Available online at www.sciencedirect.com
SCIENCE DIRECT

Journal of the European Ceramic Society 23 (2003) 2549–2552
www.elsevier.com/locate/jeurceramsoc

Phase analysis and microwave dielectric properties of LTCC TiO_2 with glass system

Sung-Hun Yoon[a], Dong-Wan Kim[a], Seo-Yong Cho[b], Kug Sun Hong[a,*]

[a]*School of Materials Science and Engineering, College of Engineering, Seoul National University, Seoul, South Korea*
[b]*Cerectron, Co., Ltd., 284, Kalgot-Li, Jinwee-Myun, PyeongTaek, Kyunggi, South Korea*

Abstract

Glass–ceramic composites containing TiO_2 (anatase, rutile) and modified borosilicate glasses were prepared and their sintering behaviour, phase evolution, interface reactions, and microwave dielectric properties were investigated as new candidates for low-temperature cofired ceramic (LTCC) materials. It was found that the addition of small amounts of borosilicate glasses lowered the sintering temperature of TiO_2 from 1400 to 900 °C. X-ray diffraction results showed that second phases, including Zn_2SiO_4, were formed when TiO_2 + zinc-borosilicate glass was used, while no crystalline phase except rutile could be found using unmodified borosilicate glass. High-density TiO_2 + zinc borosilicate glass material showed promising microwave dielectric properties: relative dielectric constant (ε_r) = 74, quality factor ($Q \times f$) = 8000 GHz, and temperature coefficient of resonant frequency (τ_f) = 340 ppm/°C. The effect of borosilicate glasses on the anatase–rutile phase transition was also investigated.

Keywords: Capacitors; Dielectric properties; Electron microscopy; Sintering; TiO_2

1. Introduction

Low-temperature cofired ceramic (LTCC) technology offers benefits for high density, high RF and fast digital applications requiring hermetical packaging and good thermal management. To fill the need for various circuit materials in RF ranges, a new lower loss, high dielectric constant LTCC system is required. There are two approaches to searching LTCC compositions sinterable below 900 °C. The first consists of adding a low softening temperature glass to the ceramic dielectrics.[1] The second is the use of low melting temperature oxides as sintering additives.[2,3]

TiO_2 has been extensively studied in electronic applications including Type I capacitors. It has a high dielectric constant (ε_r = 104) and high quality factor ($Q \times f$ > 40,000).[4] TiO_2 is also known for its polymorphism.[5,6] The most common polymorphs are rutile and anatase. Rutile has been identified as the room-temperature stable form of TiO_2, and anatase converts to rutile at the temperature range of 400–1200 °C on heating.[7]

Borosilicate glasses (BSG) are the most commonly used glass materials in glass + ceramic composites for microelectronic packaging. It was reported that the densification of glass + ceramic composites can be described by conventional three-stage liquid phase sintering.[8] Depending upon the reactivity between glass and ceramic, the densification of composites can be classified as either nonreactive, partially reactive, or completely reactive systems. It was previously demonstrated that TiO_2 with BSG was a nonreactive system.[8]

In this study the sintering behaviour and microwave dielectric properties of TiO_2 + glass-based LTCCs were investigated. Borosilicate and zinc borosilicate glass, which have different viscosities during heating, were used as additives. The sintering behaviour of the TiO_2 + glass system was studied in conjunction with phase transitions.

2. Experimental procedure

The starting materials used were anatase (Merck, Germany) and rutile (Ferro, USA) powders with 99 and 99.8% purity, respectively. BSG and zinc borosilicate glass (ZBSG) used as sintering agents were synthesized using appropriate amounts of B_2O_3, SiO_2, and ZnO. The pellets were sintered in the temperature range of 850–1000 °C for 2 h at heating rates of 5 °C/min. The bulk density of the sintered samples was determined by

* Corresponding author. Tel.: +822-880-8316; fax: +822-886-4156.
E-mail address: kshongss@plaza.snu.ac.kr (K.S. Hong).

0955-2219/03/$ - see front matter
doi:10.1016/S0955-2219(03)00144-4

the Archimedes' method. Shrinkage of the specimens during heating was measured with a horizontal-loading dilatometer with alumina rams and boats (DIL 402C, Netzsch Instruments, Germany).

Quenching experiments were conducted in air. Phase evolution was investigated by powder X-ray diffraction (M18XHF, Macscience Instruments, Japan). Polished surfaces of sintered samples were thermally etched at 850 °C for 30 min in order to examine their microstructures using a scanning electron microscopy (SEM, Jeol-6330F, Jeol, Japan).

Microwave dielectric properties of sintered samples were measured in the *x* band using a network analyser (Model HP8720C, Hewlett Packard, USA).

3. Results and discussion

Fig. 1 shows the effect of a 20 wt.% BSG and ZBSG addition on the shrinkage behaviour of anatase and rutile samples. The results demonstrate that the onset of shrinkage moves towards much lower temperatures with the addition of glasses. The shrinkage onset temperature of TiO_2 + BSG was around 700 °C, while that of TiO_2 + ZBSG was around 600 °C. In the shrinkage of anatase with glasses, a hump can be found at 850 and 700 °C for BSG and ZBSG, respectively. It is of interest that the rutile + ZBSG specimen revealed a hump in its shrinkage curve while the rutile + BSG specimen and pure rutile did not. The hump in the rutile + ZBSG specimen is related to the crystallization of ZBSG.[9] The nodes found in the anatase system are related to the phase transition from anatase to rutile.[10] Similar behaviour was reported in the anatase TiO_2–CuO system. The temperature range of the hump in the anatase + ZBSG system is larger than that of anatase + BSG, which can be also explained by the effect of crystallization of ZBSG. Considering low-temperature sintering, shrinkage curves in Fig. 1 indicate that the anatase + glass system is more suitable for LTCCs than the rutile + glass system, which is confirmed by the sintered densities in Fig. 2.

Fig. 2 shows the bulk density of TiO_2 with BSG and ZBSG as a function of temperature. Generally, TiO_2 is known to sinter only above 1200 °C,[10] but bulk density of TiO_2 with BSG and ZBSG reached the relative highest value at 900 °C. SEM images in Fig. 3 demonstrate that these specimens have dense microstructures.

In order to investigate the role of glass during sintering, dilatometric analyses of ZBSG and BSG were conducted in the temperature range of 100–800 °C. These results are shown in the Fig. 4. BSG and ZBSG started to melt at around 600 °C, i.e. softening point. However, the BSG softens more gradually than ZBSG. BSG and ZBSG completely melt down at 700 and 600 °C, respectively. In other words, melting temperature of BSG is about 700 °C and that of ZBSG is about 600 °C. The different shrinkage behaviour of TiO_2 with BSG and ZBSG shown in the Fig. 1 is related to the different melting mechanism of BSG and ZBSG.

Fig. 5 shows the XRD patterns of the quenched samples. Anatase + BSG samples (Fig. 5a), the phase transition to rutile started near 850 °C and only the rutile phase remained above 900 °C. A careful comparison of Figs. 1 and 5 revealed that the hump in the shrinkage curve of anatase + glass system is primarily related to the anatase–rutile phase transition.

In order to investigate the reactivity between TiO_2 and ZBSG/BSG, green compacts of BSG and ZBSG were placed on the top of porous TiO_2 green pellets and

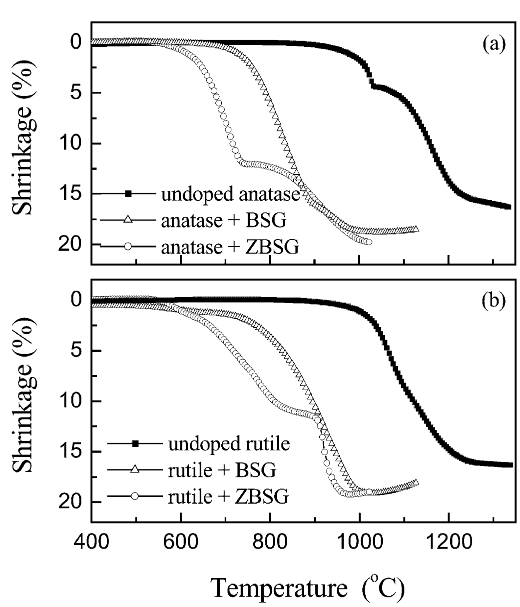

Fig. 1. Shrinkage of (a) anatase and (b) rutile with 20 wt.% BSG and ZBSG as a function of temperature.

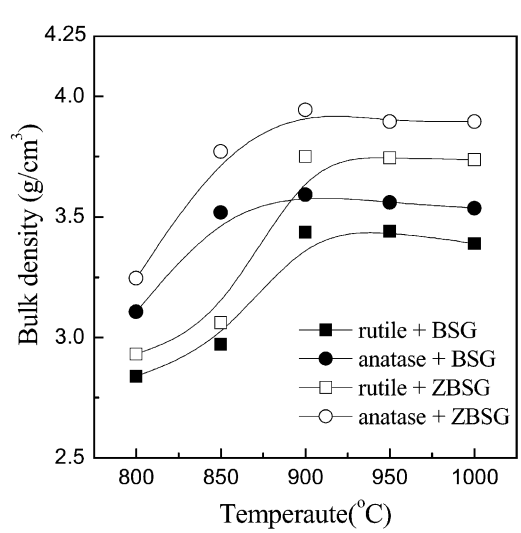

Fig. 2. Bulk density of TiO_2 with BSG and ZBSG as a function of sintering temperature.

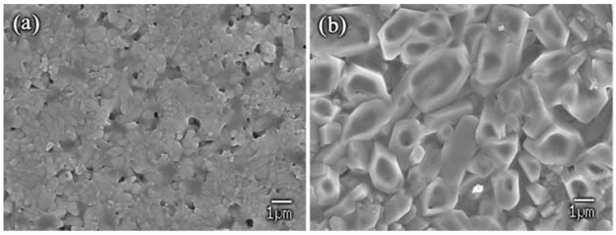

Fig. 3. SEM micrographs of the etched anatase with (a) BSG and (b) ZBSG sintered at 900 °C for 2 h.

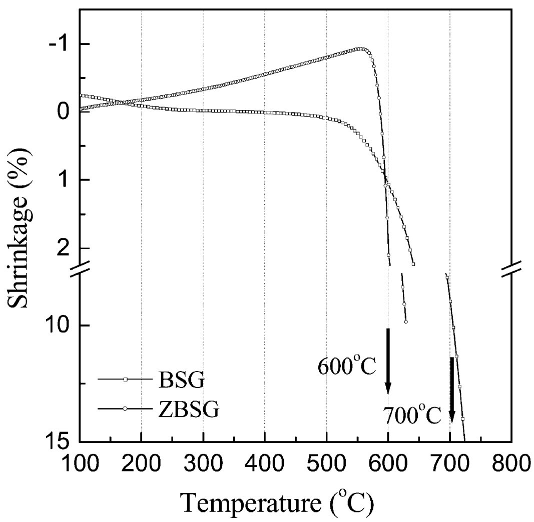

Fig. 4. Shrinkage of BSG and ZBSG as a function of temperature.

cofired at 900 °C for 2 h in air. Fig. 6 shows the samples before and after firing. BSG and ZBSG glass have different wetting behaviours with TiO_2. BSG showed nearly nonreactivity with TiO_2, while ZBSG and TiO_2 were completely reactive. That is, the wetting behaviour

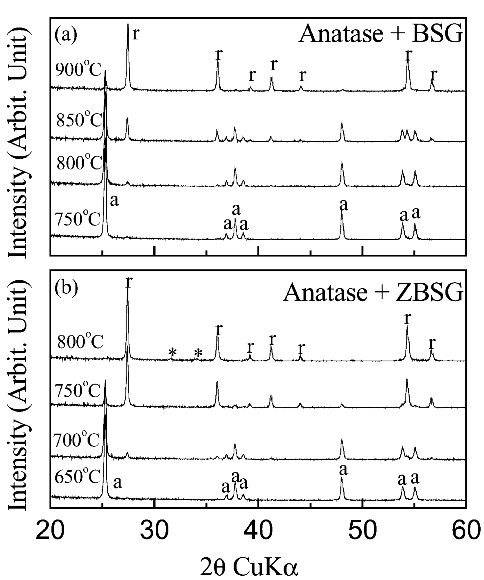

Fig. 5. X-ray diffraction patterns of quenched anatase with (a) BSG and (b) ZBSG (a : anatase, r : rutile, and * : Zn_2SiO_4).

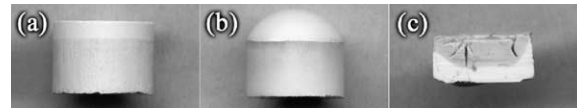

Fig. 6. Compact of glass and anatase (a) before firing, (b) BSG after firing at 900 °C for 2 h, and (c) ZBSG after firing at 900 °C for 2 h.

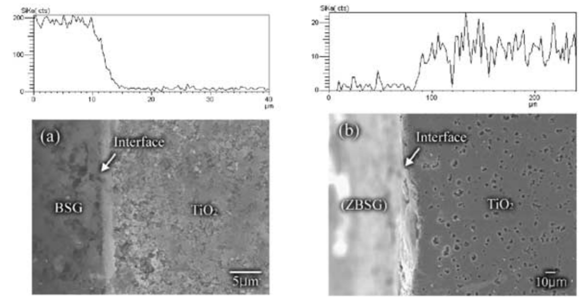

Fig. 7. SEM micrographs and EDS line scan of interface between anatase and (a) BSG / (b) ZBSG after firing 900 °C for 2 h.

of these two glasses is very different. This can also be confirmed by interface SEM images in Fig. 7. ZBSG infiltrated into the TiO_2 body, while a negligible reaction could be found in the anatase + BSG sample. These phenomena might be related to the different viscosities of ZBSG and BSG at the sintering temperature.

Microwave dielectric properties of low-temperature sintered TiO_2 using BSG and ZBSG is shown in the Fig. 8. Quality factors of TiO_2 using BSG are higher than those of TiO_2 using ZBSG. This difference in quality factor might result from the low-Q secondary phase Zn_2SiO_4 in the TiO_2–ZBSG system; however, these

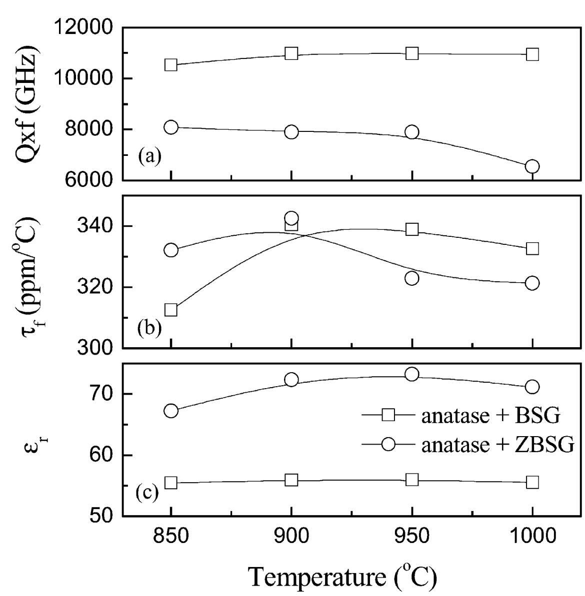

Fig. 8. Microwave dielectric properties of low-temperature sintered TiO_2 with BSG and ZBSG as a function of sintering temperature: (a) Quality factor ($Q \times f$), (b) temperature coefficient of resonant frequency (τ_f), and (c) relative dielectric constant (ε_r).

samples sintered at 900 °C for 2 h had good overall microwave dielectric properties: relative dielectric constant (ε_r) = 74, quality factor ($Q \times f$) = 8000 GHz, and temperature coefficient of resonant frequency (τ_f) = 340 ppm/°C.

4. Conclusions

The sintering behaviour, phase transition, interface reaction, and microwave dielectric properties of TiO_2-based LTCCs using modified borosilicate glasses were investigated. Dense TiO_2 + glass composites can be achieved at the sintering temperature of 900 °C. Shrinkage of anatase and rutile with glass and XRD results indicate that the melting temperature of glass and phase transition of anatase–rutile determine the sintering behaviour of TiO_2 + glass composites.

Acknowledgements

This research was supported by a grant from the Centor for Advanced Materials Processing (CAMP) of the 21st Century Frontier R&D Program funded by the Ministry of Science and Technology, Republic of Korea.

References

1. Jantunen, H., Rautioaho, R., Uusimäki, A. and Leppävuori, S., Preparing low-loss low-temperature cofired ceramic material without glass addition. *J. Am. Ceram. Soc.*, 2000, **83**, 2855–2857.
2. Takada, T., Wang, S. F., Yoshikawa, S., Jang, S. J. and Newmham, R. E., Effect of glass additions on $(Zr,Sn)TiO_4$ for microwave applications. *J. Am. Ceram. Soc.*, 1994, **77**, 2485–2488.
3. Dai, S. X., Huang, R. F. and Wilcox Sr., D. L., Use of titanates to achieve a temperature-stable low-temperature cofired ceramic dielectric for wireless applications. *J. Am. Ceram. Soc.*, 2002, **85**, 828–832.
4. Kim, D. W., Park, B., Chung, J. H. and Hong, K. S., Mixture behavior and microwave dielectric properties in the low-fired TiO_2–CuO system. *Jpn. J. Appl. Phys.*, 2000, **39**, 2696–2700.
5. Jean, J. H. and Lin, Shih-Chun, Kinetics and mechanism of anatase-to-rutile phase transformation in the presence of borosilicate glass. *J. Mater. Res.*, 1999, **14**, 2922–2928.
6. Povarennykh, A. S., *Crystal Chemical Classification of Minerals*. Plenum Press, New York, 1972.
7. Shannon, R. D. and Pask, J. A., Kinetics of the anatase–rutile transformation. *J. Am. Ceram. Soc.*, 1965, **48**, 391–398.
8. Jean, J. H. and Lin, Shih-Chun, Effects of borosilicate glass on densification and properties of borosilicate glass + TiO_2 ceramics. *J. Mater. Res.*, 1999, **14**, 1359–1363.
9. Kim, D. W., Lee, D. G. and Hong, K. S., Low-temperature firing and microwave dielectric properties of $BaTi_4O_9$ with Zn–B–O glass system. *Mater. Res. Bull.*, 2001, **36**, 585–595.
10. Kim, D. W., Kim, T. G. and Hong, K. S., Origin of a shrinkage anomaly in anatase. *J. Am. Ceram. Soc.*, 1998, **81**, 1692–1694.