CHARACTERISTICS OF LaCrO3 NANOMATERIAL : THE EFFECT OF CALCINATION TEMPERATURE

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**Abstract**. LaCrO3 nanomaterial has been prepared using sol – gel and freeze drying method, simultaneously. Preparation of material was carried out by dissolving nitrate salts of lanthanum, and chrome in pectin solution and then the sample was stirred thoroughly using magnetic stirrer while adjusting pH to 11 until the gel formed. After freeze-drying process, the precursors were subjected to the calcination treatment at 600, 700, and 800°C, respectively and subsequently characterized using the techniques of X-ray diffraction (XRD), TEM and DRS analysis. The results proved that a major crystalline phase of LaCrO3 perovskite is formed as temperature calcination increased. Crystallite size identification using Scherrer equation proved that the size greater as temperature calcination increased. Then, grain size analysis using TEM proved that calcination temperature gave a small effect to the size. DRS analysis also proved that band gap energy is affected by temperature calcination, and the value is in the range of 2.9 eV.

**Keywords**: Nano, perovskite, band-gap energy, sol-gel, freeze-drying

1. Introduction.

One of the fascinating materials which is widely used in industrial applications, such as photovoltaic solar cell [1, 2], optical coating [3, 4], ceramics [5, 6], magnetic materials [7, 8], sensors [9, 10], and catalyst [11, 12] is perovskite compound. It exhibits a peculiar physical and chemical characteristics such as conductivity, ion mobility through lattice of crystal, thermal and chemical stability, acid and base sites properties, magnetic property, electrocatalytic and photocatalytic manners.

 In principle, perovskite material presenting ABO3 general formula can be synthesized by mixing the salt or oxide of rare earth or third main group elements with the salt or oxide of the transition elements. The larger cations fitted into the A sites while the smaller cations fitted B sites in the crystalline structure. The simple ABO3 composition obeys the limits of the tolerance factor, t = 0.71(rA+ro)/(rB+ro) [13 – 15]. This t – value led to the formation of crystalline structures such as cubic, orthorhombic, and hexagonal form.

 To pronounce the characteristic of perovskite materials on its application, the choice of preparation methods such as sol-gel [16, 17], coprecipitation [18, 19], hydrothermal [20, 21], and auto-combustion [22, 23] plays an important role. Even though so many methods of preparation have been claimed to give an excellent result [24, 25], the sol-gel method offers some advantages such as homogenous product, large surface area, control its stoichiometric composition, and nanosize particles [26, 27].

 So, in this study, we report the effect of temperature calcination on the characteristics of nano size LaCrO3 which is synthesizedusing the sol-gel method by combining the use of pectin as green emulsifying agent and freeze-drying process for drying of the gel.

1. Experimental Section.

## 2.1. Materials and Instruments

La (NO3)3.6H2O, NH3, and Cr(NO3)3.9H2O used are reagent grade chemicals obtained from Merck. Pectin as the emulsifying agent was purchased from the local market and distilled water was produced in our laboratory. Characteristics of perovskite sample were studied using X-ray Diffraction, XRD (Philips-PW 1710), Transmission Electron Microscopy, TEM (JEOL, JEM-1400), and Diffuse Reflectance Spectrophotometer, DRS (Shimadzu 2450). A Nabertherm electrical furnace (Lilienthal, Germany) was used for calcining the sample.

## 2.2. Procedure

Solid LaCrO3 was prepared by dissolving specified mass of La(NO3)3.9H2O, and Cr(NO3)3.6H2O,

respectively in 100 mL pectin solution 4%. The mixture was stirred until the homogenous solution was obtained, and then freeze-dried. Dry samples were calcined to 600, 700, and 800°C, respectively, using temperature program with a temperature increase of 2 °C min-1. While the final temperature has been reached, the calcination temperature is attained for 2 hours.

## 2.3. Characterization

To compare the characteristics of LaCrO3 obtained using a mixture of both sol-gel and freeze drying methods, these samples were characterized using several techniques. The structural and crystalline phase formed were identified using X-ray diffraction analysis. The instrument was conducted using Cu Kα radiation (l = 1.5418 Å), produced at 40 kV and 30 mA, with a step size of 0.02. To evaluate the surface morphology and microstructure, the samples were characterized using TEM. The analysis was conducted on polished and thermally etched samples with different magnifications[28]. Then, the band-gap energy of the sample was analyzed by diffuse reflectance spectrophotometer.

1. Result and Discussion

Materials that have been prepared were analyzed using some instruments such as X-ray Diffraction, Transmission Electron Microscopy, and Diffuse Reflectance Spectroscopy as explained as follow :

*3.1. X-Ray Diffraction Analysis*

The XRD patterns of the samples calcined at 600, 700 and 800ºC were both collected and treated qualitatively by comparing the diffraction peaks with the standard Powder Diffraction data base of JCPD files. The investigation showed that LaCrO3 perovskite as a major phase [29]. Furthermore, in this paper, the Rietveld method in the fullprof program is used to study the effect of calcination temperature on phase composition and unit cell parameters formed. The Rietveld plot is depicted in Figure 1 below. Then, it is shown that the diffractograms, in principle, are practically similar, with the difference in the intensity, the position, and hkl plane of the highest intensity.



Figure 1. XRD Rietveld plot for LaCrO3 calcined at (a). 600°C, (b). 700°C, and (c).800°C, respectively. The observed data are shown by a solid line and calculated data by red-dot line. The vertical line (green) represents the hkl plane. The blue line is the different profile between observed and calculated data.

As shown in Fig. 1, the difference between observed and calculated data is quite small, so that Rietveld refinement took place in very good agreement. The overall Rietveld refinement results of LaCrO3 is shown in Table 1.

Table 1. Rietveld refinement results of LaCrO3 calcined at 600, 700, and 800°C, respectively

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| LaCrO3 calcined at | hkl | JCPDFile | χ2 | a (Å) | b (Å) | c (Å) | V (Å3) |
| 600°C | 110 | 44-0333 | 1.5 | 3.8842 | 3.8842 | 3.8842 | 58.6096 |
| 700°C | 121 | 33-0701 | 1.7 | 5.4788 | 7.7575 | 5.5148 | 234.3888 |
| 800°C | 112 | 24-1016 | 2.1 | 5.5162 | 5.4805 | 7.7522 | 234.3609 |

Table 1 shows the goodness of fit (χ2) values in all LaCrO3 prepared is relatively low, which is obeyed the basic principle of fit, χ2 ≤ 4 [30], so that it is accepted and satisfactory. The main phase observed in different calcination temperature is perovskite LaCrO3, however, the crystalline structure is quite different. In calcination temperature at 600°C, the structure is cubic with hkl plane 110, according to PDF 44-0333. As the temperature of calcination increased, the structure was transformed to orthorhombic. The hkl plane between the sample calcined at 700 and 800°C is also different that is 121 and 112, respectively. As a consequence, by structure transformation, the volume of the unit cell is also increased as the temperature of calcination augmounted.

## 3.2. Transmission Electron Analysis

Characterization of the samples using TEM depicted in Figure 2. This study revealed that agglomeration of the particles among the samples occurs. However, the existence of crystalline structure as a unit cell is still identified even hard. As shown in Fig. 3a, the shape of the crystal is cubic in the certain position (red-arrow). In Fig. 3b, the shape of LaCrO3 is orthorhombhohedral in certain sites (red arrow) and hexagonal (green arrow). Then, in Fig.3c, the shape of the crystal is also identified as rhombohedral (red arrow) and hexagonal (green arrow). The size of crystalline shape except the agglomerated crystalline is below 50 nm. Thus, it can be considered as nano material.



Figure 2. Micrographs of LaCrO3 calcined at (A). 600oC, (B). 700oC, and (C). 800oC

## 3.3. Diffuse Reflectance Spectroscopy Analysis

To determine the band gap of a powder sample using the diffuse reflectance spectrophotometer is a common technique [31]. So, in this study the band – gap energy is calculated using a Kubelka – Munk method [32] based on the equation below :

α(hν) ≈ β (hν - Eop)n (1)

where βis a constant, n is an index, assuming the values of 1/2, 3/2, 2 or 3, depending on the nature of the electronic transition responsible for absorption mechanism of electron transition. The exponent *n* = ½ or 3/2 for direct transition is allowed or forbidden in the quantum mechanical sense, and *n* = 2 or 3 for allowed and forbidden indirect transition, respectively [33]. The relation between (*α hv*)2 versus (*hv*) plot according to Equation (1) is shown in Fig. 3. The direct optical energy gap can be obtained from the intercept of the resulting straight lines with the energy axis at (*α hv*)2 = 0.



Figure 3. Band Gap Energy of LaCrO3 calcined at 600°C (a), 700°C (b), and 800°C (c)

The band gap energy of LaCrO3 prepared at 600, 700 and 800°C is 2.62, 2.89, and 2.98 eV, respectively. This result implied that the increase in temperature of calcination gave an effect to wider the band gap energy LaCrO3. Furthermore, the band gap energy of LaCrO3 calcined at 800°C is an agreement to the previous research [34].

1. Conclusion

This current study demonstrated the effect of calcination temperature on the LaCrO3 characteristic.

The XRD results revealed that crystalline phase formation was influenced by the calcination temperature applied. As the temperature of calcination increased to 700 and 800°C, the elongation of one side of unit cell parameter, for instance, b and c, is happened, respectively. As a consequence, the volume of unit cell increased as well as surface area. The morphology of the samples as seen by TEM is characterized by the existenceof particles with varied sizes and shapes. It can be implied that nanomaterial of LaCrO3 is formed and its smallest size is less than 50 nm. Furthermore, the band gap energy obtained is also affected by the temperature of calcination. Its value increased as the calcination temperature augmounted.

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