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Phase evolution and electrical properties of copper-electroded $BaTi_4O_9$ materials with $BaO–ZnO–B_2O_3–SiO_2$ glass system in reducing atmosphere

Kuei-Chih Feng[a], Chen-Chia Chou[a,*], Cheng-Sao Chen[b], Li-Wen Chu[c], Haydn Chen[d]

[a]*Advanced Ceramic Laboratory, Department of Mechanical Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan*
[b]*Department of Mechanical Engineering, Hwa-Hsia Institute of Technology, Taipei 235, Taiwan*
[c]*Walsin Technology Corporation, Kaohsiung 806, Taiwan*
[d]*Faculty of Science and Technology, University of Macau, Macau, China.*

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Abstract

$BaTi_4O_9$ (BT4) microwave dielectric ceramics using a copper electrode and containing 10 wt% $BaO–ZnO–B_2O_3–SiO_2$ (BZBS) glass frit were sintered under reducing atmosphere at 950 °C and were investigated on the phase evolutions, microstructures and dielectric properties of BT4 with various BaO/SiO_2 and ZnO/SiO_2 ratios of BZBS glasses. Experimental results show that the BaO/SiO_2 ratio contributes to wettability of glass with $BaTi_4O_9$ ceramics, and ZnO/SiO_2 ratio determines the densification of $BaTi_4O_9$ ceramics. The different Ba–Ti–O and Ba–Cu–O phases with various Ba/Ti and Ba/Cu ratios can be attributed to the contents of BaO in glass. $Ba_4Ti_{13}O_{30}$ and $Ba_2Cu_3O_{5+X}$ may form when BaO contents are too high, and inducing copper diffusion due to the reactions of BaO and Cu, accompanying with degrading of the dielectric characteristics. If the ZnO contents of BZBS glasses were raised, a little bit of $ZnSiO_3$ and $Ba_2Cu_3O_{5+X}$ phases appear without Cu diffusion due to non-reaction of ZnO and CuO. The high ZnO/SiO_2 ratio of glass reveals the lower softening point, indicating that the high ZnO glass could enhance the density and therefore increase the dielectric constant and quality factor.

Keywords: C. Electrical properties; D. Glass; E. Electrodes

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. Barium titanate material systems are the basic microwave dielectrics discovered by O'Bryan and other researchers in 1970s [1,2]. However, the microwave dielectric materials such as $BaTi_4O_9$ (BT4), which possess high quality factor and large dielectric constant, usually need very high sintering temperatures (~1300 °C) to achieve high density [3]. Reduction of the sintering temperature for microwave materials by using additions of low melting glasses in the ceramics is well known for its efficiency and its low cost [4]. Furthermore, use of the base metal Cu as conducting material for internal electrode layers in multilayer devices are not only reduces the cost but also is important for device design with low equivalent series resistance (ESR). Some previous studies have shown that low-melting glasses added in the ceramics, such as $B_2O_3–SiO_2$ [5], $BaO–ZnO–B_2O_3$ [6], $ZnO–B_2O_3$ [7,8] and $ZnO–B_2O_3–SiO_2$ [9], have the advantages of lowering sintering temperatures and enhancing densification of materials. For instance, $ZnO–B_2O_3–SiO_2$ glass has been demonstrated to be good flux former to reduce the sintering temperature of $BaTiO_3$ ceramics from 1300 °C to 900 °C [9]. Moreover, the addition of glass has been reported as to be an effective

*Corresponding author. Tel.: +886 2 2733314.
E-mail addresses: oaktop08@gmail.com, ccchou@mail.ntust.edu.tw (C.-C. Chou).

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sintering aid to reduce the sintering temperature of $BaTi_4O_9$ ceramics to 925 °C, and without degrading the dielectric characteristics of the materials in high frequency regime[6]. However, those reported materials were sintered in air atmosphere, but there is still no correlated investigation of low temperature co-fired ceramics materials with copper electrodes in reducing atmosphere. In this work, $BaO–ZnO–B_2O_3–SiO_2$ (BZBS) glass additives were explored to achieve high density and to permit sintering at temperatures below 1000 °C of $BaTi_4O_9$ (BT4) dielectrics, which can be co-fired with Cu. The effects of glass additions on the phase evolutions, microstructures and dielectric properties in the $BaTi_4O_9$ host materials were also investigated.

2. Experimental procedures

The $BaTi_4O_9$ material was prepared by a mixed oxide process, using $BaCO_3$ and TiO_2 powders of high purity ($>99.5\%$) with a molar ratio of nominal composition of $BaTi_4O_9$, calcined at 1250 °C for 2 h, and then ball-milled down to a size of 0.5 μm. The starting powders of BaO, ZnO, B_2O_3 and SiO_2 for BZBS glass compositions, as shown in Tables 1 and 2 with various BaO/SiO_2 and ZnO/SiO_2 ratios, 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 a 10-to-90 wt% ratio, followed by pelletization and then co-fired with a copper paste at 950 °C for 3 h in 10^{-8} atm P_{o_2} atmosphere of moist N_2–1% H_2. The sintered density of pellets was measured using the Archimedes principle. An X-ray diffractometer (XRD, Rigaku D/max-IIB and Cu Kα radiation) was employed to differentiate 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, JEOL 6500F). Energy dispersive X-ray spectroscopy (EDS) was used to analyze the interdiffusion of the electrode layers and substrates. The dielectric constant (k) and quality factor (Q) of as-sintered samples were measured using an impedance analyzer (HP4194, Hewlett-Packard, USA) and a network analyzer (HP8722A, Hewlett-Packard, USA), respectively. The dielectric properties in the microwave frequency range were also measured by a dielectric post-resonator technique suggested by Courtney [10] and Kobayash and Katohy [11].

Table 1
The BZBS glass of various BaO/SiO_2 ratios for BT4–BZBS glass composite materials. (BT4:BZBS = 90:10 wt%).

Specimen	B_2O_3	SiO_2	BaO	ZnO	BaO/SiO_2
BZBS-1	25	21.2	61.6	16.2	2.91
BZBS-2	27.2	23.3	49.5	31.7	2.12
BZBS-3	25	27.4	37.7	33.6	1.38

Table 2
The BZBS glass of various ZnO/SiO_2 ratios for BT4–BZBS glass composite materials. (BT4:BZBS = 90:10 wt%).

Specimen	B_2O_3	SiO_2	BaO	ZnO	ZnO/SiO_2
BZBS-4	27.2	23.3	49.5	17.5	0.75
BZBS-5	27.2	23.3	49.5	26.3	1.13
BZBS-6	27.2	23.3	49.5	29.2	1.27
BZBS-7	25	19.2	42.9	37.1	1.93

3. Results and discussion

It was found evidently that, among the glass components, B_2O_3 plays an essential liquid promoter and it provides a most effective melting and softening temperature reduction for the BSBZ glass materials [4], i.e. the glass softening point of BSBZ glass can be significantly decreased to 630 °C withthe B_2O_3 content up at 25 wt%. According to the foregoing results, we keep B_2O_3 content remaining unchanged in 25 wt% and vary the $BaO–ZnO–SiO_2$ contents in the BSBZ glass for studying the influence of glass compositions on the microstructural characteristics of low temperature fired BT4.

The investigations of structural variation on $BaTi_4O_9$ materials with glass of various BaO/SiO_2 ratios were carried out and are shown in Fig. 1. X-ray diffraction patterns revealed different Ba–Ti–O second phases with various Ba/Ti ratios and other Ba–Cu–O second phases, and the amounts of the second phases are shown in Table 3. It is found that only the $BaTi_4O_9$ phase appears in the material BZBS-3 of lower BaO/SiO_2 ratio, and the specimen BZBS-2 showing increased amount of BaO forms the second phases of $Ba_2Ti_9O_{20}$, and $BaCuO_2$ and Cu phase due to the copper diffusion into the matrix. In

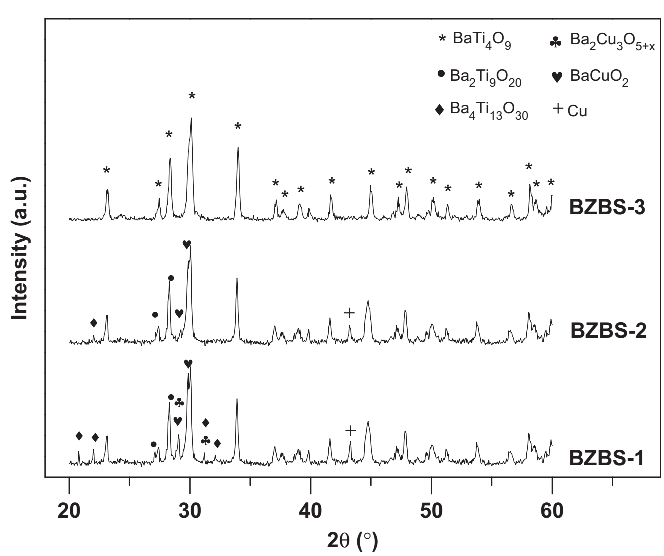

Fig. 1. The XRD patterns of the BT4 ceramics with BZBS-1 to BZBS-3 added, co-fired with copper electrodes at 950 °C for 3 hr in a reducing atmosphere.

Table 3
The physical properties, dielectric properties and phase amounts of BT4–BZBS specimens.

Specimen No.	T_s (°C)	Density (g/cm)^3	ε_r	*Qf* (GHz)	Phases					
					$BaTi_4O_9$	$Ba_4Ti_{13}O_{30}$	$Ba_2Ti_9O_{20}$	$Ba_2Cu_3O_{5+X}$	$BaCuO_2$	Cu
BZBS-1	614	4.36	34.4	3630	0.51	0.18	0.14	0.03	0.05	0.08
BZBS-2	621	4.48	30.2	4980	0.84	0.02	0.04		0.03	0.05
BZBS-3	624	4.21	33.9	6327	0.99					

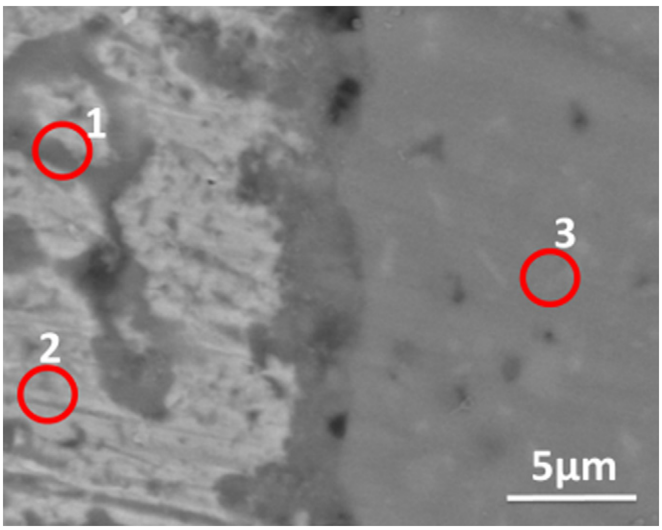

Fig. 2. Back-scattered electron imaging of the BT4 ceramics with BZBS-1 added, co-fired with copper electrodes at 950 °C for 3 hr in a reducing atmosphere.

Table 4
EDS results of the BT4 ceramics added with BZBS-1 glass.

	O K	Si K	Ti K	Cu K	BaL
1-dark					
Weight%	9.85	0.11	17.48	60.37	10.77
Atomic%	30.25	0.20	17.94	46.69	3.86
2-Electrode					
Weight%	7.37	1.28	1.71	87.96	1.54
Atomic%	23.75	2.34	1.84	71.37	0.58
3-matrix					
Weight%	22.98	3.94	36.03	0.96	35.85
Atomic%	55.06	5.37	28.84	0.58	10.01

addition, the higher BaO/SiO_2 ratio of BZBS-1 added in the BT-4 reveals the second phases of $Ba_4Ti_{13}O_{30}$ and $Ba_2Cu_3O_{5+X}$ and the enhanced Cu peak, indicating that the different Ba–Ti–O and Ba–Cu–O phases with various Ba/Ti and Ba/Cu ratios can be attributed to the contents of BaO in glass. Table 3 also shows that the gradual increase of BaO contents in BZBS glasses enhances the formation of Ba–Ti–O and Ba–Cu–O second phases. It indicates that the high BaO contents in BZBS glass easily react with BT-4 substrates and Cu electrode, and therefore the $Ba_2Cu_3O_{5+X}$ and $BaCuO_2$ formations easily induce the copper diffusion.

Comparing the dielectric properties in Table 3, the results reveal that serious chemical reactions occur and some of them may degrade the electrical properties. It is found that only the $BaTi_4O_9$ phase appears in the material BZBS-3, and the specimen show high quality factor of 6327 GHz. The quality factor of the BT4 ceramics BZBS-2 glass may drop if BT-4 transforms to other phases. Then, the Ba–rich glass material BZBS-1 reveals quality factor decrease seriously due to the higher amount of second phase formation and copper diffusion.

Furthermore, SEM micrographs show that BZBS-1 with relatively high BaO/SiO_2 ratio added in BT4 ceramics exhibit many speckles located within the copper electrode using back scattered electron imaging (Fig. 2), and EDS results of Table 4 reveal that the speckles contain relatively high amount of BaO and SiO_2, demonstrating that the second phases formation can be attributed to the serious glass flow and BaO and Cu reaction.

Fig. 3 shows XRD patterns of the samples with various ZnO/SiO_2 ratios of 10 wt% BSBZ glass added. The major phase is $BaTi_4O_9$ and there are a few second phases of $ZnSiO_3$ for the samples with added BZBS-4 to BZBS-6 glasses and ZnO/SiO_2 ratio between 0.75 and 1.27. Then, the material BZBS-7 having high ZnO/SiO_2 ratio (1.93) may produce the second phases of $ZnSiO_3$ and $Ba_2Cu_3O_{5+X}$. We also calculated the second phases, appearing in BT4 with BZBS-7. The results show that the material exhibits second phases amount less than 7 wt%, indicating that much less second phases appear in the material with high ZnO/SiO_2 ratio.

Fig. 4 reveals different softening points of BSBZ glasses and various densities of the $BaTi_4O_9$ ceramics with different series BZBS glasses addition. It is found that increase of ZnO/SiO_2 ratios in the BZBS glasses reveals a decrease of the softening point. Then, the compounds of BT4:BZBS=90:10 (in wt%) reveal the gradual enhancement of the densities with arising ZnO/SiO_2 ratio. Furthermore, the enhanced dielectric properties depend on specimen densities.Fig. 5 shows the enhancement of dielectric constant and quality factor of materials due to increase of specimen densities. We know that the dielectric constant and the quality factor of the pore sare zero [12]. Therefore, the dielectric constant and the quality factor increased with increasing densities of the specimens (decreasing pore volume). However, comparing the dielectric properties

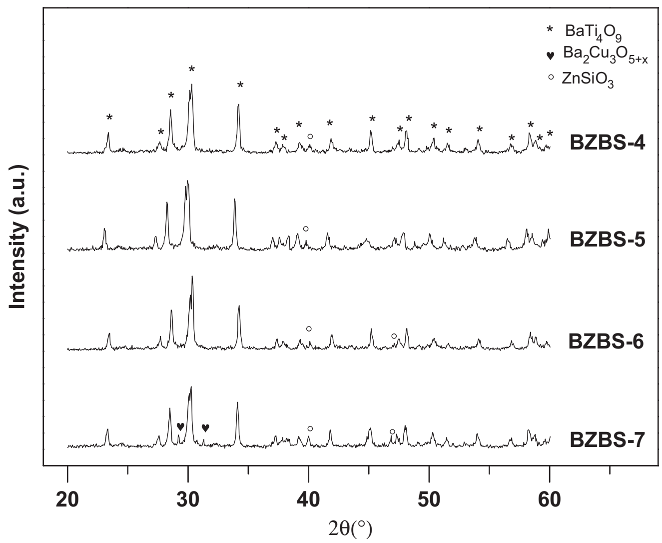

Fig. 3. The XRD patterns of the BT4 ceramics with BZBS-1 to BZBS-3 glass added, co-fired with copper electrodes at 950 °C for 3 hrs in a reducing atmosphere.

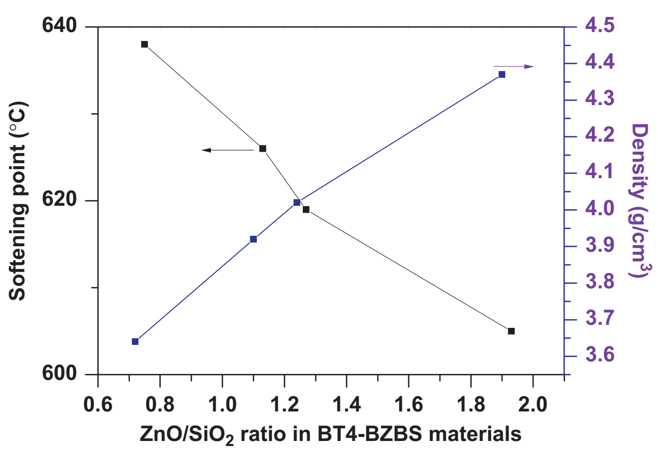

Fig. 4. The bulk densities of BT4 with BZBS-4 to BZBS-7 materials added and the softening temperatures of the glass frits as functions of SiO_2 content.

and phase transitions, the specimen BZBS-7 added in the BT-4 not only reveals the highest dielectric constant and the quality factor, but also shows the smallest amount of second phases. The experimental results imply that BaO and CuO reactions form a little $Ba_2Cu_3O_{5+X}$ phase without inducing the copper electrode diffusion due to the non-reaction of ZnO and Cu, indicating that the BZBS-7 added in the BT-4 showsoptimum dielectric properties, because of high densification.

4. Conclusions

The resultant performance of BT4–BZBS microwave dielectric materials strongly depends on the densification, phase evolution, and interaction between the glass and ceramics. XRD analysis and SEM observations indicate that rigorous chemical reaction occurs when the BT4–BZBS glass composite materials are co-fired with copper electrodes at 950 °C in a

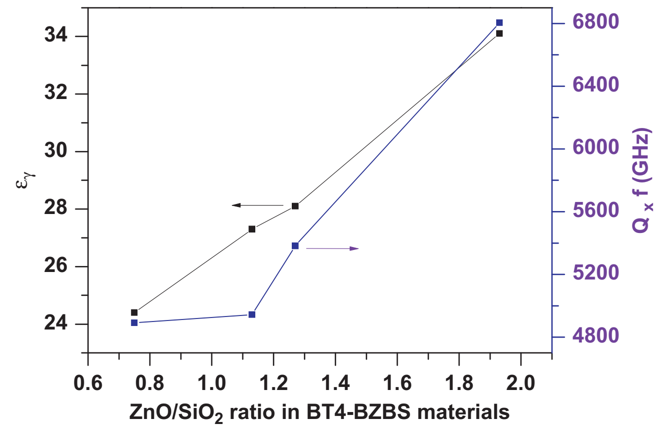

Fig. 5. The dielectric properties of BT4 ceramics added with BZBS-4 to BZBS-7 glasses, co-fired with copper electrodes at 950 °C for 3 hr in a reducing atmosphere.

reducing atmosphere, if the BZBS composition is not appropriately chosen. Accordingly, the best dielectric properties of the high ZnO/SiO_2 ratio of 1.93 reveal that the optimum $k=34.1$ and $Q \times f=6805$ GHz, can meet the requirement of microwave dielectric components for LTCC process.

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