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Influence of glass compositions on the microstructure and dielectric properties of low temperature fired $BaTi_4O_9$ microwave material with copper electrodes in reducing atmosphere

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Abstract

$BaTi_4O_9$ (BT4) dielectric ceramics, containing 10 wt% BaO–ZnO–B_2O_3–SiO_2 (BZBS) glass frit as sintering aid were co-fired with copper paste under reducing atmosphere at 950 °C and investigated on microstructures and dielectric properties. Experimental results show the microstructures and microwave dielectric properties of BT4–BZBS glass composite materials are strongly dependent on the Ba–Zn–B–Si ratio, especially for the content of SiO_2 addition, in BZBS glass. XRD and EDS results indicate that Cu reacts with BZBS glass-added BT4 ceramics seriously to form complicated reaction products such as $BaCuO_2$ phase, when the BZBS glass composition with lower content of SiO_2 (less than 20 wt%), and transformation of some $BaTi_4O_9$ into barium titanate with various ratios of Ba/Ti, which, fortunately, does not seriously degrade the dielectric properties.

Keywords: B. Microstructure-final; C. Dielectric properties; D. $BaTiO_3$ and titanates; Glass sintering aids

1. Introduction

Low temperature co-fired ceramics (LTCCs) possessing superior microwave dielectric properties have been widely investigated, due to the necessity for miniaturization of microwave devices to reduce the size of portable electronic devices [1]. However, the microwave dielectric materials such as $BaTi_4O_9$, which possess high quality factor and large dielectric constant, usually need very high sintering temperatures (~1300 °C) to achieve high enough density [2]. On the other hand, use of the base metal Cu as conducting material for internal electrode layers in a multilayer device is needed in order to lower the cost and low permittivity application in high frequency [3]. Reduction on the sintering temperature for the microwave material to a level of co-firable with Cu-electrode materials is thus called for. Adding sintering aids, optimizing the chemical processing, and reducing the particle size of the starting materials are three of the most commonly used methods to reduce the sintering temperature needed for ceramics. Among these methods, the addition of glass phase, inducing sintering in presence of a liquid phase, is well known for its efficiency and its low cost [2,4–6]. Some previous studies have shown that the addition of several glass-forming oxides and low-melting glasses has the advantages of lowering sintering temperatures and enhancing the densification, which cannot only prevent unfavorable grain growth at high temperature but also improve the dielectric properties of many microwave dielectric materials. However, contradictory results were also addressed in the literature, if the amount of borosilicate glass frit is large the network formers contained in the remaining glass materials such as B_2O_3 and SiO_2 may profoundly absorb the microwave power at high frequency regime, causing degradation of the quality factor of the final materials [7]. Furthermore, the added glasses usually exist as an amorphous phase in the specimens, which may also deteriorates the $Q \times f$ value of the specimens. In this work, BaO–ZnO–B_2O_3–SiO_2 (BZBS) glass additives were explored to modify the densification of the $BaTi_4O_9$ (BT4) dielectrics. This requires

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the development of a formulation that permits sintering at temperatures below 1000 °C, which can be co-fired with Cu. The effect of glass additions on the microstructures and dielectric properties in the $BaTi_4O_9$ host materials were investigated.

2. Experimental procedures

Pure $BaTi_4O_9$ material was first prepared by mixed oxide process. $BaCO_3$ and TiO_2 powders of high purity (>99.5%) with a molar ratio of nominal composition $BaTi_4O_9$ were mixed and then calcined at 1250 °C for 2 h. Thus obtained powders were then pulverized down to about 0.5 μm size by ball milling for 24 h. The starting powders of BaO, ZnO, B_2O_3 and SiO_2 for BZBS glass compositions, as shown in Table 1, were mixed and melted at 1300 °C in a Pt crucible. After quenching and ball milling, the fused BZBS glass powder with an average particle size of around 0.7 μm was mixed with $BaTi_4O_9$ in 10–90 wt%, followed by pelletization and then co-firing with a copper paste at 950 °C for 3 h in 10^{-8} atm Po_2 atmosphere of moist N_2-1%H_2. The sintered density was measured using Archimedes' principle. X-ray diffractometer (XRD, D/max-II B, Rigaku, Japan, and Cu Kα radiation) was employed to discriminate structural variation after glass-added $BaTi_4O_9$ materials were sintered, and then as-sintered samples were cut, cold-mounted and polished to allow the observation of cross-sectional microstructures by scanning electron microscopy (SEM, 6500F, Jeol, Japan). Energy dispersive X-ray spectroscopy (EDS, INCA system, Oxford Instruments, USA) was used to analyze the interdiffusion of the main elements along the direction perpendicular to the electrode layers. The dielectric constant (k) and quality factor (Q) of as-sintered samples were measured using impedance analyzer (HP4194, Hewlett-Packard, USA) and network analyzer (HP8722A, Hewlett-Packard, USA), respectively. The dielectric properties in the microwave frequency range were measured by a dielectric post resonator technique suggested by Courtney [8] and Kobayashi and Katohy [9].

3. Results and discussion

In order to develop a co-firable glass with low temperature fired $BaTi_4O_9$ (BT4) dielectric and Cu electrode materials for LTCC applications, the chemical compositions of BaO–ZnO–B_2O_3–SiO_2 (BZBS) glass additives were designed in consideration of physical and electrical properties. On the other hand, it is also considered that complex glass components would make the preparing process of LTCC materials difficult to control, and therefore simplifying the variations in the BZBS glass recipe is needed. In our previous studies [10], it was found evidently that, among these glass components, B_2O_3 can provide a most effective melting and softening temperature reduction for the BZBS glass materials, i.e., the glass softening point of BZBS glass can be significantly decreased to 630 °C as the B_2O_3 content up to 20 wt%. According to the foregoing results, we chose B_2O_3 content remaining unchanged at 20 wt% and varying the BaO–ZnO–SiO_2 contents in the BZBS glass for studying the influence of glass compositions on the microstructures and microwave dielectric properties of low temperature fired BT4 materials.

Table 1
The composition of BZBS glass for BT4–BZBS glass composite materials (BT4:BZBS = 90:10 wt%).

BZBS glass compositions	G19	G25	G31	G42
BaO	35.0	33.5	31.0	45.0
ZnO	30.0	28.5	27.0	10.5
B_2O_3	20.0	20.0	20.0	20.0
SiO_2	15.0	18.0	22.0	24.5
Softening point (°C)	605	615	626	630

wt%.

Experimental results show that the BZBS glass materials can reduce effectively the sintering temperature of $BaTi_4O_9$ ceramics to 950 °C and permit densification as expected, which can be attributed to liquid-phase sintering. However, it was usually found that the interface between the microwave dielectric ceramics and Cu electrode layers presented different colors after sintered in a reducing atmosphere. The results imply the glass compositions, especially for these samples contain lower content of SiO_2 (less than 20.0 wt%) such as BT4–G19 and BT4–G25, which may influence microstructural characteristics and dielectric behavior significantly. Furthermore, it was noted that these BZBS glass exhibit lower glass softening point when their SiO_2 content was reduced, as shown in Table 1, viz. glass softening temperature of the BZBS glass was raised with increasing the SiO_2 content.

Fig. 1 shows the bulk densities of BT4–BZBS glass composite materials as functions of SiO_2 content. It reveals that there was a significant reduction in the density of the materials when the SiO_2 addition was rich as shown in BT4–G42. From the procured data on the G42 glass, which consists of higher SiO_2 content compared to the other glass materials, it is revealed that higher glass softening point, about 630 °C, which may induce insufficient diffusion during sintering process, resulting in lower density of about 4.112 g/cm^3, and hence influence the apparent k and $Q \times f$ values, which are listed in Table 2. Whereas, the BT4–G19 samples, possessing a much

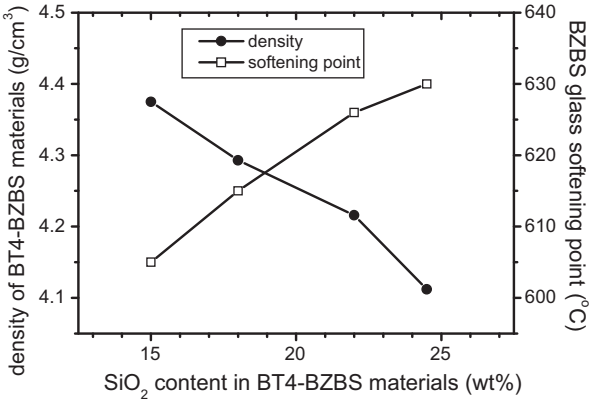

Fig. 1. The bulk densities of BT4–BZBS glass composite materials and the softening temperatures of the glass frits as functions of SiO_2 content.

Table 2
A summarized list of the sintered density, electrical properties and crystalline phases of BT4–BZBS glass composite materials, which co-fired with Cu electrodes at 950 °C for 3 h in reducing atmosphere.

LTCC composite materials	BT4–G19	BT4–G25	BT4–G31	BT4–G42
Density (g/cm^3)	4.375	4.293	4.216	4.112
k	34.1	32.9	33.9	31.8
$Q \times f$ (GHz)	6900	6500	6300	3800
Major phase	BT4	BT4	BT4	BT4
Minor phases	BCO + B4T13	BCO	–	SiO_2

BT4: $BaTi_4O_9$; B4T13: $Ba_4Ti_{13}O_{30}$; BCO: $BaCuO_2$.

lower glass softening point (605 °C) than that of BT4–G42, exhibit more effective densification and superior dielectric properties than those of BT4–G42 samples. That is, density, k and $Q \times f$ values are 4.375 g/cm^3, 34.1 and 6900 GHz, respectively. Furthermore, it has been reported that BaO addition can improve considerably wet ability between the glass and the BT4 host ceramics [4]. However, in spite of possessing large amount of BaO in glass flux, the SiO_2 content of the BT4-42 sample is rather high so that it presents deteriorated bulk density and dielectric properties. It indicates that the densification and dielectric properties of BT4–BZBS glass composite materials are strongly dependent on the BZBS glass compositions, especially for the content of SiO_2 addition in BZBS glass. The above results imply that the dielectric behavior could be mainly ascribed to the densification with lower softening temperature of glass addition for the BT4–BZBS microwave dielectric materials.

Fig. 2 shows the XRD patterns of BT4–BZBS glass composite materials co-fired with Cu electrodes in reducing atmosphere, which indicates that BT4 and the glass in the two materials (BT4–G19 and BT4–G25 samples) interact rigorously, forming some secondary phases such as $Ba_4Ti_{13}O_{30}$, and $BaCuO_2$, which are listed in Table 2. XRD patterns shown in Fig. 2 also reveals that $BaTi_4O_9$ phase in the BT4–BZBS glass composite materials was thermodynamically unstable when sintered with the BZBS glass at the sintering temperatures, and

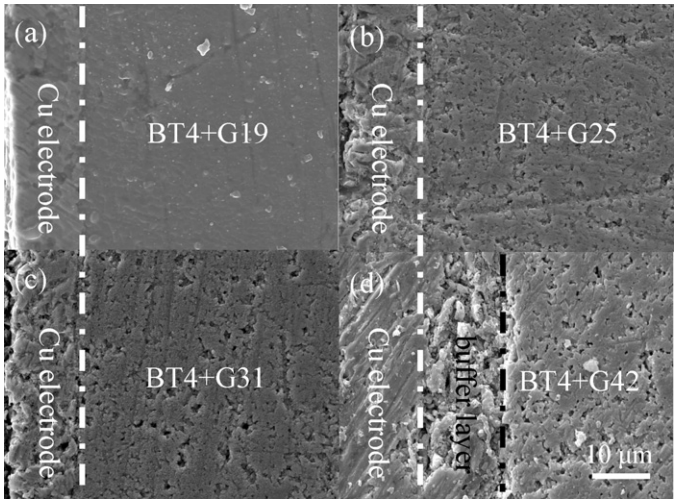

Fig. 3. SEM images of the BT4 ceramics added with (a) G19 glass, (b) G25 glass, (c) G31 glass, and (d) G42 glass, which co-fired with copper electrodes in reducing atmosphere. These micrographs were obtained from the etched surface of samples by a dilute HF solution.

therefore considerable reactions between Cu and glass additives as well as $BaTi_4O_9$ were expected to occur during sintering. Moreover, the proportion of $BaCuO_2$ phase increased with decreasing the SiO_2 content in the BZBS glass materials, and hence led to the color of as-sintered samples change from white to brown. However, no other phase was detectable in the XRD results for the BT4–G31 samples in this study, i.e., the $BaTi_4O_9$ phase was still maintained for the parent material with 10 wt% BZBS (G31) glass addition sintered at temperature as low as 950 °C. On the other hand, it could be found that the extra SiO_2 phase exists in the XRD pattern for the BT4–G42 samples. It may be attributed to over-addition of SiO_2 for the materials. Further study of the microstructures using scanning electron microscopy (SEM) would be useful to clarify the issue.

SEM observation reveals that the surface porosity decreases with decreased SiO_2 content, which is clearly illustrated by cross-sectional micrographs as shown in Fig. 3 for the BT4–BZBS materials. Note that these micrographs were obtained

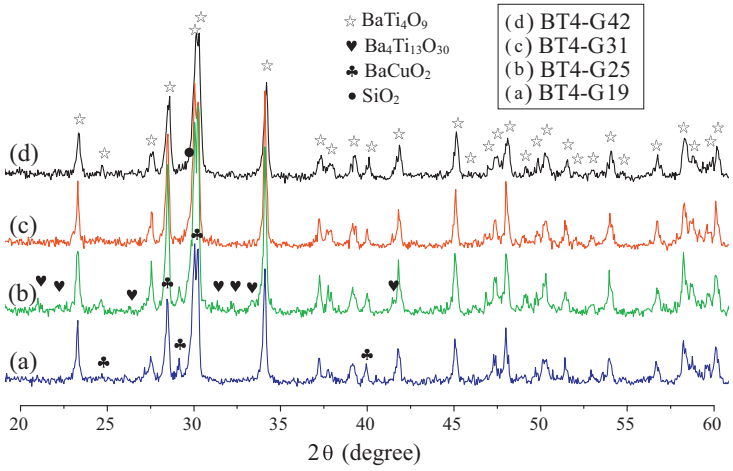

Fig. 2. The XRD patterns of the BT4 ceramics added with (a) G19 glass, (b) GA25 glass, (c) GB31 glass, and (d) GB42 glass, which co-fired with copper electrodes at 950 °C for 3 h in reducing atmosphere.

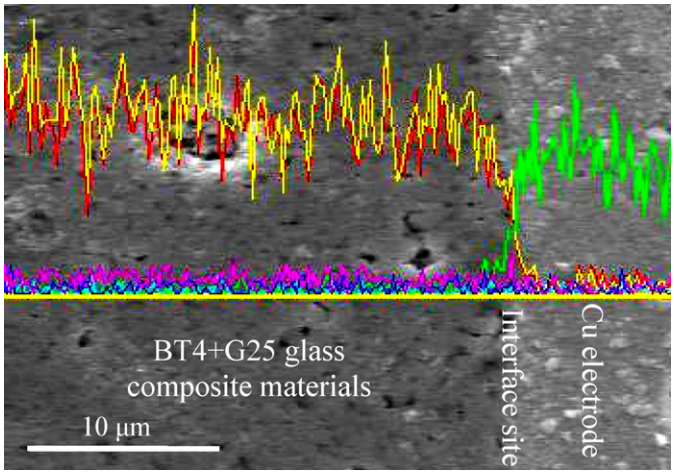

Fig. 4. A typical EDS result reveals that a phenomenon of significant diffusion existed at the interface between Cu electrode and BT4–BZBS glass composite materials with low SiO_2 content.

from the etched surfaces of samples using a dilute HF solution, which result in porous microstructures. Beside, it should also be noted that Fig. 3d shows formation of a deeply etched layer at the interface of Cu-electrode and ceramic in the BT4–G42 samples. Energy dispersive spectroscopy (EDS) results show that high concentration of Si species exist around the interface, implying that the glass did not diffuse across the boundary smoothly during sintering in a reducing atmosphere, and therefore materials exhibited poor densification and different colors. In other words, the presentation of the buffer layer can be ascribed to too abundant SiO_2 proportion in the glass. Such a phenomenon is understandable, and it is believed that higher viscosity of the glass with higher SiO_2 limits the diffusion of Ba atoms to react with Cu electrode, forming $BaCuO_2$. At the same time, network formers such as SiO_2 contained in the glass materials may absorb the microwave power profoundly at high frequency regime, degrading the quality factor for the materials [7]. Therefore, it can be concluded that the amount of SiO_2 addition in BZBS glass additives is the most significant factor to influence the sintering behavior, microstructures, and dielectric characteristics of BT4–BZBS glass composite materials.

Moreover, EDS were further used to investigate the reciprocal interdiffusion at the interfaces between Cu electrode and BT4–BZBS glass composite materials. A typical EDS result as shown in Fig. 4, it reveals that a significant diffusion or reaction layer (around several μm) existed at the interface between Cu electrode and BT4–BZBS glass composite materials, which is consistent with the results of XRD examination. That would explain the $BaCuO_2$ phase formed by a sufficient interdiffusion of Cu with low softening point of BZBS glass materials during sintering process and hence induce an evident change in color of samples. Whereas, SEM and EDS investigations of cross-section of the BT4–G31 samples show that very limited copper diffusion into the BT4–BZBS glass composite materials has occurred, indicating a suitable glass composition in the BT4–BZBS materials reduces interdiffusion and hence reactions.

4. Conclusions

The performance of BT4–BZBS microwave dielectric materials was found to depend strongly on the densification, microstructure and interaction between the glass and ceramics. XRD analysis and SEM observations indicate that rigorous reaction occurs when the BT4–BZBS glass composite materials were co-fired with copper electrodes at 950 °C in a reducing atmosphere, which does not seriously degrades the microwave dielectric properties of the materials such that $k = 33–34$ and $Q \times f = 6300–6900$ GHz were achieved for BT4–BZBS composite materials.

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