Synthesis and characterization of LaCr\((1-x)\)Mo\(x\)O\(3\)

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Abstract. LaCrO\(_3\) is a well known perovskite compound utilizing as semiconductors, catalysts, fuel cell, electronic devices, and others. In this preliminary study, the properties of LaCrO\(_3\) added by varying Mo contents were examined. The LaCr\((1-x)\)Mo\(x\)O\(3\) (with \(x=0.01\) and \(0.03\)) were synthesized by sol-gel pectin method using La, Cr nitrate, and ammonium molybdate as precursors, freeze-dried, and followed by calcination at 700 °C for 3 hours. The prepared materials were characterized using XRD, TEM, and DRS. The formation of the compounds for \(x=0.01\) are La\(_2\)Mo\(_2\)O\(_9\), LaCrO\(_3\), and Cr\(_2\)O\(_3\), and for \(x=0.03\) are La\(_2\)Mo\(_2\)O\(_9\), LaCrO\(_3\), and La\(_2\)O\(_3\). The crystallite sizes were determined using Scherrer formula and they are found to be 24 nm (\(x=0.01\)) and 33 nm (\(x=0.03\)). The TEM images showed that the obtained grains size was in the range of 24 nm (\(x=0.01\)) and 34 nm (\(x=0.03\)). The bandgap values are 2.59 eV for \(x=0.01\) and 2.68 eV for \(x=0.03\).

1. Introduction

Perovskite compound has been studied a lot because of its attractive characteristics, e.g. magnetic, dielectric\(^1\), ionic semiconductor\(^2\), catalytic, and ferroelectric\(^3\). It has been widely used for industrial applications and also can be synthesized in solution at low temperatures\(^4\). Among its widely used in application, photocatalysis became one of the interesting uses. Since perovskite compound has a capability in light absorption, and then promote electron from valence to conductance band it is suitable applied as photocatalytic material\(^5\).

Perovskite structure has a simple cubic cell with general formula ABX\(_3\) in every cell unit where A at the corners of a cube, B at the body center, and X at the center of the faces. A ion is usually derived from the alkali, lanthanide, or actinide group, while B ion is usually from 3d-5d transition metals. Their chemical and physical properties can be improved depending on the element chosen for the B site. X is an anion that is bound to A and B, usually oxygen, but can also be other ions such as halides, sulfides, or nitrides\(^6\).

The formation of a unique characteristics that could be applied to various usages is determined by the choice of both preparation method and the choice of its constituent elements. As known, sol-gel method is accustomed to be used in preparing materials. Because this method has some advantages which are...
more homogeneity and pure, lower preparation temperature, good mixing for multicomponent systems, effective to control the size, shape, particle properties, surface area, pore-volume, and pore size distribution, better gel products with special characteristics, and possible to design the structure and properties of the material through the selection of the suitable sol-gel precursors and other building blocks[5, [6]. So, in this study, the sol-gel method was chosen using pectin solution as an emulsifying agent. Furthermore, Mo cation was chosen as a dopant in the LaCrO₃ perovskite structure because Mo cation has good catalytic activity in the form of oxide [7] and composites [8] in the photocatalytic reactions. Furthermore, the use of Mo cation as a dopant in small amounts, is intended to keep the main structure of LaCrO₃ perovskite remains majority because thermodynamically, Lanthanum will more quickly combine with Molybdenum to form monoclinic La₂MoO₆ or La₂Mo₂O₉ compared to chromium to form perovskite LaCrO₃[9,[10].

So, in this chance, this paper reported on the synthesis and characterization of perovskite LaCr₁₋ₓMoₓO₃ (with x=0.01 and 0.03) nanoparticles using sol-gel method and pectin as an emulsifying agent.

2. Experimental

2.1. Materials

The precursors used were La(NO₃)₃·6H₂O, Cr(NO₃)₃·9H₂O, and (NH₄)₆Mo₇O₂₄·4H₂O. NH₃ was used to maintain the pH. The emulsifying agent used was pectin powder.

2.2. Methods

2.2.1. Synthesis of LaCr₁₋ₓMoₓO₃

LaCr₁₋ₓMoₓO₃ were prepared by sol-gel pectin method and continued by freeze-drying and calcination. 8 gram of pectin was added into 400 ml of distilled water and maintain under magnetic stirring at room temperature till homogenized. Ammonia was added at a certain volume to get pH 11. The precursors were made by dissolving La(NO₃)₃·6H₂O and Cr(NO₃)₃·9H₂O at the appropriate amount in distilled water and then introduced dropwise into pectin solution under continuous stirring. The mixture was heated on a hot plate at 70-80 °C with stirring until gel was formed. The pH is maintained at 11 during the process by ammonia addition. The gel was dried using freeze-drying method and followed by calcination at 600 °C for 2 hours. The material was ground and prepared for the next step.

1 gram of pectin dissolved into 50 mL of distilled water was used as an emulsifying agent. The pH of the solution was adjusted at 11 by ammonia addition. The stoichiometric amount of (NH₄)₆Mo₇O₂₄·4H₂O was diluted into distilled water and mixed thoroughly into the pectin solution with the ground material got before. After evaporating the solvent at 70-80 °C for several hours, the gel obtained has been freeze-dried and calcined at 700 °C for 3 hours. Finally, the product was ground and characterized.

2.2.2. Characterization

X-ray diffraction (XRD) data was used to identify the crystalline phase. Transmission electron microscopy (TEM) analysis was carried out to confirm the morphology and size of the particles. Diffuse reflectance spectrometer (DRS) was used to calculate bandgap energy.

3. Result and discussion

3.1. XRD analysis

Diffractograms of the material are represented in Figure 1. The crystallite size (D) of the materials was calculated in accordance with the Debye–Scherrer formula:
where $\lambda$ is the wavelength of the X-ray radiation, $\beta$ is full width at half maximum (FWHM), and $\Theta$ is the Bragg angle of the plane. It was found that the crystallite size for $x = 0.01$ was 24 nm and for $x = 0.03$ was 33 nm. From the detectable peaks, for $x = 0.01$ and $x = 0.03$, the same identified phase were La$_2$Mo$_2$O$_9$ and LaCrO$_3$. And the different phase detected for $x = 0.01$ was Cr$_2$O$_3$ and for $x = 0.03$ was La$_2$O$_3$. It means that the less Cr used as precursor, Cr$_2$O$_3$ will be not formed because there is not enough Cr as source but La$_2$O$_3$.

![Figure 1. XRD of samples(a) $x=0.01$ and (b) $x=0.03$: marks at some peaks stand for La$_2$Mo$_2$O$_9$ (x), LaCrO$_3$ (y), Cr$_2$O$_3$ (z), La$_2$O$_3$ (o).](image1)

3.2. TEM

As observed in Figure 2, particle size of sample a ($x=0.01$) is more uniform than sample b ($x=0.03$). Based on the obtained image in Figure 2a, the average diameter of the particle is 24 nm and there are shape of hexagonal, sphere, and cubical. While in Figure 2b the size is 34 nm with sphere form. Mo atomic size is bigger than Cr. When Cr is substituted with Mo, it causes the particle diameter bigger.

![Figure 2. TEM images of samples (a) $x=0.01$ and b $x=0.03$](image2)
3.3. DRS

By knowing the bandgap energy, the energy required to promote an electron from highest occupied molecule orbital (HOMO) to lowest un-occupied molecular orbital (LUMO) level will lead to its application. The bandgap energy is determined by using Kubelka-Munk method with this equation:

\[ F(R) = \frac{(1-R)^2}{2R} \]  \hspace{1cm} (2)

where \( R \) is the reflectance; \( F(R) \) is proportional to the extinction coefficient (\( \alpha \)). By multiplying the \( F(R) \) function by \( h\nu \) using the corresponding coefficient (\( n \)) associated with an electronic transition, we can modify Kubelka–Munk function as follows:

\[ (F(R) \times h\nu)^n \]  \hspace{1cm} (3)

where \( h \) is the Planck’s constant (J.s) and \( \nu \) is the light frequency (s\(^{-1}\)). \( E_g \) is obtained from graphical analysis, by plotting this equation as a function of the energy in eV. The recorded UV–Vis spectrum in the reflectance mode is transformed into an \( F(R) \) magnitude and plotted versus \( h\nu \) \[11\]. The \( E_g \) value was obtained by extrapolating the slope to \( \alpha = 0 \). Calculated bandgap energy from Figure 3a is 2.59 and Figure 3b is 2.68.

![Graphical representation of modified Kubelka–Munk (\( \alpha h\nu \))^2 versus Energy for (a) x=0.01 and (b) x=0.03](image)

In the LaCr\(_{1-x}\)Mo\(_x\)O\(_3\) perovskite structure, electronic properties are formed from chemical bonds between oxygen and metals (La, Cr, and Mo). Cations Cr and Mo have a greater influence on the bandgap energy value than cation La. Mo has an electronegativity of 2.16, Cr 1.66, and O 3.44. Mo is more electronegative than Cr, so a difference of the electronegativity between Mo and O (1.28) is smaller than that of electronegativity between Cr and O (1.78). The greater the difference in electronegativity, the higher the energy bandgap perovskite material. In the LaCr\(_{1-x}\)Mo\(_x\)O\(_3\) catalyst, the more substitution of Mo to Cr will cause the smaller electronegativity difference between the cation Cr and O so that the bandgap should be smaller. However, this is not in accordance with the bandgap calculation in this result. The increase in bandgap energy may be caused by two reasons: (i) bandgap tailings, a consequence of the distribution of impurities in the material especially for polycrystalline samples \[12\], and (ii) the Moss-Burstein effect \[13, 14\], which occurs when the concentration of the carrier exceeds the density of the edge of the conduction band so that absorption rises to a higher energy level. Bandgap values obtained were 2.59 and 2.68 eV. Based on the previous research, the bandgap energy value for LaCrO\(_3\) is 3.39 eV and LaCr\(_{0.90}\)Ir\(_{0.10}\)O\(_3\) is 2.66 eV \[15\]. It has an electronegativity of 2.28, while Mo is 2.16. Electronegativity values which are almost the same give an electronegativity difference between metals and oxygen the same so that it gives the same effect on the change in the bandgap energy value which is around 2.6.
4. Conclusion

LaCr\(_{(1-x)}\)Mo\(_x\)O\(_3\) synthesized by pectin sol-gel method and calcination at 700 °C with the variation of \(x=0.01\) and 0.03 has been shown the formation of that mixed oxide compounds as La\(_2\)Mo\(_2\)O\(_9\), LaCrO\(_3\), Cr\(_2\)O\(_3\), for \(x=0.01\) and La\(_2\)Mo\(_2\)O\(_9\), LaCrO\(_3\), La\(_2\)O\(_3\) for \(x=0.03\). Average crystallite size calculated from Scherrer equation as 24 nm (\(x=0.01\)) and 33 nm (\(x=0.03\)) while with the TEM estimated average particle size of 24 nm (\(x=0.01\)) and 34 nm (\(x=0.03\)). Based on the graphical analysis of modified Kubelka–Munk function, the bandgap energy of \(x=0.01\) is 2.59 and \(x=0.03\) is 2.68. LaCrO\(_3\) has been mostly employed in solid oxide fuel cells. However, the bandgap energy of engineered LaCrO\(_3\) can be used in different research areas such as electronic and optical devices, photocatalysts for water splitting, as well as solar cells.

5. References

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