Microstructure Study of Calcium Manganese Oxide (CaMnO₃) as Perovskite Materials

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Abstract. The use of metal oxide as an n-type semiconductor behavior is one of the important material in solar cells. Among the materials, these researches focus on perovskite structure of CaMnO₃. The single phase of CaMnO₃ synthesised by citrate method were studied for the microstructure of CaMnO₃. The perovskite structure of CaMnO₃ was characterized by using X-ray Diffraction (XRD), Fourier transform-infrared (FTIR) spectroscopy, Scanning Electron Microscope (SEM) and Thermogravimetric Analysis (TGA). Results indicated that the single phase of CaMnO₃ was revealed by XRD analysis. The specific interactions in the metal oxide and hence about the complexation led by FTIR. The morphological structure of the samples was studied by SEM, which confirmed the XRD analysis. While TGA analysis affirmed the CaMnO₃ was formed.

1. Introduction

The major problems that conduct to an increment contamination of environmental effected from uncontrolled use of fossil fuel [1]. There is little anxiety that modern civilization faces on expanding need for alternative energy sources. Solar energy is the most abundant and readily accessible of energy sources [2, 3]. Photovoltaic technology offers the efficient to convert the solar power into useful electrical power. Material and processing costs of photovoltaic technology were considered too expensive [4].

Currently, metal oxides are extensively use in various fields such as the semiconducting materials [5], the photocatalytic efficiency [6], the oxidative mineralization [7] and others. However, the development of a perovskite structure focused on the cost capability of the process by the use of renewable solar energy source. Calcium containing mixed oxides, such as Ca₂Fe₂O₅, CaMnO₃, CaTiO₃ and CaZrO₃ with perovskite structure considerable interest as potentials for solar energy [8, 9].

From the foregoing, perovskite structures have received much attention in electrochemical and biomimetic applications. The CaMnO₃ deserve special attention in the context of developing alternative n-type in solar cells due to the high affluence, environmental friendliness and the low cost [10]. Recent studies for the purpose of investigating the electrical properties of CaMnO₃ due to adsorption of water are necessary to synthesize CaMnO₃ at low temperature [11].
Consequently, various methods like freeze drying, combustion process and gel synthesis have been used for the preparation of highly homogenous and fine powder perovskite oxide materials. The citrate method was found for several advantages, mainly the production of starting materials form high quality [12]. Therefore, it is reasonable to believe that method requires a relatively low temperature and short duration to produce the oxide.

In the present work, with the aim of the microstructure properties of CaMnO$_3$ using the citrate method produce the perovskite structure which is can be potential for solar cells. Since, there seems to be the attention in more detailed examination of these work is discussed based on the experimental results.

2. Methodology/Materials

2.1 Preparation of CaMnO$_3$ perovskite

The powder CaMnO$_3$ perovskite structure was synthesised by citrate methods. The small amount of deionized water molar ratio of calcium acetate was mixed with manganese acetate to citric acid anhydrous were fixed at 1:2 and continuously stirring to improve the contact. The amount of citric acid used was that requisite to bind all the metal ions when all the acetate ions were replaced by citrate. The water from that solution was dried at 100 °C until a viscous gel was formed. The product was calcined at 700, 800, 900 and 1000 °C for 24 h to resulting in powder on order particle size less than 100 µm.

2.2 X-ray Diffraction (XRD) Study

The phase purity structure of CaMnO$_3$ calcined at 700, 800, 900, 1000 °C were characterized using MiniFlex II diffractometer with Cu Kα radiation. A little amount product of sample was spread uniformly on the sample holder, the diffraction angles 2θ scan were carried out at 5° to 80° due to speed 2.00°/min.

2.3 Fourier transform-infrared (FTIR) spectroscopy

The functional group of reaction (citrate process) were identified using IRTrace-100 Fourier Transform Infrared Spectrophotometer (SHIMADZU) with resolution of 4 cm$^{-1}$. The measurements were recorded at room temperature in the range 400-4000 cm$^{-1}$.

2.4 Scanning Electron Microscope (SEM)

The structural development of Calcium Manganese Oxide was analysed by using SEM, model JEOL JSM-6360LA. SEM was indicated of electron microscope that form images by scanning the microstructure of samples with a focused beam of electrons. The magnification of the SEM was at 10 kV.

2.5 Thermogravimetric Analysis (TGA)

TGA analysis measures weight change and the rate of weight change due to the aspects of temperature, time and atmosphere. Measurements are used primarily to determine the composition of materials and to predict their thermal stability. TGA measurements were conducted using the instrument in a alumina crucible about 5 mg of sample, under argon atmosphere (10 ml/min) from 30 °C to 900 °C with an increasing temperature rate 10 °C/min on the sample powder obtained by pouring a mixture of Calcium Acetate and Manganese Acetate nanopowder into a crucible and then drying at 100 °C for an hour.

3. Results and Discussion

3.1 XRD Analysis
X-ray Diffraction (XRD) is one of the functional and beneficial techniques that give the specified information about the chemical composition and crystallographic structure material of the sample. In this study, the XRD is used in command to analyse the presence of the phases of synthesized compounds whether is in crystalline or amorphous state.

The XRD pattern of CaMnO$_3$ samples due to structural changes was shown in Figure 1. There are several reaction temperatures heating known as 700, 800, 900 and 1000 °C for 24 hours [13]. For the starting temperature at 700 °C the sample became amorphous powder with some peak start appear after annealed because of the sample did not expose spontaneous combustion [14]. It was also supported due to high irregular temperature profile on the sample affected from the complication to control the combustion [15]. The peaks seen were calcium carbonate where it is a peak that wants to remove to get CaMnO$_3$. The XRD analysis was revealed the low peak intensity at 800 °C was expected that the CaMnO$_3$ was started form in intermediate phase. When the sample was heated at 900 °C, new peaks appear and finally the solid state reaction conduct to the pure CaMnO$_3$ perovskite structure phase which was also known as single phase was obtained and sharp peak exhibit the crystal phase [16].

The CaMnO$_3$ phase was affirmed by hkl values due to the literature data for corresponding perovskite structures of CaMnO$_3$ (JCPDS card no. 50-1746) [8]. The diffraction peaks at 2θ of 23.8°, 34.0°, 40.1°, 41.9°, 48.8°, 55.0°, 60.8° and 71.6° are corresponding to (020), (002), (112), (022), (040), (141), (123) and (004) crystallographic planes of orthorhombic structure, respectively. According to Kompany et al., [17] and Markovich et al.,[18] the size distribution of the CaMnO$_3$ were 24 nm and 50 nm. Moreover, the average crystallite size for the CaMnO$_3$ at 900 °C that calculated was 27 nm, as attributed from the XRD line broadening by the Scherrer equation below:

$$D = \frac{k\lambda}{\beta \cos \theta}$$

where $D$ is the average crystallite size (nm), $\theta$ is the angle of diffraction, $k$ is Scherrers constant (k=0.94), $\lambda$ is the X-ray wavelength (0.15405 nm) and $\beta$ is the full width at half maximum of the diffraction peak in radian (FWHM).

![Figure 1. XRD patterns of the synthesized CaMnO$_3$ by calcination at 700 °C, 800 °C, 900 °C and 1000 °C.](image-url)
3.2 FTIR Analysis

FTIR analysis of CaMnO$_3$ samples calcined at several reaction temperatures of 700, 800, 900 and 1000 °C respectively are illustrated in Figure 2. For starting calcined at 700 °C gives a product with strong band of CaCO$_3$ at 873 cm$^{-1}$ while the other band at 1419 cm$^{-1}$ was assigned the broad MnCO$_3$ [19]. In addition, the band for product calcined at 800 °C also corresponds to the broad MnCO$_3$ at 1419 cm$^{-1}$ and indicate loss strong band of CaCO$_3$ [20].

Besides, the products formed after calcined at 900 °C gave complex spectra. The sharp band at 513 cm$^{-1}$ presents the very strong band of CaMnO$_3$ [21]. This performance indicated the formation of a perovskite structure of CaMnO$_3$. The very strong band was assigned to the M-O stretching and O-M-O deformation modes of CaMnO$_3$. While the strong band of CaMnO$_3$ also appear at 1010 cm$^{-1}$ and the broad band of CaMnO$_3$ at 1417 cm$^{-1}$. Thus, an optimum calcination temperature is important during the synthesis perovskite structure of CaMnO$_3$. It is affirmed by performance of the product calcined at 1000 °C. The product shows the strong band of CaMnO$_3$ at 1600 cm$^{-1}$ while the broad band CaMnO$_3$ at 518 cm$^{-1}$.

![FTIR spectrum of the synthesized CaMnO$_3$.](image)

Figure 2. FTIR spectrum of the synthesized CaMnO$_3$.

3.3 SEM Analysis

The SEM images indicate that the morphology of the samples is definitely different, depending on the temperature of calcination. Through this analysis revealed the nanostructure and shows particle size of CaMnO$_3$ in SEM image correspond with XRD results. This morphological change is inherently due to the higher calcination temperature and longer reaction time of the latter process due to formation perovskite structure of CaMnO$_3$ [22].

Figure 3 shows the SEM micrographs at four different calcined temperatures 700 °C, 800 °C, 900 °C and 1000 °C respectively. SEM images reveal lesser void due to calcined temperature increased. It is also affected the elimination of porosity when grain growth in progress occurred due to Figure
3(a) and (b). The SEM image at Figure 3(c) indicates the SEM images of the CaMnO$_3$ perovskite structure with thermal annealing at 900 °C for 24 hours and shows particle size of CaMnO$_3$ image correspond with XRD results. It was also revealed the fine particle with consistent size. The small particle sizes provide the large surface attributed highly homogeneous compared with others sample. From figure 3(d) it can be seen that the sample shows a porous structure. This porous morphology act to release of a large volume gases during the calcined process.

**Figure 3.** SEM images of the CaMnO$_3$ after heat treatment at 700 °C (a), 800 °C (b), 900 °C (c) and 1000 °C (d).

### 3.4 TGA Analysis
Thermogravimetric Analysis (TGA) is functional to measure the weight loss in the material and consider their thermal stability under high temperature [23]. Commonly, thermal stability of the material is important to be investigated due to the increment stability thin film of solar cell stable under high stability thin film of solar cell stable under high temperature environment over long period of time [24].

Based on the curve of Thermogravimetric analysis pattern Figure 4 is the representative sample of CaMnO$_3$. The curve show the process of weight decomposition start with an endothermic reaction that occur between temperature 30 °C to 200 °C, the curve is considered to be due to loss of water ascribing to evaporation of adsorbed water. Further weight loss during the 200 °C to 400 °C attributed the decomposition of excess citric acid that present in the sample during the process of mixing the compound of calcium acetate and manganese acetate using citrate method. From 400 °C to 600 °C the TGA curve exhibits slow decomposition of the removal of organic impurities. On further heating over a temperature in the interval between 600 °C and 900 °C indicates the removal of the surface hydroxyls and evaporation chemisorbed water. Thus, in order to minimize energy consumption in
calcination, 900 °C was selected as calcination temperature since, the entire active crystalline phase were found to be prominent at 900 °C temperatures.

Figure 4. TGA curves of the synthesized CaMnO₃.

4. Conclusion
This study has shown conclusively that CaMnO₃ perovskite structure was successful produced at thermal annealing at 900 °C with the citrate method. Besides, the citrate method with auto ignition is a very simple and appropriate to obtain a very fine and homogenous powder of CaMnO₃ at low temperature with a drastic lower in the reaction time. XRD patterns affirmed the presence of CaMnO₃. The sharp band at 513 cm⁻¹ presents the very strong band of CaMnO₃ was observed respectively by FTIR to indicate the formation of the perovskite structure of CaMnO₃. While TGA analysis showed that stability of sample was formed at 900 °C. From these results, we can conclude that the perovskite structure of CaMnO₃ clearly formed at 900 °C.

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