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Effect of the carbothermal reaction on the pore growth of barium titanate based ceramics sintered in the reducing atmosphere

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Abstract

The sintering behavior of the $(\text{Ba}_{0.87}\text{Ca}_{0.13})_{1.000}(\text{Ti}_{0.85}\text{Zr}_{0.14}\text{Mn}_{0.01})_{1.003}\text{O}_3$ doped with Nb_2O_5 and BaCO_3 sintered in different atmospheres was investigated. When samples were sintered in the reducing atmosphere, the development of Ti-rich phase of $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ was depressed and the growth of pores was significantly developed at temperatures $> 1250^\circ\text{C}$, which are attributed to the carbothermal reaction of Ti_xO_y . A mechanism of the pore growth related to the entrapped insoluble gases CO_x derived from the carbothermal reaction of Ti_xO_y is proposed.

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1. Introduction

There are two ways to increase the volumetric efficiency of a capacitor, i.e., reduction of the thickness of each dielectric layer and increase of the room temperature dielectric constant. To achieve these goals, very fine powders are desirable. Therefore, the dielectric powders were usually synthesized by wet chemical methods. However, because the organic materials are difficult to be burnt out, residual carbon usually exists.

For the reduction of the production cost, base metals used as the inner electrodes have become the trend for the market of the multilayer ceramic capacitor. However, the base metal electrodes have to be fired in the reducing atmosphere to protect them from oxidation [1–6]. Atmosphere was known to have two important effects on the sintering of ceramics, i.e., to modify densification rate and limiting density [7]. The latter was usually attributed to the trap of the insoluble gas [8,9]. The densification process stops when the internal gas pressure counterbalances the surface tension driving force. The insoluble gas might arise directly from the atmosphere [8] or indirectly from the internal gas forming reaction [9]. In the latter case, when a soluble gas from the atmosphere diffuses through the sintering

body and reacts with an impurity to form an insoluble reaction product, there is an increase in internal pore pressure. This results in density loss and compact swelling.

Usually, the gases are generated via an oxidation reaction. However, a more complicated reaction of gas generation, i.e., carbothermal reaction of the oxide [10] may happen in a reducing atmosphere. The purpose of this investigation is to explore the effect of this new mechanism on the pore growth in sintering barium titanate based ceramics in different atmospheres.

2. Experimental procedure

The powder with a composition of $(\text{Ba}_{0.87}\text{Ca}_{0.13})_{1.000}(\text{Ti}_{0.85}\text{Zr}_{0.14}\text{Mn}_{0.01})_{1.003}\text{O}_3$ (BCTZM) was synthesized by the sol-gel method (Nippon Chemical Industrial Co. Ltd, Tokyo, Japan). For sintering study, the powder was ground for 24 h in a Nylon 6 jar with ZrO_2 balls as the medium. After grinding, the slurry was dried, and then pressed as a pellet. The green density was about 52% of the theoretical density (The theoretical density of the powder determined by the X-ray method was 5.855 g/cm^3). The pellets were sintered at a heating rate of $5^\circ\text{C}/\text{min}$ in a temperature range from 1100°C to 1400°C for 2 h in air and in 5% H_2 -95% N_2 . The sintered density was determined by the Archimedes method. The doped samples were prepared

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by mixing BCTZM with various amounts of Nb_2O_5 and BaCO_3 and followed the same procedure mentioned above.

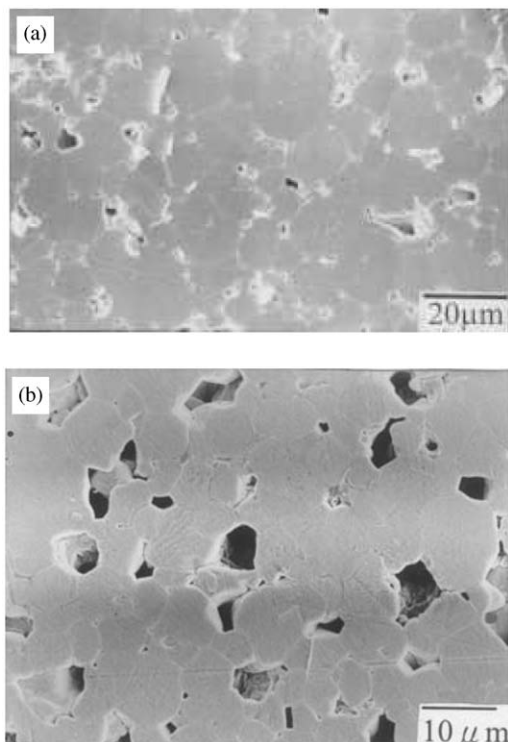


Fig. 1. Comparison of the microstructures of BCTZM doped with 1 mol% Nb_2O_5 sintered at 1400°C for 2 h in: (a) air and (b) $5\text{H}_2/95\text{N}_2$.

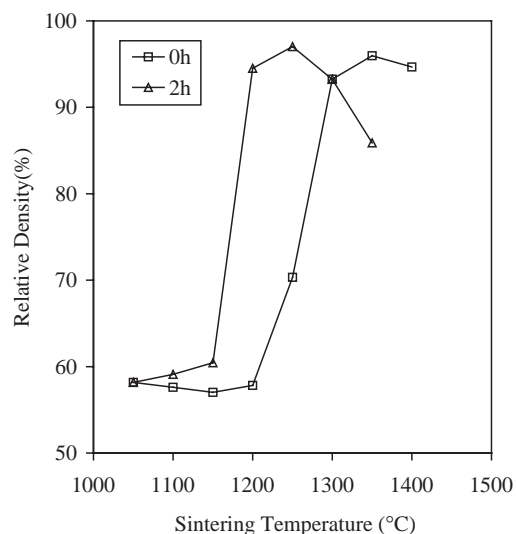


Fig. 2. Relative density versus sintering temperature for BCTZM doped with 1 mol% Nb_2O_5 sintered in $5\text{H}_2/95\text{N}_2$ for 0 and 2 h.

Scanning electron microscope (SEM) (model XL-40 FEG, Philips, Holland and model JXA-840, JEOL, Nakagami Akishima, Tokyo, Japan) was used to characterize the microstructures. Electron probe X-ray microanalysis (EPMA) (Jeol JXA-8800) equipped with wavelength-dispersive spectrometer (WDS) was used to analyze the composition of the second phase. Thermogravimetric analysis (Model Setaram TGA/DTA 24, Setaram company, France) was used to determine the weight loss of samples heated in different atmospheres.

3. Results

In the previous work [11], it was found that the densities of the samples of BCTZM sintered in $5\% \text{H}_2-95\% \text{N}_2$ started to decrease at temperatures $> 1250^\circ\text{C}$. Moreover, there are two features of the microstructures of BCTZM sintered in air and $5\% \text{H}_2-95\% \text{N}_2$, i.e., the former revealed small amount of second phase without pore growth but the latter showed pore growth without second phase. Because the powder of BCTZM is slightly Ti-rich, the amount of the second phase is too less for the compositional analysis. In order to increase the amount of the second phase, Nb_2O_5 was added to substitute Ti ion in BCTZM. Fig. 1 shows the comparison of the microstructures of 1 mol% Nb_2O_5 -doped BCTZM sintered at 1400°C in air and $5\% \text{H}_2-95\% \text{N}_2$ for 2 h. As observed, the microstructures reveal the same behavior as the undoped BCTZM, i.e., the former contains second phase without pore growth but the latter reveals pore growth without second phase. The composition of the second phase had been analyzed by WDS and is listed in Table 1, which is close to Ti-rich phase of $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$. Fig. 2 shows the comparison of the relative density versus temperature for 1 mol% Nb_2O_5 -doped BCTZM sintered in $5\% \text{H}_2-95\% \text{N}_2$ for 0 and 2 h. As observed, densities of 0-h samples do not decrease at high temperatures but those of 2-h samples become to decline at temperatures $> 1250^\circ\text{C}$. These results indicate that the occurrence of pore growth is time-dependent, which may be related to some reaction. Fig. 3 shows the microstructure of 2 mol% Nb_2O_5 -doped BCTZM sintered at 1400°C in air for 2 h. As observed, while the density still remains high, pore growth occurs but it is not as serious as in the atmosphere of $5\% \text{H}_2-95\% \text{N}_2$, i.e., the pore size is not large.

The comparisons of relative density versus temperature for samples of BCTZM doped with 1 mol% Nb_2O_5 -1 mol% BaCO_3 , 1 mol% Nb_2O_5 -2 mol% BaCO_3 , and

Table 1

Compositions of BCTZM doped with 1 mol% Nb_2O_5 sintered at 1400°C for 2 h in air

Element	Ba	Ca	Ti	Zr	Mn	Nb	O
at%	9.11	0.91	22.10	2.18	1.21	0.00	64.50

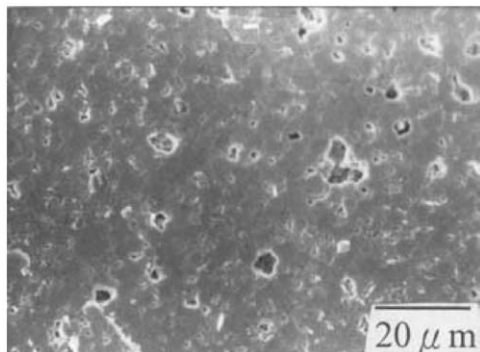
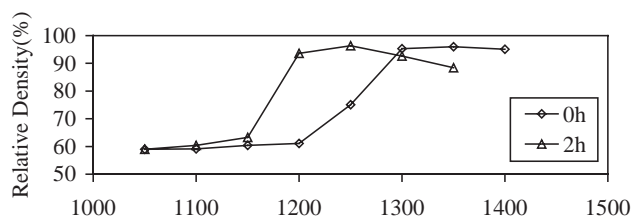
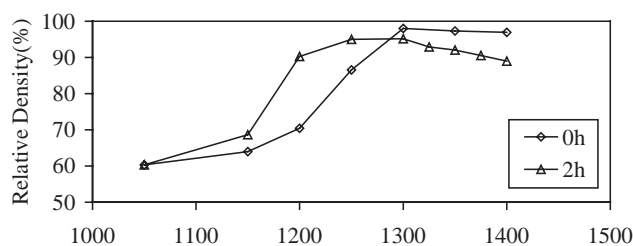


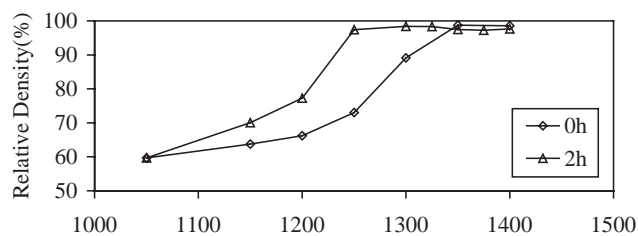
Fig. 3. Microstructure of BCTZM doped with 2 mol% Nb_2O_5 sintered at 1400°C for 2 h in air.



(a) Sintering Temperature ($^\circ\text{C}$)



(b) Sintering Temperature ($^\circ\text{C}$)



(c) Sintering Temperature ($^\circ\text{C}$)

Fig. 4. Relative density versus sintering temperature for BCTZM doped with (a) 1 mol% Nb_2O_5 and 1 mol% BaCO_3 , (b) 1 mol% Nb_2O_5 and 2 mol% BaCO_3 , and (c) 1 mol% Nb_2O_5 and 2.5 mol% BaCO_3 sintered for 0 and 2 h in $5\text{H}_2/95\text{N}_2$.

1 mol% Nb_2O_5 -2.5 mol% BaCO_3 sintered in $5\% \text{H}_2$ - $95\% \text{N}_2$ for 0 and 2 h, are shown in Fig. 4. The microstructures of these samples sintered at 1400°C in $5\% \text{H}_2$ - $95\% \text{N}_2$ for 2 h are shown in Fig. 5. As observed, for samples doped with 1 mol% Nb_2O_5 -1 mol% BaCO_3 and 1 mol% Nb_2O_5 -2 mol% BaCO_3 , density reduction or pore growth occurs at temperatures $>1250^\circ\text{C}$. However, the degree of reduction decreases with the increase of Ba content. For 1 mol% Nb_2O_5 -2.5 mol%

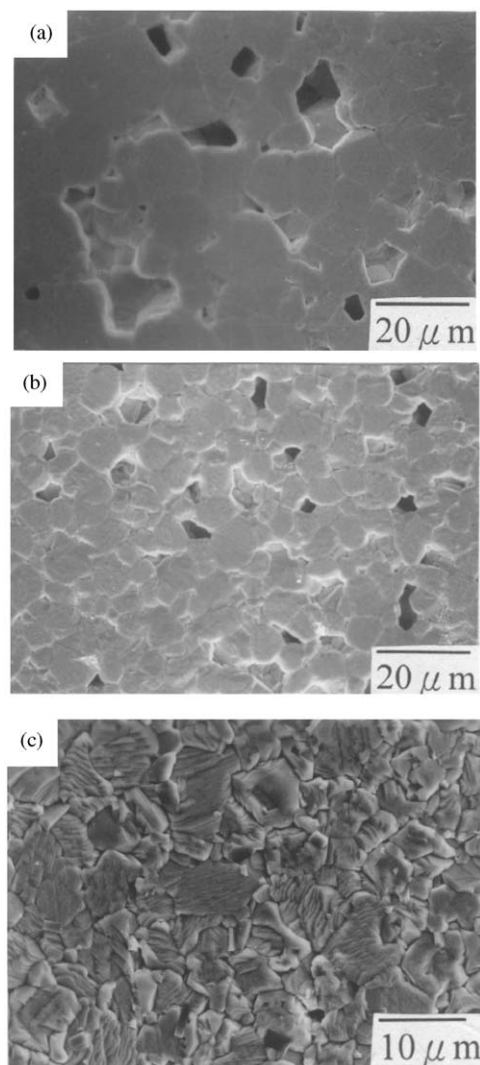


Fig. 5. Microstructures of BCTZM doped with (a) 1 mol% Nb_2O_5 and 1 mol% BaCO_3 , (b) 1 mol% Nb_2O_5 and 2 mol% BaCO_3 , and (c) 1 mol% Nb_2O_5 and 2.5 mol% BaCO_3 , sintered at 1400°C for 2 h in $5\text{H}_2/95\text{N}_2$.

BaCO_3 doped BCTZM, density reduction or pore growth is not observed. Fig. 6 shows the microstructure of the BCTZM presintered at 1200°C for 6 h in air and then sintered at 1400°C for 2 h in $5\% \text{H}_2$ - $95\% \text{N}_2$. It shows that pore growth does not occur and the density has reached 97% theoretical density. Fig. 7 shows the microstructure of 2 mol% Nb_2O_5 -doped BCTZM specimens sintered at 1400°C in O_2 for 2 h. As observed, pore growth does not occur but the second phase is present in this sample.

4. Discussion

In the recent work [11], pore growth was found to be related to the residual carbon and atmosphere in

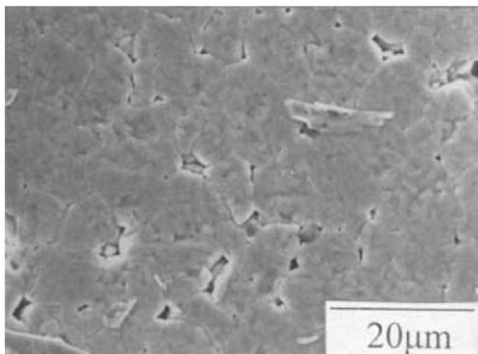


Fig. 6. Microstructure of BCTZM presintered at 1200°C for 6h in air and then sintered at 1400°C for 2h in 5H₂/95N₂.

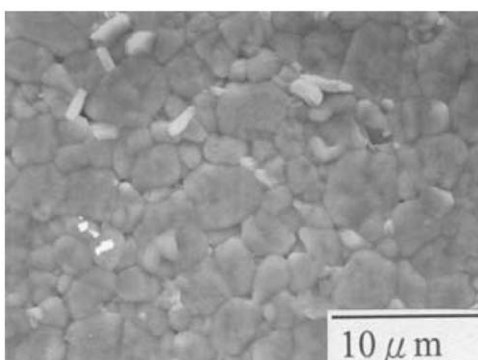


Fig. 7. Microstructures of BCTZM doped with 2mol% Nb₂O₅ sintered at 1400°C for 2h in O₂.

sintering BCTZM. However, the mechanism was not detailed. According to the literature, the major reasons for the pore growth are as follows: (i) the insoluble gas atmosphere [8], (ii) the presence of adsorbed gases [12], (iii) the action of second phase [13], and (iv) the delayed gas reaction [9,14]. It should be pointed out that there is a major difference between mechanisms (i) and (iv), namely, the former occurs at higher density >99% theoretical density [8] but the latter can occur at lower density <99% theoretical density [14], which could be attributed to the fact that the latter could generate a large amount of gases. In view of the fact that pore growth occurred at density around 95% theoretical density in this investigation, mechanism (i) can be eliminated. Moreover, it was suggested that N₂, though not soluble, would not be entrapped in the pore when it is in the dry N₂–H₂ atmospheres that contain ≥2% H₂ [15]. If so, N₂ would not be entrapped in the pore because the atmosphere used in this investigation is 5% H₂–95% N₂. The mechanism (ii) is also excluded because it does not depend on the atmospheres. Moreover, pore growth was not observed in air-sintered sample with the presence of second phases, so mechanism (iii) is also eliminated. Residual carbon might be present in the powder used in this investigation because the powder was produced via a sol–gel process [16–18].

Moreover, the residual carbon would even exist at high temperatures >1000°C when samples are sintered in an atmosphere of a mixture of hydrogen and nitrogen [19]. It is also indirectly supported by the TGA data measured in this investigation, in which the weight loss in air was 1000 ppm higher than in argon. Intuitively, the oxidation of carbon impurity in the material to form CO_x gases may be the reason for the pore growth [9,14]. However, it is in contradiction to the results of this investigation, which shows that pore growth occurs significantly in the reducing atmosphere rather than in air. Therefore, the mechanism (iv), the so-called delayed gas reaction, can be excluded.

In comparing samples sintered in air and reducing atmosphere, shown in Figs. 1 and 2, there are two features for samples sintered in 5% H₂–95% N₂, i.e., the absence of Ti-rich phase of Ba₆Ti₁₇O₄₀ and the density reduction occurring at temperatures >1250°C. It should be pointed out that excessive Ti ions segregated to the grain boundary may be in a state of Ti_xO_y before it forms Ba₆Ti₁₇O₄₀. Because the carbon residue is suggested to exist based on the TGA data, the formation of CO and CO₂ gases can be via the carbothermal reduction of Ti_xO_y species [10] when samples are sintered in the reducing atmosphere. Therefore, it is inferred that pore growth may be related to insoluble gases CO_x derived from the carbothermal reduction of Ti_xO_y. This carbothermal reaction not only induces pore growth but also depresses the development of Ti-rich phase of Ba₆Ti₁₇O₄₀ because Ti_xO_y would become TiC during the reaction. Moreover, according to the reports [10], the carbothermal reaction would occur significantly at temperatures above 1250°C, which is consistent with the temperature of density reduction for samples without or with doping (Figs. 2 and 4). As discussed above, the two features for the samples sintered in the reducing atmosphere are explained.

There are two ways to further justify the effect of carbothermal reaction on pore growth, i.e., to remove the reaction source of excessive Ti ions or residual carbon. The reduction of excessive Ti ions can be done by substituting A-site ions with foreign ions. Actually, it has been justified by the results of Figs. 4 and 5, showing that pore growth did not occur when Ba was high enough to let composition become stoichiometric or Ti-deficient. The second way to prevent the development of pore growth is to eliminate the residual carbon. When the sample was presintered at 1200°C for 6h in air, and then sintered at 1400°C for 2h in 5% H₂–95% N₂, pore growth was not observed though the second phase was present, which can be attributed to the exhaustion of the residual carbon, evidenced in Fig. 6.

In this investigation, pore growth was not observed for all the samples without doping or with low Nb content <2 mol% sintered in air. However, insignificant pore growth could be observed in the samples with high

Nb content ≥ 2 mol% sintered in air (Fig. 3). It should be noted that in this case, their densities are still higher, the pore sizes are smaller, and the pore numbers are less than those of samples sintered in 5% H_2 –95% N_2 . It is considered that when Nb content is very high, too much excessive Ti ions will exist. Because the process was not in an equilibrium state under the sintering conditions, sufficient amount of excessive Ti would not completely form $Ba_6Ti_{17}O_{40}$ but be in a state of Ti_xO_y . Thus, if the residual carbon would not be completely removed for samples sintered in the air, a small amount of CO_x gases would be generated via the carbothermal reaction of Ti_xO_y , which in turn would induce pore growth. By contrast, if the residual carbon could be completely removed, pore growth would be inhibited, which was evidenced by the result of Fig. 7 and further justifies the above discussion.

5. Conclusions

Pore growth occurs significantly for Ti-rich BCTZM sintered in the reducing atmosphere but insignificantly for BCTZM with high Nb content > 2 mol% sintered in air. The mechanism of pore growth can be attributed to the entrapment of the insoluble gases CO_x generated via the carbothermal reaction of Ti_xO_y . Moreover, when Ti-rich BCTZM is sintered in the reducing atmosphere, the development of the Ti-rich $Ba_6Ti_{17}O_{40}$ phase can be depressed owing to the occurrence of the carbothermal reaction.

Acknowledgments

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References

- [1] Y. Sakabe, Dielectric materials for based-metal multilayer ceramic capacitors, *Am. Ceram. Soc. Bull.* 66 (9) (1987) 1338.
- [2] Y.H. Han, J.B. Appleby, D.M. Smyth, *J. Am. Ceram. Soc.* 70 (2) (1987) 96.
- [3] X.W. Zhang, Y.H. Han, M. Lal, D.M. Smyth, *J. Am. Ceram. Soc.* 70 (2) (1987) 100.
- [4] H.M. Chan, M.P. Harmer, M. Lal, D.M. Smyth, in: W. Krakow, D.A. Smith, L.W. Hobbs (Eds.), *Electron Microscopy of Materials*, Material Research Society Symposium Proceedings, Vol. 31, Elsevier Science Publishing, New York, 1984, pp. 345–350.
- [5] T.T. Fang, J.T. Shuei, *J. Mater. Res.* 14 (5) (1999) 1910.
- [6] S.B. Desu, in: J. Nowotny (Ed.), *Electronic Ceramic Materials*, Trans Tech Publications, Aedermannsdorf, Switzerland, 1992, pp. 375–418.
- [7] R.M. German, *Sintering Theory and Practice*, Wiley, New York, NY, USA, 1996, pp. 442–447 (Chapter 9).
- [8] Y.K. Paek, K.Y. Eun, S.J.L. Kang, Effect of sintering atmosphere on densification of MgO-doped Al_2O_3 , *J. Am. Ceram. Soc.* 71 (1988) C380–C382.
- [9] S.J. Bennison, M.P. Harmer, Grain growth and cavity formation in MgO-doped Al_2O_3 , in: M.F. Yan, A.H. Heuer (Eds.), *Advances in Ceramics*, The American Ceramic Society, Inc., Columbus, OH, USA, 1983, pp. 171–183.
- [10] W. Gruner, S. Stolle, K. Wetzig, Formation of CO_x species during the carbothermal reduction of oxides of Zr, Si, Ti, Cr, W, and Mo, *Int. J. Refractory Metals Hard Mater.* 18 (2000) 137–145.
- [11] Tsang-Tse Fang, P.H. Wu, Effect of atmospheres on the sintering behavior and microstructural evolution of $(Ba_{0.87}Ca_{0.13})_{1.000}(Ti_{0.85}Zr_{0.14}Mn_{0.01})_{1.003}O_3$, *Mater. Chem. Phys.*, accepted for publication.
- [12] R.C. Rossi, R.M. Fulrath, Final stage densification in vacuum hot-pressing of alumina, *J. Am. Ceram. Soc.* 48 (1) (1965) 558–564.
- [13] H.A. Wang, F.A. Kroger, Pore formation during oxidative annealing of iron-doped alumina and slowing of grain growth by precipitates and pores, *J. Mater. Sci.* 15 (1980) 1978–1986.
- [14] P. Miranzo, L. Taberner, J.S. Moyo, J.R. Jurado, Effect of sintering atmosphere on the densification and electrical properties of alumina, *J. Am. Ceram. Soc.* 73 (1990) 2119–2121.
- [15] G.C. Wei, W.H. Rhodes, Sintering of translucent alumina in a nitrogen-hydrogen gas atmosphere, *J. Am. Ceram. Soc.* 83 (7) (2000) 1641–1648.
- [16] C. Miot, E. Husson, C. Proust, R. Erre, J.P. Coutures, X-ray photoelectron spectroscopy characterization of barium titanate ceramics prepared by the citric route. residual carbon study, *J. Mater. Res.* 12 (9) (1997) 2388–2392.
- [17] C. Miot, C. Proust, E. Husson, G. Blondiaux, J.P. Coutures, Ageing influence on residual carbon content in different grinded $BaTiO_3$ ceramics analyzed by $^{12}C(d,p)^{13}C$ nuclear method, *J. Eur. Ceram. Soc.* 17 (1997) 1335–1340.
- [18] C. Miot, E. Husson, C. Proust, R. Erre, J.P. Coutures, Residual carbon evolution in $BaTiO_3$ ceramics studied by XPS after ion etching, *J. Eur. Ceram. Soc.* 18 (1998) 339–343.
- [19] K. Otsuka, *Multilayer Ceramic Substrate-Technology for VLSI Package/Multichip Module*, Elsevier Science Publishers LTD, London, 1993, p. 97.