A Facile Synthesis of Mayenite Nanopowders Using Co-Precipitation Method

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ABSTRACT

Mayenite Ca$_{12}$Al$_{14}$O$_{33}$ nanopowders have been synthesized using co-presentation route. X-ray diffraction analysis (XRD), field emission scanning electron microscopy (FE-SEM), Fourier transform infrared spectrum (FTIR) and ultraviolet-visible-NIR spectroscopy are utilized to study the effect of annealing temperature and time on the structural, crystallite size, microstructure and optical properties of the formed powders. XRD profile demonstrated that well-crystalline pure cubic Ca$_{12}$Al$_{14}$O$_{33}$ phase was indexed from the precipitate precursors synthesized using ammonium carbonate as base at pH 7 then annealed at low temperature 800 °C for 2h. The average crystallite size was increased by the annealing temperature and time. It was increment in the range 54.3 to 159.9 nm. Meanwhile, lattice constant and theoretical X-ray density were found to increase with increasing temperature and time. The microstructures of the powders were appeared as nano-layers. Besides, ultraviolet-visible-NIR (UV-Vis-NIR) spectroscopy was studied. The band gap energy of the Ca$_{12}$Al$_{14}$O$_{33}$ nanopowders was diminished from 3.81 to 4.45 eV with raising temperature from 800 to 1200 °C, respectively.

Key words: Transparent conducting oxide (TCO), Mayenite, Nanocrystalline, Crystal structure, Surface microstructure, Optical Properties.

1. Introduction

Currently, there is a worldwide interest in developing transparent conducting oxides (TCOs) for the development the electronics and photonic devices. Transparent conducting electrodes (TCE) are widely used as solar cells (Das and Ray, 2004; Fortunato et al., 2007), flat panel display (He and Kanicki, 2000; Minami, 2005; Hosono, 2004), organic light emitting devices (Kim et al., 1999; Kim et al., 2000; Kim et al., 2009), surface acoustic wave device (Zhao et al., 2005) and gas sensing devices (Shukla et al., 2006). Accordingly, they are materials that combine electrical conductivity and optical transparency, having a carrier concentration of at least 1020 cm$^{-3}$ and an optical band gap of more than 3 eV (Gordon, 2000). Their optical band gaps are so large that visible photons cannot excite electrons from the topmost valence to a conduction band, resulting in light transmission (Thatribud et al., 2014).

Among them, calcium aluminium oxide (mayenite, 12CaO.7Al$_2$O$_3$, abbreviated as C12A7:O$_2^-$ or C12A7) is found to have unique physical and chemical properties based on its special crystal nanocage structure (Toda et al., 2011; Hayashi et al., 2003; Kim et al., 2011; Liu et al., 2013; Matsuishi et al., 2013). Additionally, in this insulating compound, O$^2-$ ions are caged species that compensate for the positive charge of the ~0.4 nm cage and the electrical conductivity can be simply replaced by replacing these anions with electrons (Matsuishi et al., 2013; Matsuishi et al., 2009). Alongside, mayenite is also an important material as a transparent conductive oxide (TCO) for VOCs cleaning and ionic conductor.

From the best of our knowledge, the synthesis of mayenite nanopowders is accomplished at high temperature (Tolkacheva et al., 2011). Meanwhile, the synthesis of mayenite nanopowders by co-precipitation method is not published elsewhere.

Therefore, in this study we report synthesis of mayenite nanopowders using a novel and facile co-precipitation method at relatively low annealing temperature. The crystallo-chemical aspects including, phase structure, crystallite sizes, space lattice parameters and crystal morphologies were carefully investigated. Moreover, the change in optical properties of the prepared samples using FTIR and UV-Vis-NIR was studied.

2. Experimental:

2.1. Materials:

Mayenite nanopowders have been synthesized using co-precipitation method. Chemically grade aluminum chloride AlCl$_3$ and calcium carbonate CaCO$_3$ were used as starting materials. Ammonium carbonate

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was used whereas hydrochloric acid (HCl, ADWIC 33%) was employed as leaching agent for transfer CaCO₃ into calcium chloride solution.

2.2. Preparation:

Mayenite nanoparticles have been prepared by mixing solution of aluminum chloride and calcium chloride results from dissolving calcium carbonate with 50 ml HCl at Ca:Al molar ratio 12:14. Then, a certain amount of ammonium carbonate to added gradually into the aqueous solution until pH = 7. After that, the solution was stirred gently for 15 min and filtrates with washing with deamnozied water and ethanol, and then dried at 100 °C for 24 h overnight. The dry precursors were thermally treated with different annealing temperatures ranging from 600 to 1200 °C for various times 0.5 to 2 h.

2.3. Characterization:

XRD patterns of the resulting products were identified using a Brucker D8-advance X-ray powder diffractometer with Cu Kα radiation (λ = 1.5406 Å). The crystallite size of the produced mayenite for the most intense peak (4 2 0) plane was determined from the X-ray diffraction data based on the Debye-Scherrer formula:

\[ d_{X} = \frac{k \lambda}{\beta \cos \theta} \]  

Where \( d_{X} \) is the crystallite size, \( k = 0.9 \) is a correction factor relative to account for particle shapes, \( \beta \) is the full width at half maximum (FWHM) of the most intense diffraction peak (4 2 0) plane, \( \lambda \) is the wavelength of Cu target = 1.5406 Å, and \( \theta \) is the Bragg angle. The micrographs of produced samples were performed by direct observation via filed emission scanning electron microscope (FE-SEM) model JEOL instrument (Japan) model JSM-7800F. Fourier transform infrared spectrum (FTIR) was fulfilled using Jasco 3600 spectrophotometer. The UV–Vis-NIR absorption spectrum was recorded by a UV–Vis–NIR spectrophotometer (Jasco-V-570 spectrophotometer, Japan fitted with integrating sphere reflectance unit).

3. Results and Discussion

3.1 X-ray diffraction analysis:

Fig. 1 depicts XRD patterns of the precipitated precursors annealed at different temperatures 600 to 1200 °C at 2 h. It can be obviously observed that the increasing temperature led to enhancing the formation of cubic mayenite (Ca₁₂Al₄O₃₃) phase. At low temperature of 600 and 700 °C, an impurity phase of calcite (CaCO₃) (JCPDS # 05-0586), calcium chloride (CaCl₂) (JCPDS # 49-1092) and calcium azide hydrate (Ca(N₃)₂·1.5H₂O) (JCPDS # 21-0833) were detected. Otherwise, further increasing the annealing temperature to 800 °C was ascribed the formation of single cubic Mayenite (Ca₁₂Al₄O₃₃; space group I4₃d) phase which was matched with (JCPDS card # 48-1882). The crystallite size of the formed powders was increased with increasing the annealing temperature. The crystallite size was found to increase from 54.3 to 159.9 nm with raising the temperature from 800 to 1200 °C. Besides, the lattice parameter \( a \) and unit cell volume were increased with increasing the annealing temperature. Meanwhile, by estimating the X-ray theoretical density as following (Rashad et al., 2015):

\[ d_{X} = \sum \frac{A}{N \times V} \]  

Where \( A \) is sum of the atomic weights of all the atoms in the unit cell, \( V \) is volume of the unit cell and \( N \) is the Avogadro’s number. It can apparently that the X-ray density was minified with increment the annealing temperature. The results revealed that the lattice parameters and unit cell volume were increased whereas the X-ray density was decreased with increasing the annealing temperature. The results can be imputed on basis of increasing the crystal growth of mayenite with increasing the temperature. The changes of the lattice parameter \( a \), unit cell volume \( (V_{cell}) \) as well as the average crystallite size of the Ca₁₂Al₄O₃₃ specimens were calculated and the results were listed in Table 1.
Fig. 1: XRD patterns of mayenite (Ca$_{12}$Al$_{14}$O$_{33}$) nanoparticles with different temperature

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Cry. Size (nm)</th>
<th>a (Å)</th>
<th>Cell Volume (Å$^3$)</th>
<th>X-ray density, d$_r$ (g/cm$^3$)</th>
<th>Optical band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>54.3</td>
<td>12.008</td>
<td>1731.264</td>
<td>10.640</td>
<td>3.81</td>
</tr>
<tr>
<td>900</td>
<td>88.4</td>
<td>12.017</td>
<td>1735.233</td>
<td>10.616</td>
<td>4.12</td>
</tr>
<tr>
<td>1000</td>
<td>117.5</td>
<td>12.019</td>
<td>1736.027</td>
<td>10.611</td>
<td>4.8</td>
</tr>
<tr>
<td>1200</td>
<td>159.9</td>
<td>12.023</td>
<td>1737.830</td>
<td>10.600</td>
<td>4.45</td>
</tr>
</tbody>
</table>

Fig. 2 presents XRD patterns of as prepared samples annealed at temperature 800 °C with different times from 0.5 to 3 h. It is distinctly peaks of an impurity of the aluminum oxide Al$_2$O$_3$ phase (JCPDS # 13-0373) was observed as a secondary phase with the major cubic Ca$_{12}$Al$_{14}$O$_{33}$ phase at time 0.5 and 1h. Table 2 records the changes of the lattice parameter (a), unit cell volume (V$_{cell}$) as well as the average crystallite size of the Ca$_{12}$Al$_{14}$O$_{33}$ nanoparticles. A very fine increase in both lattice parameters and hence unit cell volume was presented as the result of crystal growth with different times.

Fig. 2: XRD patterns of mayenite (Ca$_{12}$Al$_{14}$O$_{33}$) nanoparticles with different time
3.2. Microstructure:

Fig. 3 illustrates the FE-SEM image of mayenite powders synthesized using co-precipitation method annealed at temperature 800 °C for 2 h. The particles were exhibited layers structure with a narrow size range of 2.8–4.3 μm with nano-thickness ~50 nm.

![SEM micrograph of Mayenite (Ca₁₂Al₆O₃₃) nanoparticles at 800 °C for 2 h](image)

3.3. Optical properties:

3.3.1. FTIR spectrum:

Fig. 4 indicates the FTIR spectra of mayenite nanoparticles. It is fairly that the characteristic absorption regions of Al–O stretching vibrations were 650–800 cm⁻¹ for “isolated” and 700-900 cm⁻¹ for “condensed” AlO₆ tetrahedra and 400-530 cm⁻¹ and 500-680 cm⁻¹ regions for “isolated” and “condensed” AlO₆ octahedra. Indeed, the Al–O stretching vibrations for tetrahedral AlO₆ were observed in the 750-850 cm⁻¹ spectral region. Besides, the same time, the octahedral AlO₆ were indexed at 500-750 cm⁻¹ (Chang et al., 2014). The pair of peak bands assigned at 953 and 1020 cm⁻¹ may be associated with the characteristic vibrations of the Al–OH bonding. Furthermore, the absorption bands at 1500 and 3450 cm⁻¹ were corresponded to vibrations from CO₂⁻ and OH⁻ groups, respectively, due to absorption of CO₂ and H₂O in the air. The O–H stretching vibration bands (Ca/Al–OH) can be clearly observed at 3650 and 835 cm⁻¹ (Zhang et al., 2010). The broad peaks at 625 and 2100 cm⁻¹ were belonging to stretching and bending modes of AlO–(OH) (Colomban, 1988). Hence, the two strong absorptions may be attributed to AlO₂ liberation at 600-900 cm⁻¹ which deals with the previous work (Tas, 1998), in which all kinds of calcium aluminates such as Ca₁₂Al₁₆O₃₅, CaAl₂O₄₉, Ca₆Al₂O₁₇, CaAl₂O₆, CaAl₂O₇ and CaAl₂O₄ presented two groups of absorption at 400-600 cm⁻¹.
3.3.2. UV-Vis-NIR spectrum:

The optical properties of the formed powders were examined using UV–Vis-NIR spectrophotometer using integrating sphere unit and the results are indicated in Fig. 5. Clearly, the optical reflectance of the powders was highly dependent on the annealing temperature. The mayenite sample annealed at 800 °C was shown to exhibit the lowest optical reflectivity of around 75% in the visible region. Further increasing the annealing temperature resulted in highly reflective powders with an average reflectivity of around 85% in the visible region. However, the results revealed that the absorbance was observed which a characteristic peak of Al\(^{3+}\) ions. An absorption peak at 210 nm was clearly observed which confirmed the presence of Al\(^{3+}\) ions nanoparticles (Piriyawong et al., 2012; Chang and Chang, 2008). Moreover, the defect responsible for the 260 nm absorption band may be related to Al vacancies (Kortov et al., 2004; Arnold et al., 1974; Gibbs Op, 1959).

The absorption (A) is converted to the absorption coefficient (α) using the relation (Rashad et al., 2013; Rayan et al., 2013):

\[
\alpha(v) = (1/d) \ln (I/I_0) = (100-R)/2R
\]

Where ln(I/I_0) is the absorbance (A), and d is the thickness of the sample. The reflectivity R can be transformed into a value proportional to the absorption using the Kubelka–Munk function: (Viruthagiri et al., 2014; Rashad et al., 2015)

\[
K = (1-R^2)/(2R)
\]

The Tauc plot of \((Khv)^n\) against hv (with n=2, applicable for a direct band gap material), as shown in Fig. 6 change in the value of band gap as a function of temperature and time was listed in Tables 1-2. It is apparent that the band gap energy increased the annealing temperature. The results were attributed to increase in the Crystallite size from 54.3 to 159.9 nm with increasing temperature. Consequently, based on quantum confinement theory, the energy band gap of a semiconductor depends on the crystallite size. The band gap energy was increased as the result of increasing the crystallite size.
Fig. 5: Optical absorbance and reflectance spectra of mayenite nanopowders with various a) temperature and b) time synthesized using co-precipitation method

Fig. 6: Optical band gap of mayenite (Ca$_{12}$Al$_4$O$_{33}$) nanopowders with various a) temperatures and b) time synthesized using co-precipitation method

Conclusion:
Single cubic mayenite (Ca$_{12}$Al$_4$O$_{33}$; space group I43d) nanopowders have been synthesized at low temperature 800 °C for 2 hr. increasing the temperature led to increasing the crystal growth of mayenite (Ca$_{12}$Al$_4$O$_{33}$) phase. Besides, the lattice parameter and unit cell volume were increased whereas the X-ray density was diminished as function of the annealing temperature. The microstructure of the formed powders exhibited aggregated layer structure with a narrow size range of 2.8–4.3 μm and nano-thickness ~50 nm. The sample has a good electrical conductivity without charge build-up. The optical reflectance of the powders was highly subjected to the annealing temperature. Indeed, the lowest optical reflectivity of around 75% in the visible region was observed at low temperature 800 °C whereas the high reflectivity powder around 85% was realized at high annealing temperature. The energy gap was increased from 3.81 to 4.10 eV when the crystallite size was increased from 54.3 to 159.9 nm. Subsequently, based on quantum confinement theory, the energy band gap of a semiconductor depends on the crystallite size. It is noticeable that the band gap energy was increased with increasing the crystallite size.

References


