

STRUCTURAL PARAMETER AND TEM ANALYSIS OF BERYLLIUM OXIDE NANOPARTICLES SYNTHESIZED BY POLYACRYLAMIDE GEL ROUTE

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Beryllium oxide (BeO) nanoparticles were synthesized by polyacrylamide gel route followed by calcination at 700°C and 800°C and examined their structural behaviour by X-ray diffraction (XRD). The structural parameters such as dislocation density, residual stress, lattice strain, texture coefficient, lattice parameter and bond length were calculated from XRD data and discussed. The calculated crystallite size was in nanometer scale (<70 nm) and reduced when calcined at 800°C. Dislocation density was changed with respect to orientations and observed low value for (100) orientated phase when calcined at 700°C. Residual stress analysis evidenced the formation of compressive stress and dominated for calcined BeO nanoparticles. Calcination temperature did not much influence in changing the Be-O bond length. The synthesis of preferentially (002) oriented BeO nanoparticles were confirmed by texture coefficient analysis. Transmission Electron Microscopy (TEM) was attested the formation of nano particles with ellipsoid-like shape and agreed with XRD results. Stoichiometric BeO nano particles were confirmed by EDX spectra.

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1. Introduction

During the last decade, LEDs are changing the world of lighting due to their efficiencies, size, durability, and lifetime cost. LEDs have become one of the standard methods of producing lights [1]. Only 20-30% of LED's electric power was converted into visible light, the rest converts into heat. Then, the heat must be conducted from the LED to the atmosphere. Thus, heat sink is the best way to release unnecessary heat from the device by dissipates the heat generated within the LED devices [2]. However, the interface problem exists when the heat sink attached with the LED package. Therefore, thermal interface material (TIM) is required to minimize the thermal contact resistance between the heat source and the heat sink [3]. Several materials with high thermal conductivity have been suggested for TIM's material. Recently, ceramic particles filled polymer is the preferred one since it has good thermal conduction with low electrical conductivity which is magnesium oxide (MgO), aluminium nitride, boron nitride, silicon carbide and beryllium oxide (BeO) [4].

Among the oxides, BeO is unique for oxides as it combines excellent electrical insulating properties ($>10^{13}$ $\Omega\cdot\text{cm}$) with high thermal conductivity which is 330 W/(m.K) [5] compared to thermal conductivity of MgO (30 W/(m.K)) [6], AlN (220 W/(m.K)) [7], and BN (30 W/(m.K)) [8]. It is also possesses high chemical and thermal stability, good mechanical strength, high melting point and high insulation nature, low dielectric constant and corrosion resistant. Combination of physical and chemical properties of BeO will make such an outstanding combination because BeO is one of the most chemically stable oxides and at high temperatures, it will resisting both carbon reduction and molten metal attack [5]. Hence, it is widely applied in

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nuclear technology, vacuum electronics technology, microelectronics and photoelectron technology especially in thermal application [9]. BeO is most often used as an electronic substrate because it gives an effective heat sink when its high thermal conductivity and good electrical resistivity were exploited. For instance, the material was found particularly in high power devices or high density electronic circuits for high speed computers [5]. Hence, beryllium oxide powder with high performances are necessary to get advanced BeO nanoparticles ceramics. Besides that, nano particles are needed where large surface area is needed too because thermal contact conductance became more sufficient to dissipate heat from the device when the surface area increased [10]. For the development of new products, synthesis and characterization of BeO nanoparticles is important.

Mostly, the methods used to synthesize BeO nanoparticles are polyacrylamide gel route and sol-gel method. Sol-gel process is a method for producing solid materials from small molecules. The method is used for the fabrication of metal oxides [11]. Recently, polyacrylamide gel route has become a trend to synthesize nanoparticles of a variety of oxide materials [12]. In this method, a steric entrapment of stoichiometric cation solution occurs in nanocavities formed inside the gel, that is, a homogeneous micro solution with cations in the desired stoichiometry [5]. This polyacrylamide gel technique has many advantages such as a simple and convenient process, inexpensive and time-saving process and need a relatively lower calcination temperature than traditional preparation technique. Reports related to the synthesis of BeO nano particle are limited and the detailed structural analysis of synthesized BeO nano particles has not been reported. In the present work, BeO nanoparticles is synthesized by polyacrylamide gel method and size, shape, morphology and structural parameters are calculated and discussed in detail.

2. Experimental technique

BeO nanoparticles were synthesized by polyacrylamide gel method. Beryllium sulfatetetrahydrate ($\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$), Acrylamide (AM) and N, N'-Methylene-bis-acrylamide (MBAM) were prepared as the starting material. An experimental procedure of polyacrylamide gel route for preparing BeO nanoparticles is as follows. Firstly, beryllium sulfatetetrahydrate was dissolved in the distilled water with moment stirring to produce a transparent 1.5 mol/L BeSO_4 solution. 5 wt% organic agents acrylamide (AM) and N, N'-methylene-bis-acrylamide (MBAM) monomers with a mass ratio of 20 were added in the prepared solution with constant stirring until the solution became transparent. Then, 0.5 mL ammonium persulfate solution (APS: 10 wt%) was added as initiator and the temperature of the solution was increased slowly to 60 °C in water bath.

The APS initiated the free-radical crosslinking copolymerization of AM and MBAM. The mixture was turned to transparent hydrogel gradually. The condition was held for 1 hr in order to make sure that the organic monomers reacted absolutely. Then, the gel was dried at 80 °C for 48 hr in a vacuum oven. The formed xerogel was homogenized in a ceramic mortar and calcined at two different temperatures (700 °C and 800 °C) with a laboratory furnace in an oxygen atmosphere with a flow rate of 5 sccm.

An X-ray diffractometer (XRD-Siemens diffractometer D5000) was used to determine the microstructure, phase analysis and structural parameters (crystallite size, lattice constant, dislocation density, residual stress, lattice strain, texture coefficient, lattice parameter, and bond length). To confirm the presence of nano size particles by the proposed synthesis, a transmission electron microscopy (TEM) (Phillips CM12 with Docu Version 3.2 image analysis) was used. Next, surfaces and morphology of BeO nanoparticles was also captured and analysed by a scanning electron microscope (SEM) (JSM-6460 LV). Finally, energy-dispersive X-ray (EDX) spectra were used to identify the elemental composition of synthesized BeOnano particles.

3. Result and discussion

3.1. XRD Analysis

X-ray powder diffraction (XRD) spectra of BeO nanoparticles from polyacrylamide gel route calcined at 700 °C and 800 °C for 2hr are shown in fig. 1. All observed spectra are indexed and very well agreed with the characteristic of hexagonal pattern with lattice constants of $a = 2.699 \text{ \AA}$ and $c = 4.385 \text{ \AA}$ (JPCDS 78-1379) for sample calcined at 700°C and with lattice constants of $a = 2.698 \text{ \AA}$ and $c = 4.379 \text{ \AA}$ (JPCDS 76-0567) for sample calcined at 800°C.

From the fig. 1, the most three highest peak with strong Bragg reflection related to (100), (002), and (101) orientations of BeO nanoparticles can be seen for both calcined temperature. Fig.1 also reveals the presence of polycrystalline behaviour of the synthesized BeO nano particles with different orientations. In order to study the crystalline behaviour of synthesized samples, the peak intensity analysis is also carried out based on the XRD spectra (magnified) as shown in fig. 2. A significant difference in intensity could be observed for all three preferred orientations for the samples calcined at 700 °C and 800 °C. Hence, it is clearly observed from the change in intensity of the peaks that the crystallinity of BeO nanoparticles was improved at higher calcination temperature (800°C). The indication of the crystallinity is represented by the intensity of the observed peak. In the fig. 1, the highest peak intensity for the sample calcined at 700 °C can be seen at (100) orientation whereas (101) orientation is dominated for the sample calcined at 800 °C. The highest peak is a proof of a good crystallisation which is observed from the synthesized BeO nanoparticles with respect to orientations. From the fig. 2, it is concluded that the higher calcined temperature helps to grow (101) oriented BeO nano particle instead of (100) orientation by this polyacrylamide gel route.

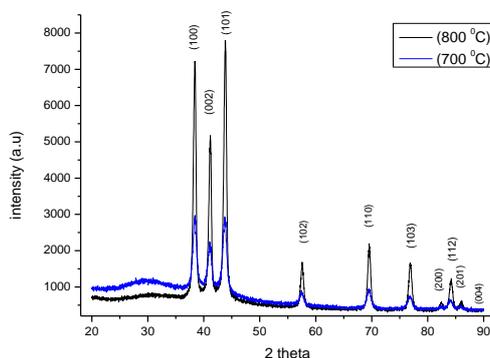


Fig 1. XRD spectra for BeO nanoparticles powder calcined at variation of temperature for 2 hr

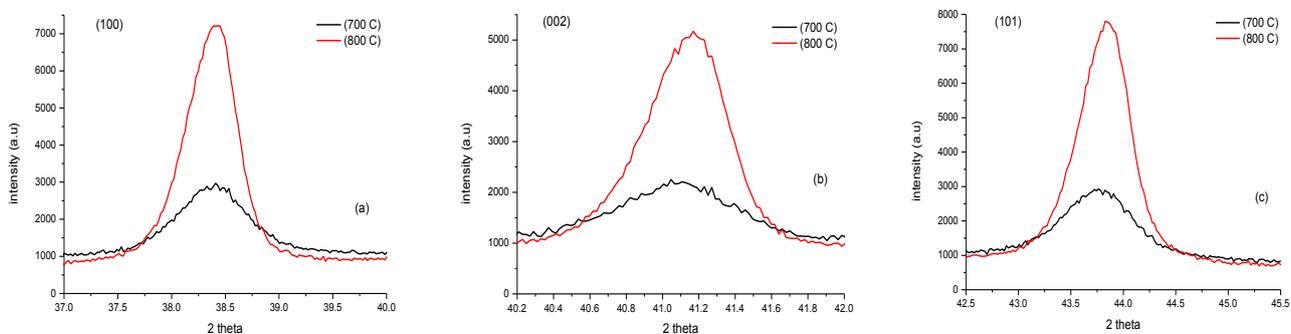


Fig 2. XRD spectra of (100), (002) & (101) oriented peaks of BeO phase calcined at various temperature for 2 hr

From the XRD data, the crystallite size of the BeO nanoparticles was calculated by using the Debye-Scherer equation [13]:

$$D = k \lambda / \beta \cos \theta \quad (1)$$

Where D is the crystallite size (nm), $\lambda = 1.5406 \text{ \AA}$ is the wavelength of the radiation used, $k = 0.94$ is a constant, β is full width half maximum (FWHM) in radian and θ is the Bragg diffraction angle of the XRD peak. The crystallite size were only calculated for the 3 dominant peaks related to (100), (002) & (101) orientations for the sample calcined at 700 °C and 800 °C and considered in this analysis. The average crystalline size of the synthesized nanoparticles is 69.07 nm and 33.51 nm for the samples calcined at 700 °C and 800 °C respectively which are summarized in table -1. The results show that the size of the particles become smaller for (100) and (200) orientations when the temperature increased from 700°C to 800°C. At (101) orientation, the particle size was decreased when the temperature increased from 700 °C to 800 °C. On considering (101) orientation, the crystallite size increases from ~13 nm to ~28 nm as the temperature increases from 700°C to 800°C whereas the value decreases from 148 nm to 34 nm and from 45 nm to 38 nm for (100) orientation and for (002) orientation respectively.

A dislocation density can be determined to define a topological defect. The dislocation density, δ stands for the magnitude of defects and it can be measured by the following equation [14]:

$$\delta = 1/D^2 \quad (2)$$

where D is the crystallite size of the BeO nanoparticles (in nm). The calculated values are also presented in table-1. It could be seen from the table 1 that the dislocation density increases as the calcination temperature increases especially for (100) and (002) orientations. A drastic reduction in δ value could be observed for (101) orientation when temperature increases. The decrement in δ values is the indication of growing perfect crystals with (101) orientation in this study. It shows that the calcination temperature did influenced the value obtained in dislocation density. The increase of dislocation density is correlated with the decreases of crystallite size [10]. Moreover, the dislocation density of other nanocrystalline such as silicon nitride powders is $0.57 \times 10^{15} \text{ m}^{-2}$ [15]. As compared to the value of silicon nitride, the value of dislocation density of BeO calcined at 700 °C almost have the same value with it at (002) orientation.

Lattice strain is also referred as the deformation of a crystal lattice. It will result in a change in the inter-atomic distances. The lattice strain, ε can be measured by the following tangent equation [16]:

$$\varepsilon = \beta / (4 \tan \theta) \quad (3)$$

Table 1: Structural parameter of BeO nanoparticles calcined at various temperature for 2 hr

Calcination temperature, (°C)	Orientation, (hkl)	Lattice constant, ($\times 10^{-10} \text{ m}$)		Crystallite size, D (nm)	Dislocation density, ($\times 10^{15} / \text{m}^2$)	Residual stress, σ (GPa)	Lattice strain, ε ($\times 10^{-3}$)	Texture coefficient, (TC)	Lattice parameter, ($\times 10^{-10} \text{ m}$)	Bond length, ($\times 10^{-10} \text{ m}$)
		a	c							
700 °C	(100)	2.6958	4.6693	148.92	0.05	-0.03	0.74	1.04	2.3346	1.6861
	(002)	2.5346	4.3900	44.96	0.49	-1.50	2.29	1.04	2.1950	1.5853
	(101)	2.3790	4.1205	13.37	5.59	-0.03	7.24	0.92	1.8427	1.4880
800 °C	(100)	2.6979	4.6729	34.32	0.85	-0.63	3.20	0.99	2.3364	1.6875
	(002)	2.5272	4.3772	37.54	0.71	-0.65	2.74	1.03	2.1886	1.5807
	(101)	2.3775	4.1180	28.67	1.22	0.37	3.38	0.98	1.8416	1.4870

where β is FWHM and θ is half of the diffraction angle. The measured value of lattice strain for all samples with respect to orientation is presented in table 1. As observed from the δ values, the lattice strain values increase for both (100) and (200) orientations with temperature increase from 700°C to 800°C. From the table - 1, it is understood that the (100) oriented BeO phase has low deformation in crystal lattice at 700°C. In the meantime, BeO phase with (101) orientations show large deformation by means of showing large value in lattice strain. Moreover, the residual stress developed in the BeO nanoparticles was also determined by using the following equation [17]:

$$\sigma = -E (d_a - d_o) / (2d_o Y) \quad (4)$$

where E is the Young's modulus (331.7 GPa) and Y is the Poisson's ratio (0.26) of BeO [18]. d_a and d_o are the d spacing of bulk and BeO nanoparticles from JCPDS data respectively. The calculated values are shown in table - 1 and the smallest value is obtained for both (100) and (101) orientations for the sample calcined at 700°C. Based on the table - 1, all the obtained values are negative other than (101) orientation at 800°C and hence, compressive stress is dominated during the growth of BeO nano particle at both temperatures. It is the indication of decreased volume of the BeO lattice in this study [19]. So it is necessary to address the change in lattice parameter value with respect to the calcination temperatures.

Calcination temperature is also influence the lattice parameter change and refines the crystal structure and hence it has to be verified here. Lattice parameter values can be obtained using the following equation (5), (6) and (7) [20]:

$$d_{hkl} = 1 / \sqrt{[(4(h^2+k^2+hk)/3a^2) + (l^2/c^2)]} \quad (5)$$

$$a = \lambda / (\sqrt{3} \sin \theta) \quad (6)$$

$$c = \lambda / \sin \theta \quad (7)$$

where d is the interplanar distance, λ is the wavelength 1.5406 Å, θ is the Bragg angle. To determine the defect level in the BeO crystal at a given strain, lattice constant is an important parameter while expansion of the crystal lattice depend on the change in lattice parameters [10,21]. The calculated lattice parameters of the BeO nano particles are also presented in table – 1 and observed the values are almost constant with respect to orientations as the temperature increases. The highest value of lattice parameter could be observed with (100) orientation whereas the lowest one is with (101) orientation. The result of lattice constant, a for (100) orientation is same as with the standard one (2.6979 Å) while the lattice constant, c for (002) orientation is same as with the standard value (4.3772 Å) [22]. These results reveal that the calcination temperatures influenced the lattice parameters of the synthesized BeO nano particles and could be observed some small deviation from the bulk BeO value.

In addition to that, the bond length analysis of Be-O is also mainly depending on the value of lattice constant as given in the following equation [23,24]:

$$L = \sqrt{[(a^2/3) + (1/2 - u)^2 c^2]} \quad (8)$$

Where

$$u = (a^2/3c^2) + 0.25 \quad (9)$$

The bond length between the elements in synthesized particles is acts as a key parameter and expected to change [19]. The value of bond length is almost constant at all of the orientation as the temperature increases. Hence, it shows that the temperature does not influence much in the value of bond length. There are no significant differences between the calculated values and the standard one (1.387×10^{-10} m)[25]. From the observed results, it can be seen that the value of the bond length is almost same with the standard one at (101) orientation.

The texture coefficient (TC) is an indication of growth of nanocrystals with their preferred orientation and could be evaluated by using the following equation [26]:

$$P_i (TC) = N (I_i/I_o) / \sum (I_i/I_o) \quad (10)$$

Where P_i is the Texture Coefficient of the plane I , N is the number of reflections considered for the analysis, I_i is the measured intensity from the XRD data of BeO nanoparticles and I_o is the intensity observed from the JCPDS powder diffraction pattern of the corresponding peak. The calculated results of TC using equation (10) are also given in table-1. The peak is chosen as the preferred orientation of the crystallites in that particular area when the P_i is greater than unity. From the table 1, the TC value of (002) orientation shows greater than 1 at two temperatures and hence exist as preferred orientation. Whereas (001) orientation shows preferred at 700°C only. On considering (101) orientation, the TC value is constant as the temperature increases and claimed as random orientation which is not influenced by the calcined temperatures.

3.2. TEM analysis

The transmission electron microscopy (TEM) micrographs of BeO nanoparticles was captured corresponding to calcined temperatures at 700 °C and 800 °C as shown in fig. 4. From the fig.4, the observed particles size is pretty much close with the values calculated from the XRD analysis and lies within 100 nm. The observed TEM image is a strong evidence of nano size particle for the synthesized samples. Fig.4 shows the shape of the BeO nanoparticles clearly. The samples annealed at 700°C and 800°C does not exhibit any well-known shape. It could be easily seen that most of the particles exhibit an ellipsoid-like shape. From the image shown in fig. 4(a), almost all parts of the particles seem to be agglomerated while partial agglomeration could be seen in fig. 4(b). Moreover, the change in particle shape could also be seen clearly with temperature increase (fig.4b). The calculated value of particle size for the sample calcined at 700 °C is 12.5 nm which is very close to value observed from the XRD result (13.37 nm).

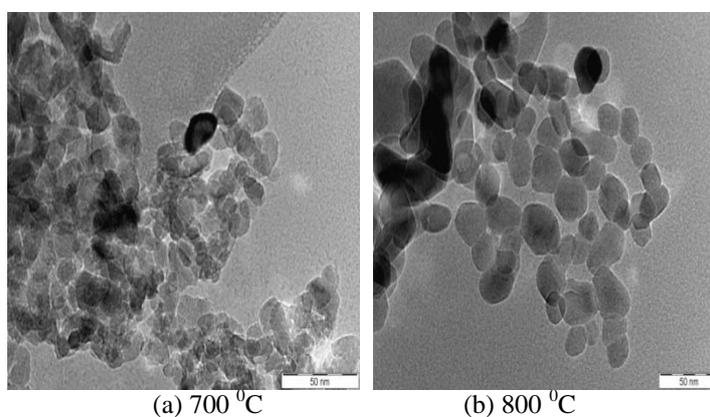


Fig 4. TEM images of BeO nanoparticles obtained by polyacrylamide gel route calcined at various temperatures for 2hr

3.4. SEM ANALYSIS

In order to investigate the morphology of synthesized BeO nanoparticles and calcined at several temperatures, SEM image of all samples is captured as presented in figure 5.

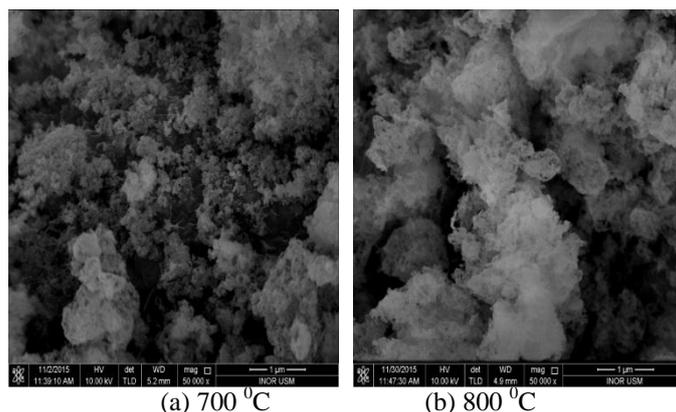


Fig 5. SEM images of BeO nanoparticles calcined at two different temperatures

In fig. 5(a), it can be observed that the synthesized BeO nanoparticles calcined at 700 °C having nanometer size particles and also showing the cluster morphology whereas the BeO nanoparticles showing bigger size with compact morphology for the samples calcined at 800°C samples. The particles agglomeration could be seen in such a large area for the samples calcined at 800°C (fig. 5(b)) compared with fig. 5(a). Based on SEM analysis, the shape of nanoparticles could not be seen clearly as a result of particle agglomeration.

3.3. EDX ANALYSIS

In order to test the composition of synthesized BeO nano particles, the prepared BeO nanoparticles was undergone for energy-dispersive X-ray (EDX) analysis and the observed results are presented in table - 2

Table 2. EDX analysis of BeO nanoparticles calcined at various temperatures in 2hrs

Temperature (°C)	Be (Wt %)	O (Wt %)
700	29.8	70.2
800	36.13	63.87

The data generated by EDX analysis consist of the elements making up the true composition of the sample and showed only the Be and O. No other elements could be identified. The standard weight percentage of Be and O are considered in this analysis for comparison which is 36.03 and 63.97 respectively [27]. It is also observed from the EDX analysis that (table 2), the sample prepared and calcined at 700°C is Be deficient and hence O rich whereas the sample calcined at 800°C shows the stoichiometric composition as compared with standard weight percentage. Hence, it is concluded that 800°C is a better calcination temperature which could be used in the synthesis of BeO nanoparticles in order to get a stoichiometric composition (weight percentage) in the particles rather than the samples calcined at 700°C.

4. Conclusion

BeO nanoparticles were successfully synthesized by polyacrylamide gel route. They exhibited with preferentially (002) orientation. The lowest calculated crystallite size for BeO nano powders was between 29-38 nm at 800 °C for 2 hr. Moreover, the calcination temperature did not influenced much in the result of bond length. Most of the particles exhibited as an ellipsoid-like shape and confirmed by TEM. There was no significant changes in shape with high calcination

temperature. The stoichiometric BeO nano particles were observed with samples calcined at 800°C. From SEM analysis, nano particles with rough surface were confirmed. Overall, the synthesized BeO nano particles could be able to increase the contact conductance in polymer matrix and will act as good filler for thermal interface material application.

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