Journal of Alloys and Compounds 509 (2011) 1192–1196

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Microwave assisted solution combustion synthesis of alumina–zirconia, ZTA, nanocomposite powder

K. Tahmasebi, M.H. Paydar*

Department of Metallurgy and Materials Science, School of Eng., Shiraz University, Shiraz, Iran

ARTICLE INFO

Article history:
Received 1 December 2008
Received in revised form
27 September 2010
Accepted 28 September 2010
Available online 8 October 2010

Keywords:
Microwave processing
Nanocomposites
Cutting tools

ABSTRACT

In the present study, the effect of microwave heating in producing alumina–20 wt% zirconia (ZTA) nanocomposite powder through metal nitrate solution combustion synthesis method, using urea as fuel, was studied. For comparison, ZTA nanocomposite powder is also synthesized using conventional heating method. To characterize the products and evaluate the effect of microwave heating system on them, X-ray diffractometry, TEM, SEM, surface area analysis (BET), and TG/DTA analysis were used. The results showed that, both ZTA powder synthesized in microwave and furnace were nanocrystalline, fine, and brittle, in which zirconia particles were homogeneously dispersed in the alumina matrix. The results also proved that, the powder produced in microwave was finer (<20 nm) with narrower size distribution and had better homogeneity of zirconia particles in alumina matrix, but lower specific surface area, in comparison with the sample which was synthesized in furnace.

1. Introduction

The addition of zirconia into alumina as a sintering aid has been in practice since the development of alumina, ceramics [1]. With developments in microstructure, the concept of dispersion strengthening gained momentum. This has lead to the development of zirconia toughened alumina, ZTA, in which zirconia particles are uniformly dispersed in alumina matrix. The toughening mechanism in ZTA ceramics is related to volume expansion and shear strain which are associated with the tetragonal to monoclinic transformation phase of zirconia, which is activated by applying external stress. This phase transformation, which is accompanied by about 6 vol% expansion, provides a compressive stress, which can reduce and eventually stop crack propagation [2]. Studies on transformation toughening in ZTA have revealed the existence of a critical size of ZrO_2 particles for the retention of metastable tetragonal phase [3].

Since nanocrystalline materials have proven superior physical and chemical properties, such as having better phase homogeneity and enhanced sinterability at relatively low temperature, a great deal of effort has been focused on synthesizing and characterizing ZTA nano-ceramics. A series of powder fabrication techniques have been investigated for synthesizing ZTA nano-ceramics such as dry milling [4], wet milling [5] of the mixture of zirconia and alumina, co-precipitation [6,7], sol–gel [8,9], etc. However, all these techniques need high temperatures and/or long processing times [10]. Among the available chemical processes, self-sustaining solution combustion synthesis, while saving time and energy consumption and utilizing simple experimental devices, has shown convenient in process over and in comparison with the above outlined techniques and is especially suitable for preparing high-tech ceramic materials, particularly nanocrystalline ceramics [11–20]. In addition, in situ synthesis of well mixed Al_2O_3/ZrO_2 nanocomposite powder can be carried out by solution combustion synthesis, so that there is no need for mixing Al_2O_3 and ZrO_2 powder particles to achieve the required homogeneity, which is absolutely difficult in the case of nano-sized constituents.

Recently, microwave has been used for processing advance materials [21]. Microwave-processing of materials is fundamentally different from the conventional processing due to its different heating mechanism. In a microwave oven, due to the interaction of micro-waves with the material, the heat is generated within the sample itself. In conventional heating, the heat is generated by heating elements and then it is transferred to the sample surface [21]. The use of microwave in combustion synthesis has several advantages. The foremost of which are the shortened periods of synthesis, enhanced reaction kinetics, and the reactant selectivity during energy transfer from the microwave field, which assists the stabilization of the metastable phase of the material. Therefore, it is possible to control both the kinetic and the thermodynamic factors of the chemical reactions using microwave in the combustion process [22].

When microwave penetrate and propagate through a dielectric material, the internal electric fields generated within the affected

---

* Corresponding author. Tel.: +98 711 2307293; fax: +98 711 2307293.
E-mail address: Paaydar@shirazu.ac.ir (M.H. Paydar).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.09.176

volume induce translational motions of free or bound charges (e.g. electrons or ions) and rotate charge complexes, such as dipoles. The resistance of these induced motions, due to inertial, elastic, and frictional forces, causes losses, attenuates the electric field, and consequently results in volumetric heating of the under-microwave material.

The present study, in which microwave was used as a heating source for initiating solution combustion synthesis of ZTA nanocomposite powder, endeavors to investigate the effects of microwave heating on the characteristics of produced powder.

2. Experimental procedure

The starting materials used in this work were: aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) and zirconyl nitrate hexahydrate ($ZrO(NO_3)_2 \cdot 6H_2O$) from Aldrich, and analytical grade of urea $CO(NH_2)_2$ from a national source. In all the reactions, the ratio between aluminum and zirconium nitrates was chosen so that the final ZTA powder contains 20 wt% of ZrO_2. That is because it is well known that both the fracture toughness and the strength of alumina ceramics are improved significantly by the dispersion of 10–20 vol.% of metastable tetragonal (t) zirconia particles [14]. The theoretical stoichiometric equations for the formation of ZTA involved in the present work and the preparation procedure are detailed as follows:

Reactions between urea and nitrates:

$$2Al(NO_3)_3 \cdot 9H_2O + 5CO(NH_2)_2 \rightarrow Al_2O_3 + 5CO_2 + 8N_2 + 28H_2O \quad (1)$$

$$3ZrO(NO_3)_2 \cdot 6H_2O + 5CO(NH_2)_2 \rightarrow 3ZrO_2 + 5CO_2 + 8N_2 + 28H_2O \quad (2)$$

For the stoichiometric reaction between urea and nitrates, i.e. reactions (1) and (2), the starting materials including stoichiometric amounts of aluminum nitrate (10 g), zirconium nitrate (0.94 g) and urea (4.3 g), were dissolved in 25 ml water. Subsequently two different processes were performed on the prepared solution; so that, in one of them the solution was put directly in a home microwave oven working at 1000 W power. As soon as the oven was turned on, the viscous solution swelled, followed by the evolution of a large volume of gases; and then self-propagating solution combustion occurred in the whole sample, yielding a foamy structure and easily crumbling to give a fine and white powder. In the other process route, first the solution was heated on a hot plate at about 80 °C to obtain a gel, and then the prepared gel was put in a microwave oven. In this case the combustion reaction, starts from a point in the sample and then propagates to other parts of the sample, and finally yields a foamy structure. For comparison purposes, a sample also was prepared using the conventional heating method, in which the starting material for combustion process was the gel. Details of this experimental procedure are reported elsewhere [23].

The crystallinity and phase identification of the produced powders were performed on a Bruker Advance D8 X-ray diffractometer using Cu Kα as the radiation source and Ni as the filter. The crystallite size distribution was calculated using measured line-broadening of the mean peaks. For this purpose, Winfit software was used and a PearsonVII shape function was fitted on the peaks, corresponding to $2\theta = 30^\circ$ and 36° reflections of tetragonal zirconia and α-alumina phases, respectively. Subsequently size-distribution of the crystallites was determined from the second derivative of the Fourier-coefficient plots. To evaluate the derivative, a Savitzky–Golay polynomial was used.

Transmission electron microscopy, TEM, (CM200 FEG PHILIPS) was used to determine the shape and the average size of the crystallites. The size and morphology of the agglomerated particles were determined by means of a SEM (CamScan MV2300). For evaluating the nature of combustion reactions, the DTA/TG analysis of the gels was conducted in flowing air up to 400 °C at a heating rate of 20 °C/min using a L70/2171 LINSEIS thermal analyzer. BET surface area analysis of produced nanopowders was also performed using Gemini 2375 V4.02 surface area analyzer.

3. Results and discussion

The microwave power, P, absorbed to produce internal heating, is proportional to the relative dielectric constant ε_r of the material expressed by the following relation:

$$P = 2\pi f \varepsilon_0 \varepsilon_r \tan \delta |E|^2 \quad (3)$$

where "f" is the frequency of the microwave, "ε_0" the permittivity of the space, "$\tan \delta$" the loss factor and "E" the electric field. The power absorbed is directly correlated to the permittivity of the interacting material, ε_r. Metal nitrates having an ε_r of ca. 18–25, absorb microwave radiation effectively [24]. In addition, zirconia possesses in relatively high loss factor which causes the heating up of the mixture to be more efficient [25].

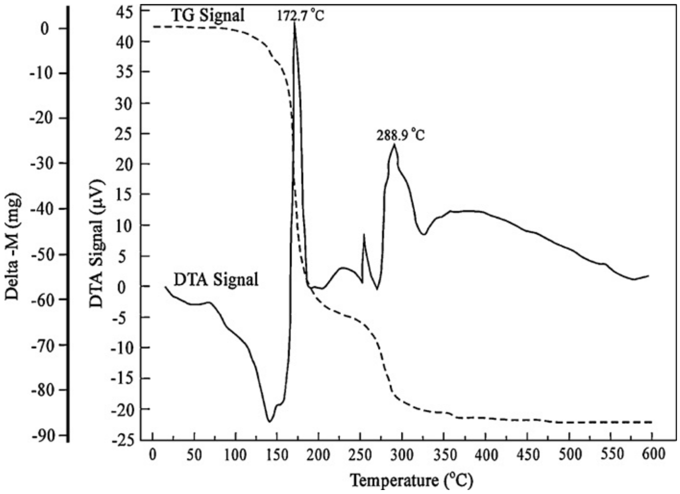


Fig. 1. TG/DTA analysis of a gel sample containing stoichiometric amount of nitrates and urea.

The Al/Zr oxides formation process in a microwave oven is consisted of the supersaturating of the solution; containing metals nitrate salts mixture and urea, and subsequently its conversion to a semisolid (gel) precursor, after rapid solution removal under microwave irradiation. Due to the fast heating under microwaves irradiation, gel type precursor changed to a foamy shape product through successive steps of rapid nucleation and slow growth. Zirconium oxides are efficient microwave receptors and can absorb 2450 MHz microwave frequency strongly [25]. Due to the presence of zirconium oxides, which are homogeneously distributed in the Al_2O_3, rapid synthesis of α-alumina/t-zirconia composite powder can take place.

Fig. 1 shows the result of thermal analysis performed on the gel prepared by heating the starting solution on a hot plate. As it can be seen, there is a first endothermic peak on DTA signal, followed by the reduction of weight indicated on TG signal, which must be due to dehydration of aluminum nitrate and decomposition of urea in the sample, that are related to the following reactions:

$$Al(NO_3)_3 \cdot 9H_2O \rightarrow Al(NO_3)_3 + 9H_2O \quad (4)$$

$$CO(NH_2)_2 \rightarrow NH_3 + HCNO \quad (5)$$

The next two DTA peaks in the temperature ranges of 170–190 °C and 280–320 °C, correspond to the main combustion reactions, that can be the result of different reactions including reactions (6)–(8). However, with regard to the TG analysis results, it can be concluded that the main combustion reactions happen in this temperature range. So that a large amount of gases release, as the result of combustion reactions. The first sharp peak of exothermic reaction is followed by a huge amount of gas release, while during the second exothermal broad peak lesser amount of gas evolves.

The XRD patterns of the samples are shown in Fig. 2. As it can be seen, all the samples are completely crystallized, although for the samples produced in microwave, the crystalline peaks are weaker. The lower crystallinity is probably due to the difference between starting raw materials in these two synthesizing methods. In fact, as it was mentioned in the last section, in microwave synthesis in which the solution mixture was used directly as the starting material, partial decomposition of urea, which happens before gelation and during the removal of water from the sample, decreases the amount of urea, needed for combustion reaction, and consequently the exothermicity of the reaction also decrease [23]. In the sample prepared in microwave oven using gel as starting material, the peaks are also weak. In this case, although there is lower amount of

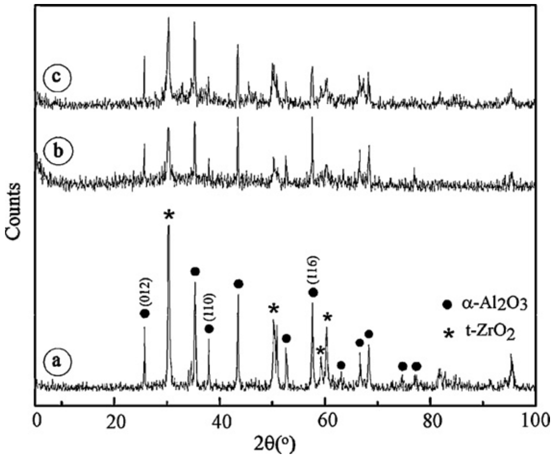


Fig. 2. XRD patterns of ZTA prepared by (a) conventional heating method, and (b) microwave heating system.

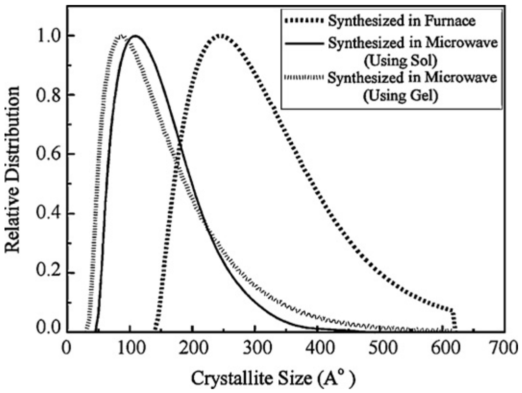


Fig. 3. Size distribution of alumina crystallites in the samples prepared by conventional and microwave heating methods.

water, its lower amount leads to weaker interaction of microwave signals with the gel sample. In fact dipoles of polar H_2O molecules have a strong interact with the microwave [26]. Therefore also in this case the exothermicity of the reaction is low. So it is reasonable that the microwave products were less crystallized in comparison with the samples prepared in furnace using gel as a starting material. However as Fig. 2 shows, crystalline phases in all samples are α-alumina and tetragonal zirconia which are the proper phases for the ZTA composite. Therefore there is no need for usual calcination process of the produced powders.

Fig. 3 compares the size distribution of alumina crystallites in three crystalline samples prepared in microwave and furnace. As it is shown, heating mechanism has a significant effect on crystallite size and size distribution of products. This figure also shows that the crystallite sizes of the ZTA powder produced by microwave heating are smaller and has a narrow distribution ranging from 5 to 30 nm with a maximum around 10 nm. While in the case of the sample prepared in furnace there is a wide range of crystallite size in the range of 15–65 nm with a maximum at 27 nm. These results support the fact that there is lower exothermicity of combustion reaction in microwave in comparison with furnace, which results in smaller crystallite size and narrow distribution.

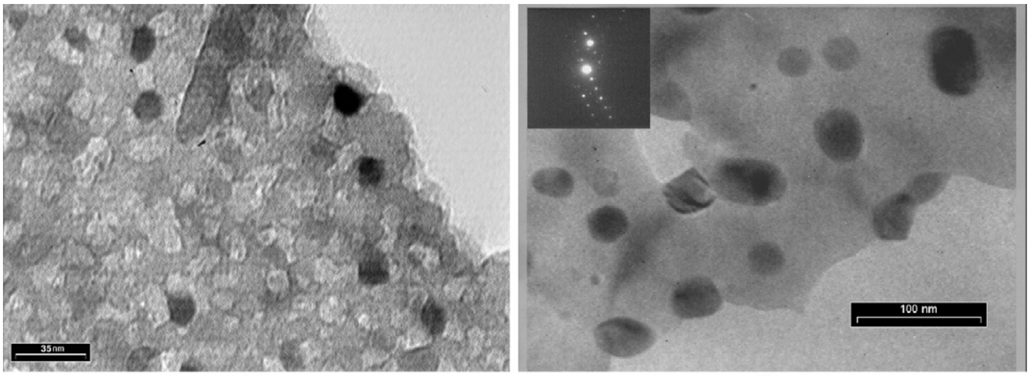
BET analysis showed that, specific surface area for the sample prepared in microwave using solution as the starting material, is $1.75\,m^2\,g^{-1}$, which is lower than that obtained for the sample synthesized in furnace ($3.56\,m^2\,g^{-1}$). At the first sight these results may seems in contrast with the results of crystallite size distribution in Fig. 3. But in this case specific surface area is related to the number and size of the particles and agglomerates, not the size of the crystallites. We can justify the result of BET analysis based on a difference in the nature of the reactions in two samples. Based on TG/DTA analysis, there are three possible exothermic chemical reactions on combustion process, which are listed below. As the following reactions also indicate, reaction between metal (Al and Zr) nitrates and urea (reactions (6) and (7)) releases more volume of gases than is produced by the reaction of the product produced by decomposition of urea with the nitrates (reaction (8)), which is dominated in the case of microwave synthesis. The release of a lower amount of gas means creating lower porosity and less efficiency in preventing particles from joining with each other in the final foamy powder product. Therefore, it is reasonable to obtain a final product with lower specific surface area in the case of microwave heating.

$$2Al(NO_3)_3 + 5CO(NH_2)_2 \rightarrow Al_2O_3 + 5CO_2 + 8N_2 + 10H_2O \quad (6)$$

$$2Al(NO_3)_3 + CO(NH_2)_2 \rightarrow Al_2O_3 + 6NO_2 + CO_2 + N_2 + 2H_2O \quad (7)$$

$$2Al(NO_3)_3 + 2HCNO \rightarrow Al_2O_3 + 6NO_2 + 2CO_2 + N_2 + H_2O \quad (8)$$

TEM results are summarized in Fig. 4, in which the dark spots on the TEM images are zirconia particles and bright matrix composed of α-alumina particles (based on EDX analysis (Fig. 5)). Using an image analysis software, the average size of the zirconia particles is estimated, based on the difference of color with the matrix in the TEM images. These results show a reduction of average zirconia particles size from 32 nm to 15 nm, using microwave heating system, in which the solution (sol) is used as starting precursor instead of furnace. This value is even lower in comparison with the sample prepared using modified fuel, composed of the combination of urea and starch [23]. As discussed before, lower heat of the reaction gen-



(a) (b)

Fig. 4. TEM images of ZTA powder, prepared by (a) using microwave heating system and (b) conventional heating method.

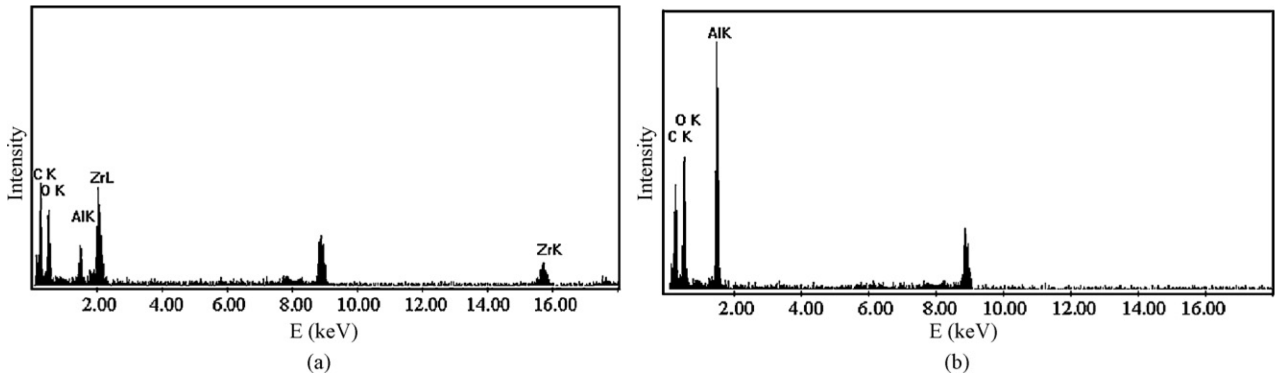


Fig. 5. EDX analysis of (a) the dark spots and (b) the bright matrix.

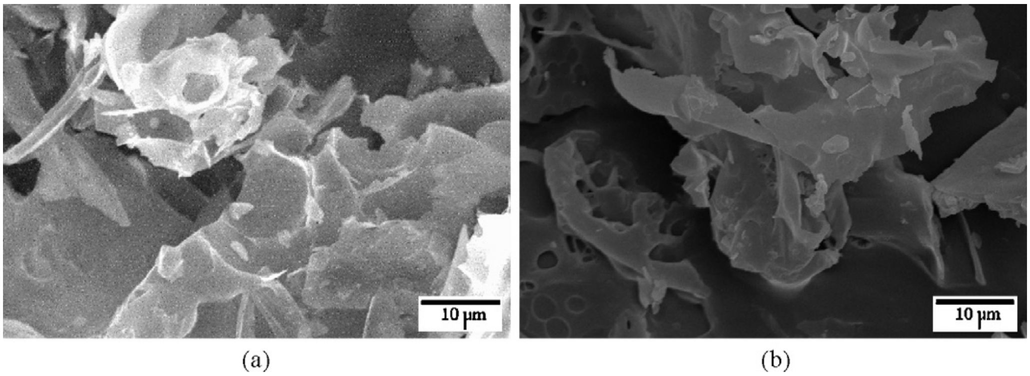


Fig. 6. SEM micrographs of ZTA agglomerates, prepared by (a) using microwave heating system and (b) conventional heating method.

erated in microwave synthesis leads to finer crystallites. Probably, in microwave system, radiation type of heating that leads to simultaneous beginning of the reaction from several points within the solution is another reason for the reduced size of the zirconia particles. In some literatures [21], it is even proposed that the reaction in microwave solution sample starts in gas system, which means infinite reaction points.

Fig. 6 shows the agglomerate morphology's of the final foamy shape powder just after synthesis process. As it can be seen, agglomerates are flake-like with a lot of voids, which is likely the result of releasing large amount of gas during combustion reaction. There is no sharp difference between samples prepared in furnace and microwave in this case. The average agglomerate size is about 20 μm.

4. Conclusion

Microwave and conventional heating systems are used successfully for synthesizing of alumina–20 wt% zirconia nanocomposite powder via solution combustion synthesis, using metal nitrates and urea as raw materials. For both the heating method, the resultant powder was fine, brittle and nanocrystalline, in which zirconia particles were homogeneously dispersed in the alumina matrix. The results proved that the microwave heating system is a fast and easy synthesis method, in which there is no need for preparing the gel; and the solution can directly interact with the microwave signals and results in a well-developed combustion reaction. While in the conventional heating, the sol should be changed to gel and then converted to the product due to high temperature heating in a furnace. Furthermore the final powder produced in microwave heating system has finer crystallites with narrower size distribution in contrast with the sample prepared in the furnace with the same starting raw materials. Nevertheless the specific surface area of the sample prepared in furnace, using gel as starting precursor, is higher in comparison with the sample prepared in microwave, in which the sol was used as the starting precursor.

Acknowledgement

The authors would like to acknowledge the financial support of Shiraz University through the grant number of 88-GR-ENG-16.

References

[1] J. Wang, R. Stevens, J. Mater. Sci. 24 (1989) 3421.
[2] E. Dow Whitney, Ceramic Cutting Tools, Noyes/William Andrew Publishing, 1994, p. 183.
[3] R.C. Garvie, Advances in ceramics – science and technology of zirconia III, Am. Ceram. Soc. 24 (1988) 55.
[4] B. Kibbel, A.H. Heuer, J. Am. Ceram. Soc. 69 (1986) 231.
[5] D.J. Green, J. Am. Ceram. Soc. 65 (1982) 610.
[6] T.Y. Peng, P.W. Du, B. Hu, Z.C. Jiang, J. Inorg. Mater. 15 (2000) 1097.
[7] S. Ramanathan, S.K. Roy, R. Bhat, D.D. Upadhaya, A.R. Biswas, J. Alloys Compd. 243 (1996) 39.
[8] S. Kureti, W. Weisweiler, J. Non-Cryst. Solids 303 (2002) 253.
[9] N. Hong, N. Chen, Gongneng. Cailiao. 26 (1995) 181.
[10] T. Ring, Fundamentals of Ceramic Powder Processing and Synthesis, Academic Press, 1996, p. 307.
[11] L.C. Pathak, T.B. Singh, S. Das, A.K. Verma, P. Ramachandrarao, Mater. Lett. 57 (2002) 380.
[12] J.J. Kingsley, K.C. Patil, Mater. Lett. 6 (1988) 427.
[13] R.H.G.A. Kiminami, M.R. Morelli, D.Z. Folz, D.E. Clark, Am. Cream. Soc. Bull. 79 (2000) 63.
[14] S. Biamino, P. Fino, M. Pavese, C. Badini, Ceram. Int. 32 (2006) 509.
[15] S.T. Aruna, K.S. Rajam, Mater. Res. Bull. 39 (2004) 157.
[16] N. Dasgupta, R. Krishnamoorthy, K.T. Jacob, Int. J. Inorg. Mater. 3 (2002) 143.
[17] T. Mimani, K.C. Patil, Mater. Phys. Mech. 4 (2001) 134.
[18] J. Chandradass, M.H. Kim, D.-S. Bae, J. Alloys Compd. 470 (2009) L9.
[19] G. Fagherazzi, S. Polizzi, M. Bettinelli, A. Speghini, J. Mater. Res. 15 (2000) 586.

[20] G.E. Lascalea, D.G. Lamas, E. Djurado, E.D. Cabanillas, N.E. Walsöe de Reca, Mater. Res. Bull. 40 (2005) 2029.
[21] Y.-P. Fu, C.-W. Liu, Y.-S. Chang, S.-B. Wen, C.-H. Lin, Mater. Res. Bull. 41 (2006) 2260.
[22] H. Mohebbi, T. Ebadzadeh, F.A. Hesari, J. Power Sources 178 (2008) 64.
[23] K. Tahmasebi, M.H. Paydar, Mater. Chem. Phys. 109 (2008) 156.
[24] D.E. Clark, W.H. Sutton, Annu. Rev. Mater. Sci. 26 (1996) 299.
[25] D.M.P. Mingos, D.R. Baghurst, J. Br. Ceram. Soc. 91 (1992) 142.
[26] Z. Chen, Y. Yan, J. Liu, Y. Yin, H. Wen, J. Zao, D. Liu, H. Tian, C. Zhang, S. Li, J. Alloys Compd. 473 (2009) L13.