bixbyite formed at the diffraction angle of 18.87°, 38.28°, and 65.95°. Braunite is formed at the diffraction angle 23.25°, 26.70°, 33.01°, 45.23°, 49.56°, 55.34°, 85.16° and 91.14°. In addition, the non-manganese oxide phase contained is the coesite formed at the diffraction angle 96.32°.

![Figure 1. Spectra XRD of manganese powder with sintering at 600°C](image-url)
Figure 2 shows the diffraction pattern of the sintered manganese sample at a temperature of 700°C. The diffraction results show in bical samples of bixbyite, braunite, hausmannite, rhodonite, braunite. The most dominant phase is braunite. The type of manganese oxide phase contained when sintered at a temperature of 700°C is Bixbyite which is seen at angles of 18.89°, 38.28°, 64.06°, and 94.21°. Braunite is visible at angles, 33.00°, 45.29°, 49.56°, and 55.32°. At diffraction angle 26.71°, 28.56°, rhodonite phase of rhodonite is formed

![Figure 2. Spectra XRD of Manganese Powder with sintering at 700°C](image)

Figure 3 shows the diffraction pattern of the sintered manganese sample at a temperature of 800°C. Results The diffraction pattern showed in samples containing braunite and bixbyite phases, hausmannite. The most dominant phases are braunite and bixbyite. The type of manganese oxide phase contained in the sample disinterring at a temperature of 800°C is bixbyite formed at an angle 18.89°, 38.28°, 45.18° and 55.21°. Rhodonite formed at an angle 26.70° and 28.66°. Braunite formed at an angle 23.21°, 49.46°, 65.84°, 69.48°, 91.42°, dan 94.05°.

![Figure 3. Spectra XRD of Manganese Powder with sintering at 800°C](image)
Figure 4 shows the diffraction pattern of the sintered manganese sample at a temperature of 900°C. The type of manganese oxide phase present in the sample disinterring at a temperature of 900 °C is a bixbyite formed at an angle 49.43°, 55.25°, braunite formed at an angle 23.18°, 26.68°, 33.00°, 69.39°, 74.12°, 80.23°, and 91.22°. Hausmannite formed at an angle 18.07°, 32.39°, 36.17°, 38.27°, 45.41° and 58.7447°.

![Figure 4. Spectra XRD of manganese powder with sintering at 900°C](image)

The type of manganese oxide phase present in the sample disinterring at 1000°C is shown in Figure 5. The phase type is a braunite formed at an angle 25.56°, 26.64° and 36.12°. Hausmannite formed at an angle 18.04°, 28.94°, 31.02°, 32.39°, 38.04°, 44.48°, 50.85°, 55.31°, 58.54°, 59.91°, 60.7981°, 64.6520°, 74.22°, 80.03°, and 89.59°.

![Figure 5. Spectra XRD of manganese powder with sintering at 1000°C](image)
Based on XRD data analysis for each sample it can be seen that sintering temperature variations influence the formation of manganese oxide phase. At a temperature of 1000ÅC the other phases begin to disappear and the most dominant stay is hausmannite. The phase change starts at the sintering temperature of 600ÅC, where the pyrolusite phase undergoes phase transformation to bixbyite. At 600ÅC sintering temperatures all pyrolusite phases undergo phase transformation to bixbyite as a whole. This is evident from the absence of pyrolusite peaks on XRD patterns. At the sintering temperature of 700ÅC-1000ÅC there is also a phase transformation of bixbyite that joins the rhodonite phase to form braunite phase. At a sintering temperature of 1000ÅC all bixbyite phases undergo transformation as a whole to be hausmannite, as can be seen from the increasing number of hausmannite peaks. The manganese oxide phase formed by the sintering temperature is shown in Table 1.

Table 1. The manganese oxide phase formed by the sintering temperature

| Temperature | Pyrolusite | Hausmannite | Rhodonite | Bixbyite | Braunite | Coesite |
|-------------|------------|-------------|-----------|----------|----------|---------|
| 26ºC        | √          |             |           |          |          |         |
| 600ºC       | √          | √           | √         | √        | √        |         |
| 700ºC       | √          | √           | √         | √        |          |         |
| 800ºC       | √          | √           | √         |          |          |         |
| 900ºC       | √          | √           |           |          |          |         |
| 1000ºC      | √          |             |           |          |          |         |

The occurrence of phase changes due to temperature changes is caused by the growth and alteration of one phase in manganese ore. Manganese oxide minerals are minerals formed from a combination of manganese elements with anion oxide (O) groups. Mineral manganese oxide is formed as a result of compounds between oxygen and manganese elements. The formation of these new phases is due to the pyrolusite oxidation process to bixbyite and hausmannite. While the braunite phase appears due to the bond between bixbyite and rhodonite [8]. The pyrolusite transformation reaction to bixbyite, begins in pyrolusite phase built on Mn³⁺ Ion arranged with tetragonal pattern and Mn²⁺ ions are arranged cubic. As a result of thermal energies causing atoms, in manganese ore especially pyrolusite vibrates. At that time there is a transfer of cations to the surface of the crystal and at the same time there is a cation vacuum. On the surface of the crystals the Mn²⁺ ion oxidizes into Mn³⁺ ions. The Mn³⁺ ion interacts with the binding of oxygen to form the edges of the bixbyite. Such a condition causes the presence of Mn³⁺ ions with tetragonal geometry and there is also a Mn³⁺ ion with cubic geometry paired with oxygen this is a feature of bixbyite. Based on the ion dissolution or dissolution reaction Mn2⁺ occurs due to the free electrons moving. The dissolution of the ion or the dissolution can be processed on Mn atoms present on the surface either in the oxidation or ion-exchange areas. When pyrolusite phase transformation occurs to bixbyite and then to hausmannite, there is also a change of structure of the manganese ore. The structural changes that occur are tetragonal structured pyrolusite phase with a 4.4000 Å and c = 2.8700Å axis cellular units to a cubic structured bixbyite phase with a cell unit a = b = c = 9.4091 Å and then to tetragonal a = b = c = 9.4091 Å and tetragonal phase structures c = 9.4560Å. This structure change is caused by the continuous oxidation process in the sample. The oxidation process causes the emergence of Mn³⁺ ions, each pair of Mn³⁺ ions coupled with a cation vacuum. This thus affects the coordination of the atoms in the cell unit. The Mn²⁺ ion with tetragonal geometry and also the Mn³⁺ ion with cubic geometry paired with oxygen is characteristic of bixbyite. As the temperature is increased, the unit cell contains most of the Mn³⁺ ions this is a feature of hausmannite.

3.2. Grain size
The grain size of the sintered manganese samples at various temperature variations has been investigated simultaneously. Figure 6 shows that the grain size of the manganese oxide crystal changes with increasing temperature. The bixbyite and rhodonite phase increased grain size up to 600°C sintering temperature, then dropped and at 700°C and rose again at 800°C, then decreased and lost at 900°C. However, the grain size of the rhodonite phase drops at 800 °C and disappears at 900°C. The hausmannite phase has an increase in grain size from a temperature of 700 °C to a sintering temperature of 1000°C.

![Graph showing grain size vs sintering temperature](image)

**Figure 6.** Grain size of manganese samples due to variation of sintering temperature 600°C, 700°C, 800°C, 900°C, dan 1000°C.

The size of coesite phase crystalline grains has increased. This increase occurs because at 600 °C there is no phase transformation, so that the thermal energy provided by the manganese ore compounds to join each other and form a new bond. During the heating occurs there will be union between the particles. The increase in grain size is due to the transformation of the bixbyite phase to the hausmannite, so that the given thermal energy is used by bixbyite to join the other. The incorporation mechanism is preceded by pore-separated nuclei, due to continuous temperature, the pores.

### 4. Conclusion

Manganese powders were synthetized by dried method using natural manganese ores phase as the starting material. The crystal structure and grain size of manganese are depending on the sintering temperature. Giving variation of sintering temperature on manganese which influences change of structure of manganese oxide formed. The structural change that occurs is a tetragonal tetra-structured phase pyrolusite with a 4.4000 Å and c = 2.8700Å axis cell units to a cubic-structured bixbyite phase with a cell unit a = b = c = 9.4091 Å and then to a tetragonal a tethered phase a phenomenon = b = 5.7630 Å and c = 9.4560Å. In addition, the sintering temperature affects the size of the manganese oxide grains formed. For the hausmanite phase, the grain size increases with increasing sintering temperature

**Acknowledgment**

The authors thank to RISTEK DIKTI for financial support through Hibah MP3EI 2016-2017 for this work.
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