Structural analysis of the hausmannite thin film (Mn$_3$O$_4$) by spin coating method

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Abstract. Recent research on Hausmannite is becoming more interesting to be examined because of its advantages that can be used in a variety of applications. The purpose of this research is to investigate the influence of temperature variation of calcination on thin film structure of Hausmannite. This type of research is an experimental research. The Hausmannite used was derived from manganese ore which had been sintered for 3 hours at a temperature of 1000 $^\circ$C and milling for 8 hours. This sample is made in the form of a thin layer with Sol-Gel Spin Coating method. In this research, the variation of calcination temperature is 200 $^\circ$C, 300 $^\circ$C, 400 $^\circ$C and 500 $^\circ$C. Then to analyze the structure of thin film Hausmannite formed used X-ray diffraction. Based on characterization results using X-ray diffraction the thin layer formed based on the result of X-ray diffraction is Mn$_3$O$_4$ and Mn$_2$O$_3$. As for the variation of calcination temperature, the difference of intensity of the diffraction peaks formed then the crystal size for each calcination temperature 200 $^\circ$C, 300 $^\circ$C, 400 $^\circ$C and 500 $^\circ$C were 41.06 nm, 52.37 nm, 47.73 and 47.87 nm

1. Introduction

Manganese is one of the minerals of 12 elements that are quite abundant in the earth's crust. Manganese minerals worldwide are present with 0.1% of the Earth's crust content (Anshori, 2010). One of the manganese ore presence is found in Nagari Kawai District of Tuleh Regency of Pasaman Barat Regency. From the research (Putri, 2015) the manganese ore structure of the manganese ore from the sinter yield at a temperature of 700-1000, yielded some mineral composition one of them Hausmannite. Hausmannite has a tetragonal crystalline system with its cell dimensions = 5.76, b = 5.76, c = 9.45 Å and group space 141 / amd. Specific gravity 4.7-4.8 g cm$^{-3}$ is brownish-black. Hausmannite has a luster like metal. Hausmannite was applied as an electronic material of ceramic magnets and semiconductor materials (Feng, 1999). Currently hausmannite has been widely used in industry as a catalyst, magnetism, electrochemistry, or for air decontamination. In order to be applied as mentioned above it is necessary to improve the properties of hausmannite as it has been done (Prasetyo, 2014) which produces hausmannite nanoparticles at 8 hours milling with grain size of 90,50 nm. However the morphology of the resulting hausmannite nanoparticles has an erratic shape with an uneven size distribution. For the morphology of the nanoparticles to be irregular, the writer wants to convert these nanoparticles into thin layers which are often called thin films.

Thin film is a layer of very thin material that is between the scale of nano to millimeter. The synthesis of thin films has enormous benefits in the material world as a material to cover the weaknesses of coated materials such as anti-corrosion, the preparation of new materials before being applied as well as in the development of new materials (Dadan 2014). The method of making thin layers in general is grouped into two ie vacuum and non-vacuum method. The vacuum method consists of PVD (Phisical Vapor Deposition), Ablation Laser, Ion Planting, and CVD (Chemical Vapor Deposition). While for non vacuum method that is CSD (Chemical Solution Deposition) like sol gel.

Spin coating method can be interpreted as a method of forming a thin layer through the process of playback or spin. Spin coating method is the easiest and quickest method of thin layer growth. The thin
layer produced by this method has a high degree of homogeneity. The desired layer thickness can be controlled based on the time and spin speed of the spin coater tool. The spin coating process includes 4 stages consisting of deposition, spin up and spin off as well as an evaporation stage that determines the final thickness of the thin film (Muhlis, 2013).

2. Experimental

In the preparation of thin films of Mn₃O₄ used Manganese Acetate precursor (Mn(NO₃)₂·4H₂O). Precursor preparation was done by mixing 0.6 gram Mn₃O₄ with 15 ml 1M HNO₃. Then the precursor was mixed with C₂H₂N₂ (ethylene diamin) based on Ningsih (2013) study with a 1:2 ratio while stirring to form a homogeneous solution. Stirring is carried out at 110 °C for 3 hours using a constant-speed magnetic stirrer. A thin layer is made by a spin coating method, in which the solution is dripped on a 1 cm by 1 cm glass substrate, the substrate is rotated for 30 seconds with swivel speed of a 1000 rpm spin coating tool intended to spread the gel throughout the substrate surface and to form a flat and homogeneous layer. Then a thin layer is dried at 100 °C for 15 minutes. Further calcined with temperature variations of 200 °C, 300 °C, 400 °C and 500 °C for 1 hour to obtain manganese oxide. Furthermore, to know how the structure of the thin layer formed used X-ray difraction tool.

3. Result and discussion

The results consisted of identification of the structure of the Mn₃O₄ thin film. The process of making this thin film is done with variations of calcination temperature that is 200 °C, 300 °C, 400 °C and 500 °C. After that each thin film is characterized using X-ray diffraction.

![Figure 1. X-ray diffraction spectra of Mn₃O₄ thin film with variations of calcination temperature 200 °C, 300 °C, 400 °C and 500 °C.](image)

Figure 1 shows a diffractogram that expresses the relationship between the diffraction angle (2θ) and the intensity (I). Diffractogram shows several significant intensity peaks at a certain angle. Based on the above picture we can see from the diffraction peaks that formed the phase Mn₃O₄ and Mn₂O₃. The data obtained from the measurement results are not only the diffraction angle (2θ) and the intensity (I), but the results can also show the distance between the fields (d), the relative intensity and FWHM that we can see in Table 1. Measurements of X-rays difraction can also be used to determine the crystal structure and the size of the thin film grain.

| Table 1. Data of measurement result using X-ray diffraction with variation of calcination temperature |
| No | Temperature (°C) | Pos. [°2θ.] | d-spacing [Å] | I_r (%) | FWHM |
|----|------------------|-------------|---------------|--------|-----|
| 1  | 200              |             |               |        |     |
|    | 23,1119          | 3,84843     | 11,4          | 0,4093 |     |
|    | 33,3024          | 2,69046     | 98,61         | 0,3582 |     |
|    | 35,9584          | 2,4976      | 15,55         | 0,8187 |     |
|    | 38,5799          | 2,3337      | 10,42         | 0,614  |     |
|    | 42,1028          | 2,14623     | 18,52         | 0,307  |     |
|    | 44,5754          | 2,03275     | 21,74         | 0,307  |     |
|    | 48,767           | 1,86739     | 9,11          | 0,614  |     |
|    | 55,6217          | 1,65241     | 28,51         | 0,3582 |     |
|    | 66,1598          | 1,41247     | 8,75          | 0,8187 |     |
|    | 72,6429          | 1,30157     | 100,00        | 0,4605 |     |
|    | 88,5128          | 1,1047      | 20,56         | 0,3582 |     |
| 2  | 300              |             |               |        |     |
|    | 23,3664          | 3,80709     | 11,37         | 0,307  |     |
|    | 33,2575          | 2,69399     | 100,00        | 0,2047 |     |
|    | 38,4674          | 2,34027     | 17,57         | 0,307  |     |
|    | 44,5865          | 2,03227     | 15,83         | 0,307  |     |
|    | 55,5419          | 1,65459     | 26,59         | 0,307  |     |
|    | 59,3061          | 1,55825     | 5,31          | 0,4093 |     |
|    | 66,345           | 1,40898     | 9,89          | 0,8187 |     |
|    | 72,6744          | 1,30108     | 64,03         | 0,307  |     |
|    | 88,1641          | 1,10816     | 11,75         | 0,614  |     |
| 3  | 400              |             |               |        |     |
|    | 16,3951          | 5,40681     | 8,43          | 0,614  |     |
|    | 21,0115          | 4,22816     | 6,82          | 0,8187 |     |
|    | 26,8673          | 3,31843     | 17,04         | 0,4093 |     |
|    | 33,3086          | 2,68997     | 100,00        | 0,2047 |     |
|    | 36,192           | 2,48201     | 11,82         | 0,614  |     |
|    | 38,4859          | 2,33919     | 14,80         | 0,307  |     |
|    | 44,6071          | 2,03138     | 18,66         | 0,2558 |     |
|    | 49,0811          | 1,85617     | 15,18         | 0,4093 |     |
|    | 55,5769          | 1,65363     | 25,60         | 0,3582 |     |
|    | 69,0285          | 1,36061     | 5,85          | 0,5117 |     |
|    | 72,6814          | 1,30097     | 81,41         | 0,307  |     |
|    | 88,4271          | 1,10555     | 15,23         | 0,3582 |     |
| 4  | 500              |             |               |        |     |
|    | 23,3288          | 3,81314     | 10,28         | 0,307  |     |
|    | 26,8322          | 3,3227      | 11,59         | 0,307  |     |
|    | 33,1549          | 2,70209     | 95,68         | 0,307  |     |
|    | 36,0521          | 2,49132     | 8,89          | 0,8187 |     |
|    | 38,3885          | 2,3449      | 16,48         | 0,3582 |     |
|    | 42,0412          | 2,14923     | 16,82         | 0,3582 |     |
|    | 44,5806          | 2,03253     | 13,10         | 0,307  |     |
|    | 49,3095          | 1,84811     | 10,64         | 0,614  |     |
|    | 55,3649          | 1,65946     | 23,95         | 0,2558 |     |
|    | 66,3064          | 1,4097      | 7,39          | 0,7164 |     |
|    | 72,5745          | 1,30262     | 100,00        | 0,307  |     |
|    | 88,3237          | 1,10657     | 20,08         | 0,4093 |     |
Based on Table 1 we can see by the change of temperature of calcination which is used intensity of the diffraction peaks almost the same. This shows the difference in the phase shape of the tupis layer is almost the same. Measurements of X-ray diffraction can also be used to determine the crystal structure and the size of the thin film grain seen in Table 2.

Table 2. Relation Data of Variation of Calcination Temperature on Crystal Size

| No | temperature calcinsasi | crystal size (nm) |
|----|-------------------------|-------------------|
| 1  | 200                     | 41.06             |
| 2  | 300                     | 52.37             |
| 3  | 400                     | 47.73             |
| 4  | 500                     | 47.87             |

Based on the data in Table 2 showing the crystallite size of the thin film formed has a minimum value at 200 °C and a maximum value at 300 °C. Then at a temperature of 400 °C there is a decrease in the size of the crystal formed and this value again rises at a temperature of 500 °C. This indicates that a change in calcination temperature causes a change in crystal size of the formed Mn$_3$O$_4$ thin film.

4. Conclusions

Synthesis of Mn$_3$O$_4$ thin layer can be dilakukan with sol-gel process then continued with spin coating method. The preparation process of sol-gel is used ethylene diamin solution. The thin layer formed based on the result of X-ray diffraction is Mn$_3$O$_4$ and Mn$_2$O$_3$. As for the variation of calcination temperature, the difference of intensity of the diffraction peaks formed then the crystal size for each calcination temperature 200 °C, 300 °C, 400 °C and 500 °C were 41.06 nm, 52.37 nm, 47.73 and 47.87 nm.

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