Dislocation, crystallite size distribution and lattice strain of magnesium oxide nanoparticles

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Abstract. The oxide of magnesium nanoparticles synthesized using sol-gel method and analysis of the structural properties was conducted. The functional groups of nanoparticles has been analysed by Fourier Transform Infrared Spectroscopy (FT-IR). Dislocations, average size of crystal, strain, stress, the energy density of crystal, crystallite size distribution and morphologies of the crystals were determined based on X-ray diffraction profile analysis. The morphological of the crystal was analysed based on the image resulted from SEM analysis. The crystallite size distribution was calculated with the contention that the particle size has a normal logarithmic form. The most orientations of crystal were determined based on the textural crystal from diffraction data of X-ray diffraction profile analysis. FT-IR results showed the stretching vibration mode of the Mg–O–Mg in the range of 400.11–525 cm⁻¹ as a broad band. The average size crystal of nanoparticles resulted is 9.21 nm with dislocation value of crystal is 0.012 nm⁻². The strains, stress, the energy density of crystal are 1.5 x 10⁻⁴; 37.31 MPa; 0.72 MPa respectively. The highest texture coefficient value of the crystal is 0.98. This result is supported by morphological analysis using SEM which shows most of the regular cubic-shaped crystals. The synthesis method is suitable for simple and cost-effective synthesis model of MgO nanoparticles.

1. Introduction

Oxide materials such as MgO nanoparticles have attracted some researchers for a variety of unique properties owned by this material. In general, the properties of the solid material can be determined using computational methods or conventional (laboratory method) [1–3]. Various methods can be used to produce these nanoparticles in accordance with the raw materials and processes used such as through the process of emulsion with assisted by microwave [4], using a hydrothermal process [5], through the process of co-precipitation [6], and through the formation of sol and followed by gel formation [7].

The results of nanoparticles synthesis obtained should be conducted the analysis of advanced characteristics. Characterization of further properties of nanoparticles is needed to ensure the success of the synthesis process as well as other characters possessed by these materials. The results of calculating characteristic values such as dislocations and microstructures of MgO nano crystals are important factors in determining the physical properties to ensure the success of the formation process of these nanomaterials [8]. Various types of instrument have been used to define the microstructure of solid nanomaterials and to understand the character of nanomaterials [9]. X-ray diffraction is one of the most
effective instruments for estimating average crystal size, dislocations and microstructures. Estimated values are based on FWHM data (full width at half maximum), intensity obtained and result of integration analysis of X-ray diffraction profiles. The stress, strain, and energy density values possessed by the crystals were calculated using the Williamson-Hall analysis method [10,11].

The crystal size distribution parameter can be illustrated using the calculation of the log-normal function from the angle of X-ray diffraction results from nanocrystallite. In addition, to know the formation of functional groups contained in the resulting nanoparticles is required FT-IR (Fourier Transmittance Infra-Red) instrument that will provide information about the functional groups of the compounds contained. The best authors know, based on the literature study, there has been no report on the analysis of nanoparticles synthesis results using methanol for the sol-gel formation process and calcination process at high temperatures.

In this paper, the analysis and determination of microstructural properties, crystal value textures, the size of crystal, the distribution of size and the dislocation of structures, which occur during the calcination process to produce nanocrystalline MgO materials have been studied by X-ray diffraction. It is then supported by FTIR analysis to know the functional group changes contained in the resulting nanoparticles and SEM to analyse the morphology of the crystals.

2. Experimental

2.1 Materials
Oxalic acid dihydrate (Merck, >98 % purity), Magnesium acetate tetra hydrate (Merck, 99.5% purity), and methanol (Merck, 99.9% purity) were used in the synthesis of the MgO nanoparticles.

2.2 Synthesis of MgO nanoparticles
Firstly, magnesium acetate tetrahydrate is dissolved using methanol followed by constant stirring until a clear mixture is produced. The mixture is then adjusted to a pH value of 5 using 0.1 M oxalic acid and stirred vigorously until a white gel is formed. The resulting gel is left for 12 hours for further gelation process then dried in an oven at 200°C for 24 hours. Subsequently, the resulting solid is crushed and sieved to produce a magnesium oxalate complex powder [12]. Then, it was calcined at 950 °C for 6 hours in the furnace to produce MgO nanoparticle crystals. The crystals obtained are then characterized by FT-IR, X-ray diffraction and SEM.

3. Results and discussion

3.1 FTIR Analysis
The analysis of functional groups present on MgO nanoparticle materials was scanned in the range of 350 cm⁻¹ to 4000 cm⁻¹. The results of the analysis show that the broad vibration band has seen in the range of wavenumber 3250-3550 cm⁻¹ resulted by stretching vibration from the O-H group of water molecules absorbed into the solid and hydroxyl groups on the solid surface. This is due to the adsorption of water molecules in the air to the surface of MgO when the nanomaterial is in the free air.

In addition, the wave numbers appearing at 1018.24-1062.51 cm⁻¹ and 1225-1512 cm⁻¹ are generated by the bending vibration of the hydroxyl group (-OH) water molecules absorbed on the surface (-OH). While the functional groups of the Mg-O-Mg compound bonds were seen in the range 400.11-525 cm⁻¹ as wide band. The absorption peaks of FT-IR seen at wavenumber 1417.68 cm⁻¹ were assigned to asymmetric stretching of carbonate ion species (CO₃²⁻).
3.2 XRD Analysis
Further nanoparticle analysis was performed using XRD. Results of XRD diffractogram of calcined MgO nanoparticles at 950 °C for 6 hours are shown in Figure 2. Based on the diffractogram there are several peaks that characterize MgO nanoparticles. The presence of a strong and sharp diffraction peak lies in the values of 2θ 38.73°, 43.09°, 55.82°, 62.44°, 74.79°, and 78.73° which have Miller Index (1 1 1), (2 0 0), (2 2 0), (2 2 0), (3 1 1), and (2 2 2) are derived originally from MgO nanoparticles, whereas the diffraction peak lies in the value of 2θ 37.13° derived from Mg(OH)₂ which is a hydroxyl group absorbed in the solid material.

3.3 Determination average the particle size and the dislocation density
To determine the average particle size and density of nanoparticle dislocations based on XRD analysis results was done using the following Debye-Scherer equation 1 [13].
\[ D_{ave} = \frac{K\lambda}{\beta \cos \theta} \]  

\( D_{ave} \) is the average crystallite size of the particles, \( K \) is Debye – Scherrer’s constant (0.94), \( \lambda \) is the wavelength of the CuK\(_\alpha\) radiation (0.154 nm), \( \beta \) is the full width half maximum (FWHM) of the peak, \( \theta \) is the Bragg’s angle samples. The average crystal size obtained for the synthesis of MgO nanoparticles at a temperature of 950 °C 6 h is 9.21 nm. Based on the results obtained shows that the synthesis process with sol-gel method and continued with the calcination process in this procedure can produce nanoparticles with average size lower than 10 nm.

Based on the average particle size values obtained from equation 1, the dislocation density value of the MgO nanoparticles can be determined. The dislocation density (\( \delta \)) can be calculated using equation 2 [14]. The dislocation density value (\( \delta \)) denotes the number of dislocation lines per unit volume of crystal, which is the size of the crystal defects possessed by a crystal. In other words, the dislocation density value will illustrate the degree of crystallinity of the nanoparticles profile.

\[ \delta_{np} = 1/D^2 \]  

The result of the dislocation density (\( \delta_{np} \)) of the MgO nanoparticles is 0.012 (nm)\(^2\). Based on the results of this calculation is known that the dislocation density (\( \delta_{np} \)) of the nanoparticles obtained in this study is quite small. Small dislocation density value is indicates that MgO nanoparticles have been produced had a high degree of crystallinity.

### 3.4 Crystallite Size Distribution

Crystallite Size Distribution (CZD) of a crystal is determined using the assumption that the crystal particles have a size distribution with a normal distribution in all planes. The CZD function is defined as equation 3 [11].

\[ f(y) = \frac{1}{\sqrt{2\pi}\sigma y} \exp \left\{ -\left[ \frac{\ln(y/m)}{2\sigma^2} \right]^2 \right\} \]  

The \( y \) value is the size of a crystallite from the size distribution, \( \sigma \) is the variance and \( m \) is the median of the size distribution function. The crystallite size distribution function of the MgO nanoparticles was calcined at temperature 950 °C is plotted in Figure 3. The resulting CZD function can also be used to determine the area and the volume of the mean of crystallite size. The area, volume means crystallite size is obtained on equation 4 and 5[8].

\[ \langle y \rangle_{area} = m \exp(2.5 \sigma^2) \]  

\[ \langle y \rangle_{volume} = m \exp(3.5 \sigma^2) \]  

The MgO nanoparticles have particle size distributions lower than 12.5 nm. The median values and variance of the crystal size distribution based on CZD function calculations are 9.21 and 0.72 respectively. Using the median and the variant obtained the value of the area and the volumes of the crystal are 34.08 and 57.51 nm respectively. Referring to the value of crystal volume is 57.51 nm, it indicates that the amorphous portion of the specimen does not give impact to the overall material properties or nanocrystalline properties produced has a good crystal form. This is also supported by XRD results showing that the resulting diffractogram with a sharp peak and a flat background [8].
3.5 Determination of the stress of crystal ($\sigma$)
The strain calculation of nanoparticle crystals resulted conducted using the Williamson-Hall equation is modified into a model of uniform voltage deformation (USDM). In USDM, the deformation of the lattice strain in all directions of the uniform crystal plane. In addition, the Hook Law equation used only maintains linear proportionality between stress and strain ($\sigma = \varepsilon Y$), $\sigma$ is the crystal voltage and $Y$ is the Young (or) modulus of elasticity, $\beta_i$ is an instrumental FWHM.

$$\beta_i \cos \theta = \frac{K\lambda}{D} + \frac{4\sigma \sin \theta}{Y}$$  \hspace{1cm} (6)
The young’s modulus ($Y$) for cubic MgO nanoparticle is 248.73 GPa. The USDM plots for MgO nanoparticle calcined at 950 °C are shown in Figure 4. The calculated result of the stress values calculated using slope of the straight line of the graph is 37.31 MPa.

3.6 Determination of the strain of crystal ($\epsilon$)

The strain value of a crystal shows the alignment of a crystal that was produced. The crystalline strain was determined by using the diffraction pattern relationship of the line broadening that obtained in the measurement using XRD [10]. $\beta_{hkl}$ is resulted by each the diffraction peak of MgO. The total peak broadening is the sum of the crystallite size and strain present in the material.

$$\beta_{hkl} = \left[ (\beta_{hkl}^2)_{\text{measured}} - (\beta_{hkl}^2)_{\text{standard}} \right]^{1/2}$$  \hspace{1cm} (7)

$$\beta_{hkl} = \beta_a + \beta_b$$  \hspace{1cm} (8)

$\beta_a$ is the contribution of crystallite size, $\beta_b$ is strain-induced broadening and $\beta_{hkl}$ is the width of the full wide half-maximum (FWHM) intensity of the instrumental corrected broadening.

$$\beta_{hkl} \cos \theta = \frac{k^2}{D} + 4\epsilon \sin \theta$$  \hspace{1cm} (9)

The solution of equation 8 uses the assumption that the crystalline strain is uniform in all directions of crystallography. The use of this assumption is known as a uniform deformation model (UDM). All crystals are regarded as having isotropic properties and have independent properties in all directions along their measurements [10].

![Figure 5. Plot $\beta_{hkl} \cos \theta$ versus $4\sin \theta$.

The strain value of $\epsilon$-crystal nanoparticles of MgO estimated from the slope (Figure 5) is $1.5 \times 10^{-4}$. The calculation result of strain value is very low and the slope of the line MgO calcined at 950 °C is $R^2 = 0.6772$. The value indicates that all the crystals are not far apart. In addition, this result also shows that the nanoparticle product is a lack of strain [15].

3.7 Determination of The Energy Density of crystal ($U_{ed}$)

Based on the reference that the nanoparticle crystals are of the same nature and are isotropic, to determine the magnitude of the energy streams possessed by the crystals can be used a model of energy density having a uniform deformation (UDEDMD). On the elastic system that follows Hooke’s law, the
energy density $U_{ed}$ (energy per unit) can be calculated from the strain function $U_{ed} = (\varepsilon^2 Y)/2$. The equation (9) can be modified according to the energy and strain relation.

$$\beta_{hkl} \cos \theta = \frac{k \lambda}{D} + \left(4 \sin \theta \left(\frac{2U_{ed}}{Y}\right)^{1/2}\right)$$  \hspace{1cm} (10)

Plots of $\beta_{hkl} \cos \theta$ versus $4 \sin \theta \left(\frac{2U_{ed}}{Y}\right)^{1/2}$ were constructed and the data fitted to lines (Fig. 6). The anisotropic energy density $U_{ed}$ was estimated from the slope of the linear fit is 0.712 MPa.

![Plot of $\beta_{hkl} \cos \theta$ versus $4 \sin \theta \left(\frac{2U_{ed}}{Y}\right)^{1/2}$](image)

**Figure 6.** Plot $\beta_{hkl} \cos \theta$ versus $4 \sin(2/Y)^{1/2}$.

### 3.8 Analysis Texture coefficient $TC_{(hkl)}$

Quantitative information of crystal orientation preference can be analyzed using the texture coefficient calculation. The texture coefficient will give a percentage value for each X-ray diffraction of the MgO nanoparticles. The coefficient of texture can be calculated using equation 11 [16,17]:

$$TC_{(hkl)} = \frac{I_{(hkl)} / I_{o(hkl)}}{\sum I_{(hkl)} / I_{o(hkl)}} \times 100\% \hspace{1cm} (11)$$

$I_{(hkl)}$, $I_{o(hkl)}$ and $N$ are the intensity relative of diffraction peak, the intensity of standard measurement results and the number of diffraction peaks resulted respectively.

| No. | h k l  | I$_{(hkl)measured}$ | I$_{o(hkl)standard}$ | TC$_{(hkl)}$ |
|-----|-------|---------------------|----------------------|-------------|
| 1   | (2 0 0) | 100                | 100                  | 0.19        |
| 2   | (2 2 0) | 10                  | 9                    | 0.43        |
| 3   | (2 2 0) | 47                  | 45                   | 0.61        |
| 4   | (3 1 1) | 5                   | 5                    | 0.78        |
| 5   | (2 2 2) | 12                  | 12                   | 0.97        |

The TC (hkl) values calculated for MgO nanoparticles calcined at 950 °C for 6 hours show at Table 1. The calculation result showed that the highest of $TC_{(hkl)}$ value at (2 2 2) plane is 0.97. The results indicates that most of the crystal MgO nanoparticles resulted is preferred orientation of (2 2 2).
3.9 Morphological analysis

The SEM image of the MgO nanoparticles is shown in Figure 7. SEM analysis is a method for showing the surface morphology of the sample. Figure 7 shows that the results of MgO nanoparticles have a good agreement on the results that have been done by previous researchers with other methods [18,19].

![SEM image of MgO nanoparticles](image)

**Figure 7.** SEM of micrograph of MgO nanoparticles.

The results of SEM analysis showed that the crystal structure of MgO nanoparticles has a regular morphology. The shape of the crystal structure of the nanoparticles is dominated by crystals of the cubic shape. The MgO nanoparticles produced through these pathways are capable to produce the highest quality crystals with dominating cubic structures.

4. Conclusions

FTIR and XRD results show that MgO nanoparticles are formed through this synthesis process. This can be seen in the FT-IR wavelength range of 400.11-525 cm\(^{-1}\) as the broad band produced by the stretching vibration mode for the Mg-O-Mg compound. The average crystallite of MgO nanoparticles was 9.21 nm with a crystalline dislocation value is 0.012 nm\(^2\) whereas the distribution of the MgO nanoparticle crystallite size showed a particle size of the distribution lower than 12.5 nm. Strain, stress, and density of crystal energy are 1.5 x 10\(^{-4}\); 37.31 MPa; 0.72 MPa respectively. The highest texture coefficient value of the crystal is 0.98 in the crystal plane (2 2 2). This result is supported by morphological analysis using SEM which shows most of the regular cubic-shaped crystals. The synthesis method is suitable for a simple and cost-effective synthesis model of the MgO nanoparticles.

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