Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 34 (2008) 551–555
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Studies of drying and sintering characteristics of gelcast $BaTiO_3$-based ceramic parts

Zhiping Zheng *, Dongxiang Zhou, Shuping Gong

MOE Engineering Research Center for Information Functional Ceramics, Department of Electronic Science & Technology, Huazhong University of Science & Technology, No. 1037, Luoyu Road, Hongshan District, Wuhan City, Hubei Province 430074, PR China

Received 9 October 2006; received in revised form 6 November 2006; accepted 14 December 2006
Available online 30 January 2007

Abstract

Drying green gelcast parts is an essential step in the gelcasting manufacturing process. In this work, the liquid desiccant method was used for drying of $BaTiO_3$-based semiconducting ceramic gelcast parts. The results show that the loading level of ceramic powders and the liquid desiccant concentration significantly effect the drying process and the sintering characteristics of the ceramic parts. Lowering the loading level of ceramic powders and increasing the concentration of the liquid desiccant, non-uniform and differential drying in various regions due to great solvent gradient, induces structural and residual stresses which cause defects, such as cracking, bending and other malformations, which make the articles useless during the drying process and sintering procedure. However, when the solid loading of green gelcast parts is increased to more than 45 vol.%, the stresses developed during drying can be greatly reduced, and a higher concentration of the liquid desiccant can be used without inducing defects in the drying process and defect free ceramic with a smooth surface can be obtained. Moreover, the effects of loading level of ceramic powders and thickness of parts on the density of ceramic parts were studied. Higher solid content in the gel, and lower thickness of parts, increase the density of ceramics.

Keywords: A. Drying; Gelcasting; $BaTiO_3$-based ceramic; Liquid desiccant

1. Introduction

Gelcasting is a relatively new near-net-shape ceramic forming process that is used in manufacturing advanced structural and functional ceramic parts for various industries [1–4]. The gelcasting process involves the dispersion of ceramic powders in a polymerizable aqueous monomer solution to form a fluid, castable slurry which is then gelled in a mold. Resulting from this *in situ* polymerization, the crosslinked polymer gels, which are three-dimensional network structures, hold the ceramic particles together. After removal from the mold, the gelled part, which is very homogeneous, contains moisture, as about a quarter of its mass, which should then be removed by drying. Then, binder removal and sintering are carried out as in other ceramic processes.

Drying, i.e. solvent removing from green gelcast parts, is an essential step in the gelcasting process [5–7]. Recently liquid desiccant drying has been used as a novel method in drying gelcast ceramic parts [8–10]. The green bodies are brought into contact with an appropriate liquid desiccant, by immersion. The reason for the effect of the liquid desiccant on a gelcast part is the osmotic difference between the liquid desiccant and the gelled polymer in the part.

Although studies about liquid desiccant drying of gelcast ceramic parts are available in the literature, there is no further investigation about the sintering characteristics of gelcast ceramic parts dried by the liquid desiccant method. In this investigation, we are concerned with polyacylamide gels which are filled by various solid loading of $BaTiO_3$-based ceramic powder undergoing drying (collapse) in various isothermal solutions of liquid desiccant, and the sintering characteristics of corresponding ceramic parts.

---

* Corresponding author. Tel.: +86 27 87557447x604; fax: +86 27 87545167.
E-mail address: pinger87@163.com (Z. Zheng).

0272-8842/$34.00 © 2007 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2006.12.001

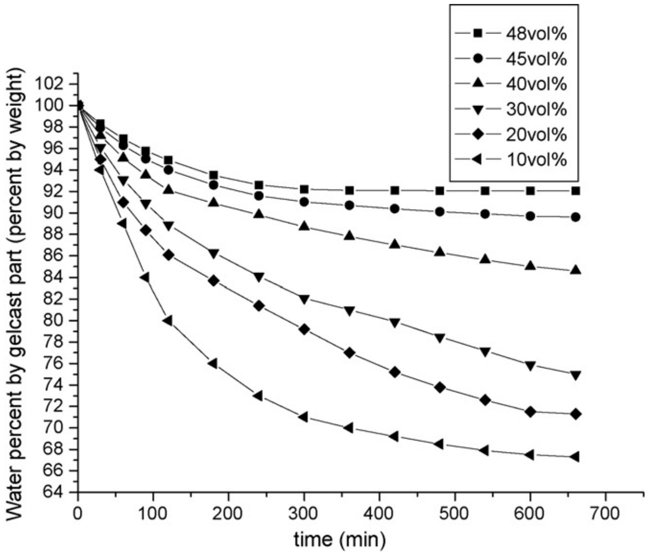

Fig. 1. Comparison of drying for gelcast parts with various loading levels of $BaTiO_3$-based ceramic in 20 wt% aqueous solution of PEG1000.

2. Experimental

$BaTiO_3$ aqueous slurry for gelcasting was composed of $BaTiO_3$-based ceramic powder, dispersant (ammonium polymethacrylamide, a self-made 10% aqueous solution), a monomer (acrylamide) and a crosslinker (*N*,*N*′-methylenebisacrylamide), a pH adjustor (ammonia) and deionized water. A small amount of ammonium persulfate and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine were added as an initiator and a catalyst, respectively, for the free-radical polymerization reaction of the monomer and the crosslinker. The starting $BaTiO_3$-based PTCR ceramic powder has a nominal composition of $Ba_{0.78}Sr_{0.22}Ti_{1.01}O_3 + 0.15\ \mathrm{mol\%}Y_2O_3 + 2.0\ \mathrm{mol\%}SiO_2 + 0.08\ \mathrm{mol\%}Mn(NO_3)_2$, consisting of $Mn(NO_3)_2$ and the calcined mixture of $BaCO_3$, $SrCO_3$, TiO_2, SiO_2, and Y_2O_3, and has an average particle size of 3.0 μm.

After casting and gelling, the samples were remoulded and immersed in an aqueous solution of PEG1000 as liquid desiccant solution. Each 30 min, samples were removed from the container and washed with deionized water. Excess water on the surface of the sample was drained off with tissue and then weighed. Shrinkage of the sample was measured using vernier caliper (0.02 mm accuracy). All of the samples were of cylindrical shape in this work.

3. Results and discussion

Experiments were designed as follows: all of the samples were $BaTiO_3$ gelcast cylinders of 13 mm diameter. Several sets of experiments were performed on these samples. In each set, one of the two parameters (i.e. solid loading level and liquid desiccant concentration) varied while the other was kept constant. Six levels of solid loading (i.e. 10 vol.%, 20 vol.%, 30 vol.%, 40 vol.%, 45 vol.% and 48 vol.%) and five levels of liquid desiccant concentration (i.e. 20 wt%, 40 wt%, 60 wt%, 80 wt% and 90 wt%) were used. In all the experiments, the concentration of liquid desiccant on the surface of the sample remained constant during the drying cycle.

It is known that the kinetic behavior of the drying of pure gel is a Fickian diffusion with volume change. Change in the amount of solid loading of the gel at a constant concentration of liquid desiccant solution has no effect on the type of diffusion and the drying of gel in a constant concentration of liquid desiccant [7]. The experiments showed that changing the solid loading level in the gels has a significant effect on the drying rate of gelcast parts. The results obtained from drying samples with the above six levels of solid loading (i.e. 10 vol.%, 20 vol.%, 30 vol.%, 40 vol.%, 45 vol.% and 48 vol.%) in 20 wt% aqueous solution of PEG1000 are compared in Fig. 1. As expected, lower solid loading in the gel creates higher drying potentials and higher drying rates, accordingly more shrinkage, whereas relatively higher solid loading creates lower drying potentials and lower drying rates, therefore less shrinkage, as shown in Fig. 2.

The concentration of aqueous solution of liquid desiccant is another parameter which affects the drying rate of the gelcast parts. The results obtained for gelcast parts of 48 vol.% solid loading, dried in various concentration of liquid desiccant, are shown in Fig. 3. Higher concentration of the liquid desiccant creates higher drying rates. This could be attributed to the difference between the concentration of water in the gel and the liquid desiccant solution. This difference results in a gradient of chemical potential between the two media. Higher the gradients, cause more diffusion of water from gel to the solution. As a result, the rate of drying increases accordingly.

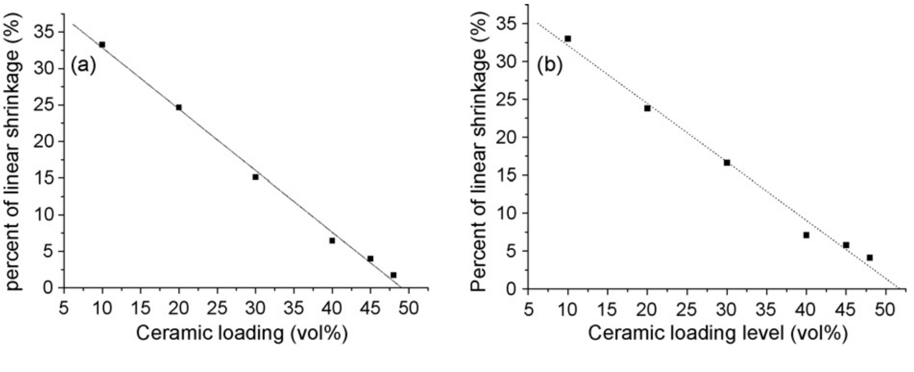

Fig. 2. Comparing the variation of linear shrinkage of gelcast parts in various loading levels of ceramic (a) in the diameter directions, (b) in the length.

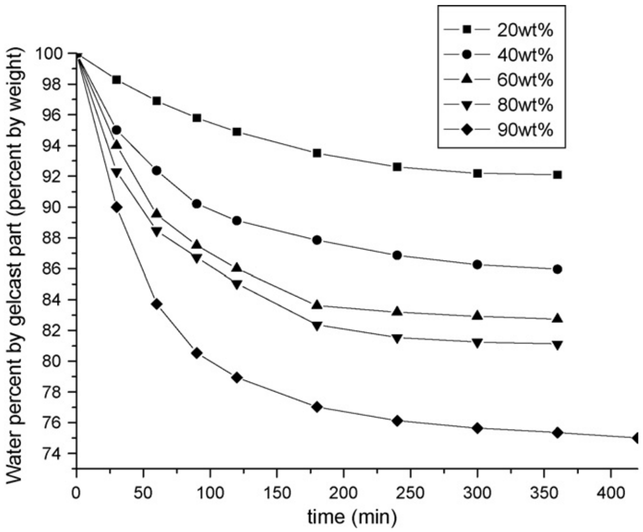

Fig. 3. Comparison of drying for 48 vol.% gelcast $BaTiO_3$-based ceramic parts in various concentrations of liquid desiccant.

In the experiments, some parts were cracked and became useless during drying or after sintering because of cracking or crazing on the surface or across the width of the samples. In order to understand the cause of cracks in gelcast parts during the drying process and sintering procedure, a detailed investigation was made on the state of the samples.

As for the samples with 10 vol.% solid loading, all were cracked across the width, when immersed in 40 wt%, 60 wt%, 80 wt% and 90 wt% aqueous solution of PEG1000 within 30 min. Only the sample immersed in 20 wt% aqueous solution of PEG1000 kept its shape while it lost 50 wt% of its interior solvent. Then it was moved to room atmosphere until losing 90 wt% of its interior solvent safely, and it continued drying in an oven with higher temperature, but in this period it deformed and lost its dimensional stability and a longitudinal crack was observed.

In samples with 20 vol.% solid loading, surface cracking which penetrated to some extent across the depth was observed, when the samples immersed in 60 wt%, 80 wt% and 90 wt% aqueous solution of PEG1000 after about 120 min, 65 min and 15 min, respectively. When immersed in 20 wt% and 40 wt% aqueous solution of PEG1000, the samples kept their shape losing 40.9 wt% and 44.3 wt% of their interior solvent. Then they were moved to room atmosphere until losing more than 90 wt% of their interior solvent safely, and continued drying in an oven with higher temperature without any longitudinal cracks.

As regard to samples with solid loading of 30 vol.%, 40 vol.%, 45 vol.% and 48 vol.%, no warpage or longitudinal cracking was observed when the samples were immersed in the above five levels of liquid desiccant concentration respectively. After 720 min, the parts were removed from the solution. Finally, drying was continued in the air at room temperature and humidity until more than 70 wt% of their interior solvent was lost, and their drying continued safely in an oven with higher temperature.

From Fig. 4, it can be seen, when increasing solid loading to 48 vol.%, and drying in high concentration of liquid desiccant (90 wt%), samples can safely lose about 25 wt% of interior water in a short time (about 5 h) and complete most of the shrinkage associated with drying, then continue their drying in an oven with higher temperature safely.

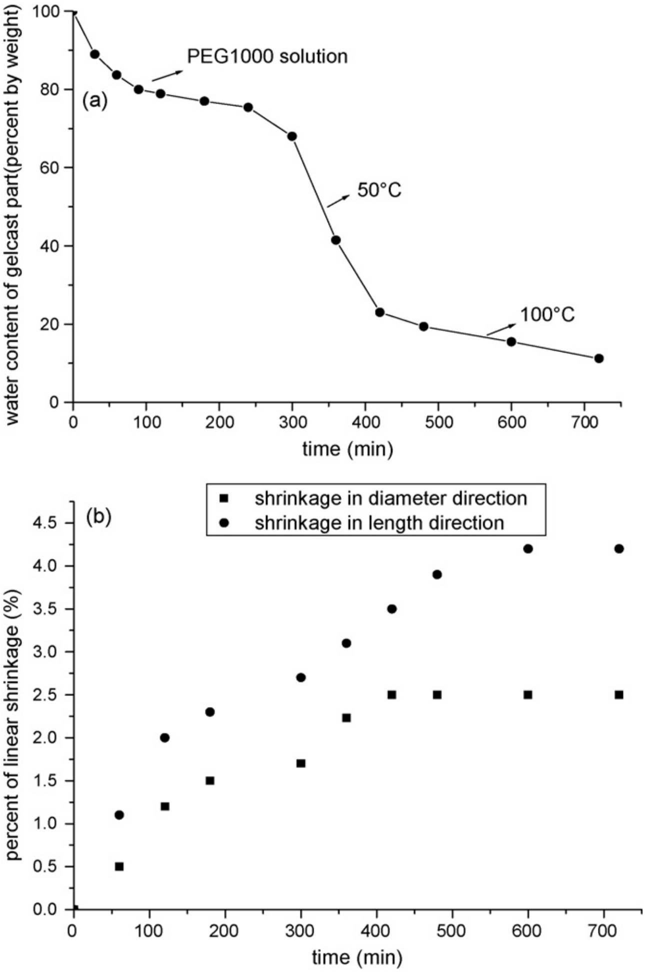

Fig. 4. (a) Drying of 48 vol.% $BaTiO_3$ gelcast cylinder in an aqueous solutions of PEG1000, followed by drying in an oven at 50 and 100 °C, (b) linear shrinkage in length and diameter of $BaTiO_3$ gelcast cylinder.

The result of the pyrolysis study of the gelcast $BaTiO_3$-based ceramic in air showed that pyrolysis occurred mainly between 260 °C and 410 °C [11], heating rate on the order of 1 °C/min to temperatures as high as 600 °C has been used successfully for gelcast $BaTiO_3$-based parts. Such slower heating rate is dictated because the gelcast parts are large. Appropriate time at temperature is required to pyrolyze the polymers and to allow gases to escape from the body.

Based on the above pyrolysis study, all parts, which safely shrank during drying process, were sintered according to the sintering schedule shown in Fig. 5. It can be seen, the schedule has a low increasing rate from room temperature to 600 °C for the binder removal, and a long soaking time at the sintering temperature of 1330 °C for densification. After sintered, the surface status of the sintered samples was observed. The results were shown as follows:

The ceramics with loading level of 48 vol.% and 45 vol.%, dried in various concentration of aqueous solution PEG1000,

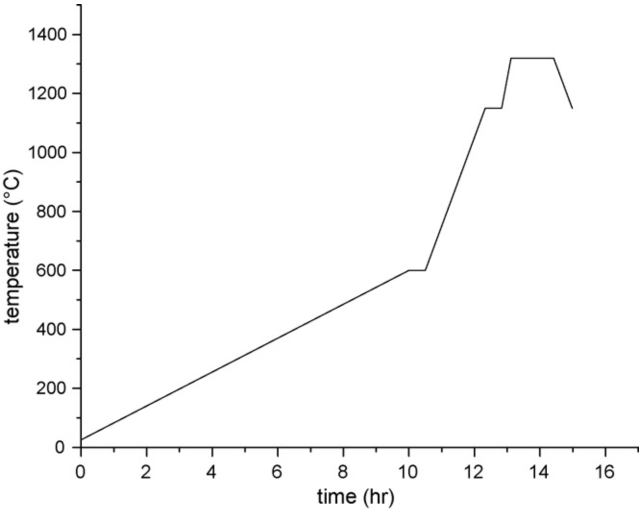

Fig. 5. The firing schedule for gelcast ceramics.

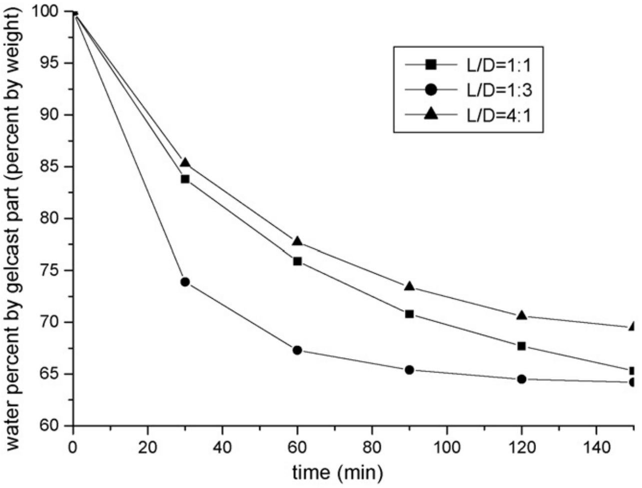

Fig. 7. Effect of dimensions of cylindrical gelcast parts on the time and the rate of drying.

have smooth surface and no crack. While the ceramics with 40 vol.% loading, the ones, dried in 20 wt% and 40 wt% aqueous solution of PEG1000, also have smooth surface and no crack, whereas the others dried in higher concentration solution of PEG1000, appear many crazing on the surface of the samples. As for ceramic samples with loading level of 30 vol.% and 20 vol.%, dried in various concentration of aqueous solution PEG1000, severely crack or the surface peel off, although the critical stage of drying process of the gelcast parts could be carried out safely (i.e. no cracks, warp or uncontrolled shrinkage) by using liquid desiccant method, and the part safely continues its drying in air at room conditions or in an oven.

From the results above, it can be concluded that samples with lower loading level, when immersed in higher concentration of the liquid desiccant, create higher drying rates near the drying surface owing to great solvent gradient, resulting in greater compressive stresses on the network in that region. This produces non-uniform and differential shrinkage in various regions of the samples (especially between the drying surfaces and the center of the samples), and induces structural and residual stresses which is the cause of cracking during drying, and crazing on the surface or even severely cracking, the surface peeling off and other malformations during sintering procedure, although these ceramics with low solid loading experienced the critical stage of drying process in low concentration of the liquid desiccant and perform most shrinkage, and finished their drying in higher temperature.

From Fig. 6, it is seen that the solid loading level of gelcast part obviously affects the density of gelcast ceramics sintered using the same systems. For green gelcast parts of cylindrical shape with 13 mm diameter and aspect ratio 4:1, as the solid loading increases greatly from 20 vol.% to 48 vol.%, density of corresponding ceramic increases from 90.2% to 93.8%. This result is in good agreement with the study by Hu et al. [4].

The thickness of sample is another factor that has considerable effect on the time and the rate of drying. With 40 vol.% solid loading, green $BaTiO_3$ gelcast parts of cylindrical shape with 15 mm diameter and different thickness were prepared based on conventional aqueous gelcasting methods. Fig. 7 shows drying curves for the $BaTiO_3$ gelcast

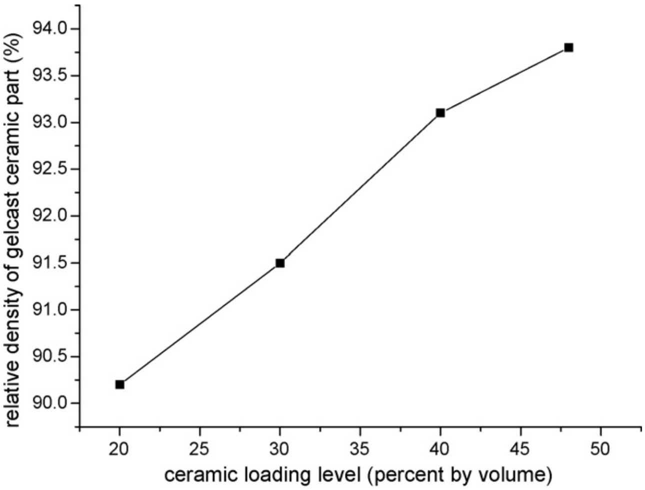

Fig. 6. Comparison of density of gelcast part with various ceramic-loading levels.

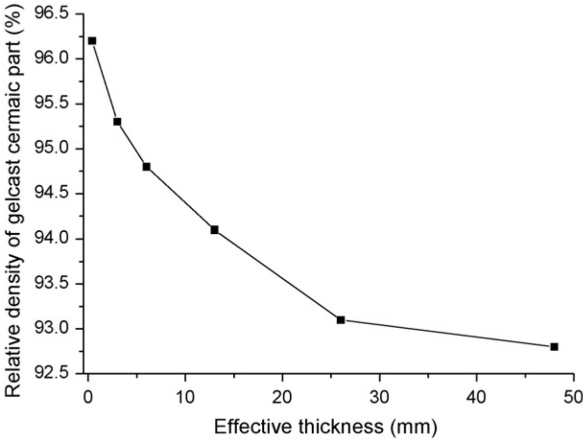

Fig. 8. Comparison of density of ceramic parts with various effective thickness.

parts with different thickness (i.e. aspect ratio of L/D = 1:1, 1:3, and 4:1) dried in liquid desiccant solution. It can be seen, rate of drying decreases with increase in sample thickness. Thicker samples correspond to longer transport distances and hence result in drying rates that are much smaller than those for thin gelcast parts, which is reasonable. As shown in Fig. 8, thickness of gelcast parts also has considerable effect on the density of ceramics sintered using the same systems. With increase in the thickness of gelcast parts, the density of ceramics decreased considerably.

4. Conclusion

The loading level of ceramic powders and the liquid desiccant concentration significantly effect the drying process and the sintering characteristics of the ceramic parts. Lowering the loading level of ceramic powders and increasing the concentration of the liquid desiccant, non-uniform and differential drying in various regions due to great solvent gradient, induces structural and residual stresses which cause defects, such as cracking, bending and other malformations, which make the articles useless during the drying process and sintering procedure. However, when increasing the solid loading of green gelcast articles to more than 45 vol.%, the stresses developed during drying can be greatly reduced, and a high concentration of the liquid desiccant can be used without inducing defects. After the critical stage of drying process in liquid desiccant, gelcast parts can safely continues their drying in air at room conditions or in an oven.

The loading level of ceramic powders and the thickness of parts have a considerable effect on the density of ceramic parts. Higher solid content in the gel, and lower thickness of parts, increase the density of parts.

Acknowledgment

This work was partly financially supported by Science and Technology R & D Program of Hubei Province, China (Project: 2004AA102A01).

References

[1] O.O. Omatete, M.A. Janney, R.A. Strehlow, Am. Ceram. Soc. Bull. 70 (10) (1991) 1641–1649.

[2] A.C. Young, O.O. Omatete, M.A. Janney, et al. J. Am. Ceram. Soc. 74 (3) (1991) 612–618.

[3] S.P. Gong, Z.P. Zheng, D.X. Zhou, et al. Mater. Sci. Eng. B 99 (2003) 408–411.

[4] Y.X. Hu, D.X. Zhou, D.L. Zhang, et al. Sens. Actuators A 88 (2001) 67–70.

[5] S. Ghosal, A. Emami-Naeini, Y.P. Harn, et al. J. Am. Ceram. Soc. 82 (3) (1999) 513–520.

[6] O.O. Omatete, R.A. Strehlow, C.A. Walls, in: M.A. Cima (Ed.), Forming Science & Technology for Ceramics, Am. Ceram. Soc., Westerville, OH, 1992, pp. 101–107.

[7] W.S. George, J. Am. Ceram. Soc. 73 (1) (1990) 3–14.

[8] M.A. Janney, J.O. Kiggans, US Patent 5,885,493 (March 1999).

[9] A. Barati, M. Kokabi, N. Famili, Ceram. Int. 29 (2003) 199–207.

[10] A. Barati, M. Kokabi, N. Famili, J. Eur. Ceram. Soc. 23 (2003) 2265–2272.

[11] Y.X. Hu, Study on gelcasting of $BaTiO_3$-based semiconducting ceramic, Dissertation, 2001.