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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

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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

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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

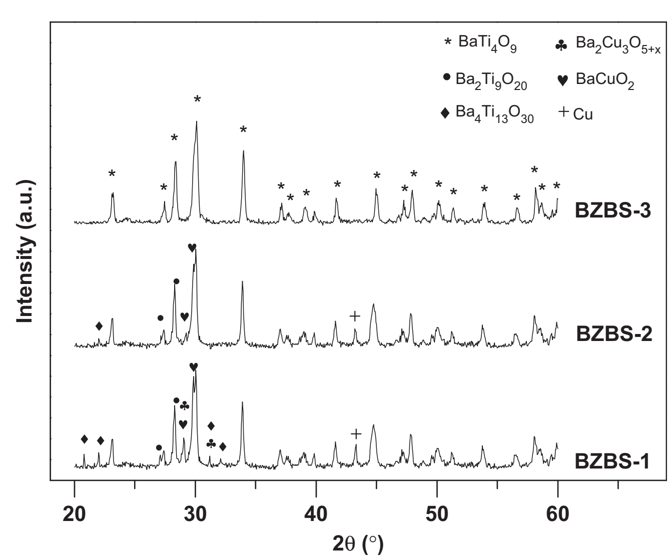

Fig. 1. The XRD patterns of the BT4 ceramics with BZBS-1 to BZBS-3 added, co-fired with copper electrodes at 950 °C for 3 hr in a reducing atmosphere.