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Low temperature processing of $(Zr_{0.8}Sn_{0.2})TiO_4$ ceramics with improved Q factor

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ABSTRACT

Polycrystalline $(Zr_{0.8}Sn_{0.2})TiO_4$ (ZST) ceramics have been synthesized by solid-sate reaction method. The effect of B_2O_3, $ZnO–B_2O_3$ or $5ZnO–2B_2O_3$ glass addition (0.2–1.0 wt.%) on microwave dielectric properties of ZST ceramics are investigated. The increase in average grain size via growth of large grains and dissolution of small grains is explained by Ostwald ripening phenomena. The highest $Q \times f_o$ values are found to be 61,500, 48,500 and 51,900 GHz for the ZST dielectric resonators added with B_2O_3, $ZnO–B_2O_3$ and $5ZnO–2B_2O_3$ respectively. The effect of liquid phase sintering on microstructure and microwave dielectric properties of ZST ceramics is discussed.

1. Introduction

Microwave ceramics are increasingly used for resonators, filters, duplexers and antenna systems for wireless communications. Especially, multilayer microwave devices are being investigated to let those devices increase volume efficiency. Multilayer chip inductors (MLCI) are one of the key surface mounted devices and have been extensively developed in recent years. These components are fabricated by lamination of ferrite and Ag electrode paste alternately and then co-fired to form a monolithic structure [1]. To keep up with the trend in miniaturization of electronic equipments and related components, particularly with the rapid development of integrated circuits and surface mounting technology, the demand for multilayer ceramic capacitors is increasing drastically [2]. Accordingly, low temperature co fired ceramics (LTCC) technology becomes more important for cost effectiveness. Often LTCC is used as substitute for multi chip modules (MCM). Integration proceeds by combining thick film and LTTC materials [3]. The sintering temperatures of microwave dielectrics such as ZST are too high to use low melting point electrodes. It was imperative to lower the sintering temperature of these microwave ceramics in order to use silver or copper electrodes i.e., the sintering temperature of co firing with high conductivity metals should be lower than the melting temperature of Ag (961 °C) or Cu (1064 °C) [4].

Lowering sintering temperature with glass additions is generally a most effective and least expansive technique. The motivation of this study with glass additions are (a) to reduce the sintering temperature of ZST and thereby the cost of production without any deterioration in the microwave dielectric properties, (b) to probe the relation between microstructure and quality factor, (c) to suppress the secondary phases and (d) to improve the microwave dielectric properties of ZST. The influence of these additives on phase, densification, microstructure and microwave dielectric properties on ZST is discussed. However, no systematic study on the effect of these additives to ZST ceramics has been reported previously.

2. Experimental

2.1. Sample preparation

Samples of $(Zr_{0.8}Sn_{0.2})TiO_4$ were synthesized by conventional solid-state reaction method from individual high-purity oxide powders ZrO_2, SnO_2 and TiO_2 all with 99.9% purity, Sigma Aldrich, USA. The staring materials were mixed according to the desired stoichiometry of $(Zr_{0.8}Sn_{0.2})TiO_4$ ceramics, with 1 wt.% addition of ZnO as a sintering aid. A planetary ball mill (Retsch, PM100) was used to prepare these powders. These powders were mixed at the wheel speed of 100 rpm for 1 h using zirconia balls and deionized water as milling media. The powders were dried and calcined at 1300 °C for 1 min. The calcined powders were again ball milled at the wheel speed of 300 rpm for 15 h to reduce the particle size. The particle size of the milled powder was obtained using a particle size analyzer (Zeta Sizer 3000 HSA). The glass additives were weighed stoichiometrically and mixed for 2 h in agate mortar using deionized water as a medium. Then it was melted above their deformation temperature and powdered (450 °C for B_2O_3, 610 °C for $ZnO–B_2O_3$ and 570 °C for $5ZnO–2B_2O_3$). The formation of the glassy phases was confirmed using X-Ray diffraction method. The calcined powders were remilled with different amounts (0.2–1.0 wt.%) of B_2O_3, $ZnO–B_2O_3$ or $5ZnO–2B_2O_3$ additions for 1 h. After remilling with different amounts (0.2–1.0 wt.%) of B_2O_3, $ZnO–B_2O_3$ or $5ZnO–2B_2O_3$ with the calcined powder, the fine powder is compacted in to cylindrical specimens by uniaxial pressing at 110 MPa pressure. The pellets were sintered at temperatures of

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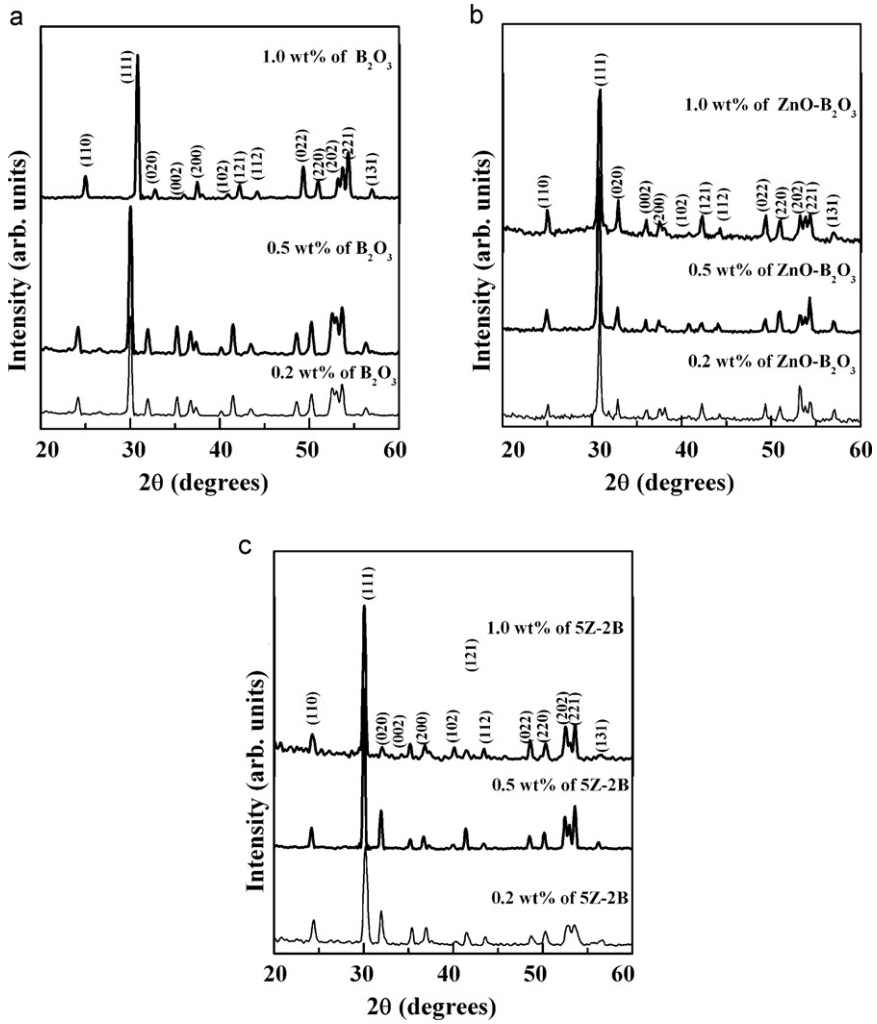

Fig. 1. (a) XRD patterns of the ZST ceramics added with (a) B_2O_3, sintered at 1150 °C for 3 h, (b) ZnO–B_2O_3, sintered at 1200 °C for 3 h, (c) 5ZnO–$2B_2O_3$, sintered at 1250 °C for 3 h.

1100–1250 °C for 3 h. The heating and cooling rates were 15 °C/min and 2 °C/min, respectively.

2.2. Characterization techniques

The crystalline phase of the calcined ZST powders and the sintered ZST ceramics was identified using X-Ray Diffractometer (Philips PW 1830). The microstructure of the sintered ZST ceramics was observed by Scanning Electron Microscopy (Philips XL 30 ESEM).

The theoretical relative bulk density (D) of the ZST–glass ceramics was calculated using the following equation:

$$D = \frac{W_1 + W_2}{\left[W_1/D_1 + W_2/D_2\right]} \quad (1)$$

where W_1 and W_2 are the weight percentage of the ZST matrix and glass with bulk densities D_1 and D_2 in the mixture, respectively [5]. The bulk densities of the ZST ceramics were measured by Archimedes method.

A vector network analyzer (Agilent 8722ES) was used to measure the microwave dielectric properties. Dielectric constant (ε_r) of the ZST dielectric resonators (DRs) was measured by using Hakki–Coleman method [6] as modified and improved by Courtney [7]. The Q factor was measured using reflection method with a cylindrical cavity having dimensions 3.0 times the DR. The rigid coaxial cable was provided at center of the cavity for electromagnetic field coupling and it can be moved in and out for adjusting between weak coupling and strong coupling. The cavity was connected to the network analyzer and rigid coaxial cable was adjusted in such a way that weak coupling exists between the rigid coaxial cable and DR. Weakly coupled condition was used to minimize the coupling losses. The unloaded Q_u value was calculated using the coupling coefficient and loaded Q_l value, using $Q_u = Q_l(1 + k)$, here k is the coupling coefficient, when the DR was in weakly coupled condition [8]. The temperature coefficient of resonance frequency (τ_f) at microwave frequency was measured using an invar cavity by heating the ZST ceramics from +25 °C to +80 °C.

3. Results and discussion

3.1. Crystal structure

The XRD patterns of the ZST ceramics added with B_2O_3, ZnO–B_2O_3 and 5ZnO–$2B_2O_3$ with different concentrations, sintered at 1150, 1200 and 1250 °C, for 3 h are shown in Fig. 1(a–c), respectively. All the samples showed a homogeneous phase with α-PbO orthorhombic structure and the space group of the structure is D_{2h}^{14} = pbcn. The average initial particle size of the milled powder is 220 nm. The crystallite sizes of glassy additives added ZST ceramics were calculated from the Williamson-Hall plot (β$\mathrm{Cos}\,\theta$ vs. $\mathrm{Sin}\,\theta$). The mean crystallite sizes of glassy additives added ZST ceramics ranged between 40 and 65.5 nm. The lattice constants of the glassy additives added ZST ceramics were calculated and it is observed that there is no deviation from the pure ZST ceramics. Secondary phases were not observed up to the 1.0 wt.% level of these additives due to the fact that the detection of minor secondary phases by X-ray diffraction is extremely difficult. Even though no secondary phase is observed there are variations in peak intensities and splitting of the peaks.