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# Surfactant effect on synthesize of BaAl<sub>2</sub>O<sub>4</sub> nanoparticles prepared by reverse micelle process

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Barium aluminate (BaAl<sub>2</sub>O<sub>4</sub>) spinel nanoparticles were prepared by a reverse micelle method using micro-reactors made of different nonionic surfactants (Span 20, Span 40 and Span 60) in a nonpolar solvent benzene. The synthesized nanomaterials were characterized by X-ray diffraction (XRD) technique. The morphology of the synthesized materials was studied by field emission scanning electron microscope (FESEM). Particle size was estimated by XRD and transmission electron microscope (TEM) with using software of ImageJ. The effect of different surfactants on the particles size and morphology was determined. The results revealed, that particle size was increased by decreasing HLB (Hydrophilic-Lipophilic Balance) of surfactants and also particle size was increased from 23 to 35 nm. HLB of surfactants is a major factor in controlling the final particles size of BaAl<sub>2</sub>O<sub>4</sub> powder. The X-ray powder diffraction analysis indicated, all the formation of hexagonal phase on calcinations. Dislocation of peaks ( $2\theta$ ) in XRD with decreasing HLB of surfactant was decreased slightly.

Key words: Barium aluminate, Reverse micelle, Nanoparticle, Span 20, 40 and 60, X-ray diffraction, Hydrophilic-lipophilic balance.

## Introduction

Nanotechnology employs knowledge from the different scientific fields of physics, chemistry, biology, materials science, health sciences and engineering. It has immense applications in almost all the fields of science and human life. It is expected that nanotechnology causes revolutionary changes in the field of life sciences such as drug delivery, production of bio-materials and diagnostics. Nanoparticle materials use in electronics, cosmetics, magnetic pharmaceuticals, energy, catalytic and materials industries. Nanoparticles have unique properties as compared to macro particles. There are several processes to create nanomaterials [1].

The technique of microemulsion is a multi-purpose method for preparation nanoparticles, that it can control their properties such as geometry, homogeneity, mechanisms of particles size, morphology and surface area [2]. One of the best definitions of microemulsions is from Danielsson and Lindman [3] "a microemulsion is a system of water, oil and an amphiphile which is optically transparent and a thermodynamically stable system". The boundaries between phases of microemulsions are stabilized by surfactant and co-surfactant monolayers [2].

Barium aluminate is an inorganic material that have been widely applied in different industries. One of the most important properties of  $BaAl_2O_4$  is its optical properties [4-6]. BaAl<sub>2</sub>O<sub>4</sub> is used in the field of energy saving, safety improvement, emergency, traffic signs, advertising and safety clothes [7-14]. BaAl<sub>2</sub>O<sub>4</sub> nanoparticles widely use in cements, pigments, ceramic glazes and as industrial catalysts [15]. Barium aluminate (BaAl<sub>2</sub>O<sub>4</sub>) is applied in the catalysis that is used in the treatment of air pollution [4, 15, 16]. Also, it can be used for the preparation of phosphor materials and humidity sensors [17-23]. Rare earth ion-doped aluminates show good luminescent properties with high stability and brightness [14, 24].

 $BaAl_2O_4$  nanoparticles have synthesized by different methods, such as via the solid-state reactions [25-28], co-precipitation [15], combustion with different starting temperature [29-31], sol-gel route [32, 33], microwave combustion [34] and combustion [35].

Microemulsion is a method for preparation of nanoparticles. In these processes, micelles can be described as "nanoreactors". It was reported that the particles size is affected by different surfactants and co-surfactants [36-38]. Also, the effect of solvent type has been investigated [36, 39-41]. Many articles show the final particles size is dependent on the initial water to surfactant molar ratio  $W_0 = [H_2O]/[Surfactant]$  [42-50]. The studies were reported that reactant concentration is effective on particles size [51-53]. Several studies have shown that the size of final particles is changed insignificantly by the addition of electrolyte [54, 55].

In this paper, barium aluminate nanoparticles were synthesized by microemulsion method and influence of different surfactants on the particles size of  $BaAl_2O_4$  powder was reported. XRD was used in order to check the crystalline phases of the particles, morphology and

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size of particles are characterized using FESEM and TEM.

## **Experimental**

Barium nitrate (Ba(NO<sub>3</sub>)<sub>2</sub>, 99.5 %, Merck), aluminum nitrate nonahydrate (Al(NO<sub>3</sub>)<sub>3</sub>, 9H<sub>2</sub>O, 98.5%, Merck) were used as the precursor of barium and alumina, respectively. The required amount of barium nitrate and aluminum nitrate salts (Ba:Al = 1:2) was dissolved in deionized water to a concentration of 0.1 M. Benzene (99.7 %, Merck) was used as organic solvent.

A solution of reverse microemulsion was prepared by mixing 0.09 M of sorbitan monolaurate (Span 20, Merck) a nonionic surfactant, 0.93 M of benzene and 0.1 M of mixed aqueous salt solution.

B solution of reverse microemulsion was prepared by mixing 0.09 M of sorbitan monopalmitate (Span 40, Sigma Aldrich) a nonionic surfactant, 0.93 M of



Fig. 1. Flowchart for the preparation of nanoparticles by reverse micelle processing.

benzene and 0.1 M of mixed aqueous salt solution.

C solution of reverse microemulsion was prepared by mixing 0.09 M of sorbitan monostearate (Span 60, Sigma Aldrich) a nonionic surfactant, 0.93 M of benzene and 0.1 M of mixed aqueous salt solution. The microemulsion was mixed rapidly, and after 30 min of equilibration 0.2 M of NH<sub>4</sub>OH (28 %, Merck) was injected into the microemulsion. Then, the microemulsion was centrifuged to extract the particles and they were subsequently washed with ethanol to remove any residual surfactant. The powders were dried at 60 °C in an oven for 24 h, then ground and calcined at 900 °C for 2 h. Fig. 1 shows the flowchart for the preparation of BaAl<sub>2</sub>O<sub>4</sub> nanopowders by reverse micelle processing. The phase identification of calcined powders was recorded using X-ray diffractometer (STOE STADI, MP) that is shown in Fig. 2. The morphology of the calcined powder was observed by FESEM operating at an accelerating voltage of 30 kV (MIRA3 TESCAN) that is shown in Fig. 3.

The particles size of the calcined powders was analyzed using TEM operating at an accelerating voltage of 200 kV (Philips, CM30) by placing the powder on a copper grid to get the details about the



Fig. 2. X-ray diffraction patterns of  $BaAl_2O_4$  powder calcined with different solvents, a: Span 20, b: Span 40 and c: Span 60.



Fig. 3. FESEM micrographs of BaAl<sub>2</sub>O<sub>4</sub> powder calcined for 2 h at 900 °C, a: Span 20, b: Span 40 and c: Span 60.

morphology and size of the powders that is shown in Fig. 4.

Particle size was estimated from the TEM micrographs

using standard software ImageJ that is shown in Fig. 5. The crystallite size of the calcined BaAl<sub>2</sub>O<sub>4</sub> powder

was calculated from full width at half maximum



Fig. 4. TEM micrographs of BaAl<sub>2</sub>O<sub>4</sub> powder calcined for 2 h at 900 °C, a: Span 20, b: Span 40 and c: Span 60.



Fig. 5. Diagram of particles distribution of BaAl<sub>2</sub>O<sub>4</sub> was estimated by using software IMAGE J, a: Span 20, b: Span 40 and c: Span 60.

(FWHM) peak using Scherrer's equation [56].

#### **Results and discussion**

The XRD patterns of the calcined samples are shown with different surfactants at 900 °C for 2 h in Fig. 2. The detected diffraction peaks are corresponded to the standard patterns of BaAl<sub>2</sub>O<sub>4</sub> (ICSD card 00-017-0306). All the samples were found to have a hexagonal crystal structure. According to this analysis, all three patterns show the formation of single phase BaAl<sub>2</sub>O<sub>4</sub>.

No other crystalline phase was found in the calcined samples. Location of peaks  $(2\theta)$  in XRD with decreasing hydrophilic-lipophilic balance of surfactant was decreased. The average nanoparticles size was calculated by the following Scherrer's equation:

$$D = \frac{k\lambda}{\beta \cos \theta}$$

In the equation, *D* is the size of the crystallite sample,  $\lambda$  is the wavelength of X-ray source of Cu-K<sub>a</sub> (1.54 Å), *k* is the Scherrer's constant (0.9),  $\beta$  of FWHM is the width at half its maxium intensity and  $\theta$  is the half diffraction angle at which the peak is located.

The result shows that the size of the synthesized nanoparticles with decreasing HLB of surfactant from HLB = 8.6 (Span 20), HLB = 6.7 (Span 40) and to HLB = 4.7 (Span 60) were increased from 23 to 35 nm, respectively. Table 1 shows the data of Scherrer's equation and the dislocation value.

The surface morphology of samples was reported by FESEM. The FESEM micrographs of  $BaAl_2O_4$  nanopowders in different surfactants show that the particles are not uniform in shape and also the boundary between phases is clear at Span 20 and Span 40. It can be seen that density of the particles at span 40 is more than the other images. Meanwhile, in the images due to the presence of moisture in the environment, agglomeration between nanoparticles is observed.

Fig. 4 shows the TEM micrographs and size distribution of nanoparticles. These samples were synthesized with different surfactants and benzene as a nonpolar solvent and then they were calcined at 900 °C for 2 h. All the particles are very fine. TEM images show that the most of BaAl<sub>2</sub>O<sub>4</sub> nanoparticles synthesized at Span 20 are nearly spherical, at Span 40 and Span 60 are completely spherical. Particle size estimated from the TEM image

Table 1. Scherrer's data information for BaAl<sub>2</sub>O<sub>4</sub> nanoparticles.

Samples	$\beta \text{ obs}$ (2 $\theta$ )	Peak position $(2\theta)$	Crystallite size (nm)	Type of crystallite
Span 20	0.354	28.382	23	hexagonal
Span 40	0.280	28.301	29	hexagonal
Span 60	0.236	28.305	35	hexagonal

using standard software ImageJ is found to increase with decreasing hydrophilic-lipophilic balance of surfactants. Nanoparticles size from HLB = 8.6 (Span 20), HLB = 6.7 (Span 40) to HLB = 4.7 (Span 60) is increased, respectively. The nanoparticles size distribution in different surfactants is similar to each other Fig. 5. Increasing of nanoparticles size is agreement with crystallite size data of the targets calculated by Scherrer's equation.

Results of experiment show that the hydrophiliclipophilic balance of surfactants control the diameter of the nanoparticles in the microemulsion.

#### Conclusions

BaAl<sub>2</sub>O<sub>4</sub> nanoparticles can be synthesized by reverse micelle processing at 900 °C for 2 h. All the calcined powders show the presence of hexagonal phase and no other crystalline phase are found in the samples. The surfactant of Span 20, Span 40 and Span 60 is effective on the particles size distribution of nanoparticles. The particles size can be controlled by changing HLB of different nonionic surfactants. Dislocation of peaks  $(2\theta)$  in XRD with decreasing hydrophilic-lipophilic balance of surfactants was decreased. The results of the TEM are agreement with the XRD results. The presence of moisture in the environment causes agglomeration of nanoparticles. Particle size of BaAl<sub>2</sub>O<sub>4</sub> was found to increase with decreasing of surfactant hydrophiliclipophilic balance.

### References

- M.A. Godwin, K.M. Shri, and M. Balaji, Int. J. Res. Eng. Biosci. 3 (2015) 11-29.
- M.A. Malik, M.Y. Wani, and M.A. Hashim, Arab. J. Chem. 5 (2012) 397-417.
- I. Danielsson, and B. Lindman, Colloids Surf. A. 3(1981) 391-392.
- M.V.D.S. Rezende, C. Arrouvel, S.C. Parker, J.F.Q. Rey, and M.E.G. Valerio, Mater. Chem. Phys. 136 (2012) 1052-1059.
- J. Holsa, T. Laamanen, M. Lastusaari, M. Malkamaki, E. Welter, and D.A. Zajac, Spectrochim. Acta Part B: At, Spectrose. 65 (2010) 301-305.
- M.V.D.S. Rezende, M.E.G. Valerio, and R.A. Jackson, Mater. Res. Bull. 61 (2015) 348- 351.
- R.H. Krishna, B.M. Nagabhushana, B.N. Sherikar, N.S. Murthy, C. Shivakumara, and T. Thomas, J. Chem. Eng. 267 (2015) 317-323.
- H. Ryu, B.K. Singh, and K.S. Bartwal, Phys. B: Condens. Matter. 403 (2008) 126-130.
- R. Stefani, L.C.V. Rodrigues, C.A.A. Caravalho, M.C.F.C. Felinto, H.F. Brito, M. Lastusaari, and J. Hölsä, Opt. Mater. (amst). 31 (2009) 1815-1818.
- M.R.M. Shafiee, M. Ghashang, and A. Fazlinia, Curr. Nanosci. 9 (2013)197-201.
- 11. M. Ghashang, Curr. Org. Synth. 9 (2012) 727-732.
- M.R.M. Shafiee, A. Fazlinia, N. Yaghooti, and M. Ghashang, Lett. Org. Chem. 9 (2012) 351-355.

- 13. M. Ghashang, Lett. Org. Chem. 9 (2012) 497-502.
- M.A. Gomes, A.B. Andrade, M.V.D.S. Rezende, and M.E.G. Valerio, J. Phys. Chem. Solids. 102 (2017) 74-78.
- M. Momayezan, M. Ghashang, and S.A. Hassanzadeh-Tabrizi, Bulg. Chem. Commun. 47 (2015) 809-815.
- H. Lin, Y. Li, W. Shangguan, and Z. Huang, Combust. Flame. 156 (2009) 2063-2070.
- 17. S. Hodjati, P. Bernhardt, C. Petit, V. Pitchon, and A. Kiennemann, Appl. Catal. B: Environ.19 (1998) 209-219.
- M. Mohapatra, D.M. Pattanaik, S. An, and R.P. Das, Ceram. Inter. 33 (2007) 531- 535.
- M. Casapu, J.D. Grunwaldt, M. Maciejewski, M. Wittrock, U. Gobel, and A. Baiker, Appl. Catal. B: Environ. 63 (2006) 232-242.
- J.J. Vijaya, L.J. Kennedy, G Sekaran, and K.S. Nagaraja, Sens Actuators B: Chem. 124 (2007) 542-548.
- R.S. Yadav, S.K. Pandey, and A.C. Pandey, J. Lumin. 131 (2011) 1998-2003.
- 22. V. Singh, V. Natarajan, and J.J. Zhu, Opt. Mater. 29 (2007) 1447-1451.
- 23. Z. Qiu, Y. Zhou, M. Lu, A. Zhang, and Q. Ma, Acta. Mater. 55 (2007) 2615-2620.
- 24. A.H. Wako, F.B. Dejene, and H.C. Swart, J. Rare Earths. 32 (2014) 806-811.
- 25. G. Blass, W.L. Wanmaker, J.W. TerVrugt, and A. Brill, Philips. Res. Rep. 23 (1968) 189-200.
- 26. H.S. Roh, I.S. Cho, J.S. An, C.M. Cho, T.H. Noh, D.K. Yim, D.W. Kim, and K.S. Hong, Ceram. Int. 38 (2012) 443-447.
- 27. H. Ryu, B.K. Singh, and K.S. Bartwal, Phys. B: Condens. Matter. 403 (2008) 126-130.
- 28. H. Ryu, and K.S. Bartwal, Mater. Chem. Phys. 111 (2008) 186-189.
- M.A. Lephoto, O.M. Ntwaeaborwa, S.S. Pitale, H.C. Swart, J.R. Botha, and B.M. Mothudi, Phys. B: Condens. Matter. 407 (2012) 1603-1606.
- L.C.V. Rodrigues, J. Hölsä, J.M. Carvalho, C.C.S. Pedroso, M. Lastusaari, M.C.F.C. Felinto, S. Watanabe, and H.F. Brito, Phys. B: Condens. Matter. 439 (2014) 67-71.
- 31. R. Ianos, R. Lazău, and R.C. Boruntea, Ceram. Int. 41 (2015) 3186-3190.
- 32. J. Zhong, J.L. Wang, L. Tao, M. Gong, L. Zhimin, and Y. Chen, J. Hazard. Mater. 140 (2007) 200-204.
- 33. R.J. Wiglusz, and T. Grzyb, Opt. Mater. (Amst). 36 (2013) 539-545.
- C. Ragupath, J. JudithVijaya, and L. John Kennedy, Mater. Sci. Eng. B. 184 (2014) 18-25.

- R. Manigandan, R. Suresh, K. Giribabu, L. Vijayalakshmi, A. Stephen, and V. Narayanan, Adv. Mater. Res. 584 (2012) 263-266.
- M.A. Lopez-Quintela, C. Tojo, M.C. Blanco, L. Garcia Rio, and J.R. Leis, Curr. Opin. Colloid Interface Sci. 9 (2004) 264-278.
- V. Uskokovie, and M. Drofenik, Surf. Rev. Lett. 12 (2005) 239-277.
- A. Bumajdad, M. Zaki, J. Eastoe, and L. Pasupulety, Langmuir, 20 (2004) 11223-11233
- 39. C.L. Kitchens, M.C. McLeod, and C.B. Roberts, J. Phys. Chem. B. 107 (2003) 11331- 11338.
- 40. J.P. Cason, M.E. Miller, J.B. Thompson, and C.B. Roberts, J. Phys. Chem. B. 105 (2001) 2297-2302.
- 41. R.P. Agwe, and K.C. Khilar, Langmuir, 13 (1997) 6432-6438.
- 42. Y. Berkovich, A. Aserin, E. Wachtel, and N. Garti, J. Colloid Interface. Sci. 245 (2002) 58-67.
- 43. D.E. Zhang, X.M. Ni, H.G. Zheng, Y. Li, X.J. Zhang, and Z.R. Yang, Mater. Lett. 59 (2005) 2011-2014.
- 44. K. Kimijima, and T. Sugimoto, J. Colloid Interface Sci. 286 (2005) 520-525.
- 45. A. Nanni, and L. Dei, Langmuir, 19 (2003) 933-938.
- 46. D. Markovec, A. Kosak, A. Znidarsic, M. Drofenik, and M.J. Magn, J. Magn. Magn. Mater. 289 (2005) 32-35.
- 47. J.L. Lemyre, and A.M. Ritcey, Chem. Mater. 17 (2005) 3040-3043.
- L. Levy, D. Ingert, N. Feltin, V. Briois, and M.P. Pilieni, Langmuir, 18 (2002) 1490- 1493.
- 49. J. Chandradass, M. Balasubramanian, D. Sik Bae, J. Kim, and K. Kim, J. Alloys Compd. 491 (2010) L25-L28.
- 50. J. Chandradass, and K. Kim, J. Cryst. Growth. 311 (2009) 3631-3645.
- 51. I. Lisiecki, and M.P. Pileni, Langmuir, 19 (2003) 9486-9489.
- J. Eastoe, S. Stebbing, J. Dalton, and R.K. Heenan, Colloids Surf. A Physicochem. Eng. Asp. 119 (1996) 123-131.
- 53. M. Maillard, S. Giorgio, and M.P. Pileni, J. Phys. Chem. B. 107 (2003) 2466-2470.
- 54. C. Kitchens, M. McLeod, and C. Roberts, Langmuir, 21(2005) 5166-5173.
- 55. C. Saiwan, S. Krathong, T. Anukulprasert, and E. O'RearIII, J. Chem. Eng. Jpn. 37 (2004) 279-285.
- B.D. Cullity, Elements of X-ray Diffraction, 2nd ed, Addison-Wesley, London, UK, (1978).