Journal of the European Ceramic Society xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Original Article

Investigation on low-temperature sinterable behavior and tunable dielectric properties of BLMT glass-$Li_2ZnTi_3O_8$ composite ceramics

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ARTICLE INFO

Keywords:
B_2O_3-La_2O_3-MgO-TiO_2
Glass
$Li_2ZnTi_3O_8$ ceramic
Sintering behavior
Dielectric properties
LTCC

ABSTRACT

The novel low-temperature sinterable ceramic composites were fabricated by mixing B_2O_3-La_2O_3-MgO-TiO_2 (BLMT) glass with $Li_2ZnTi_3O_8$ ceramic. All composites could be well sintered at 900 °C for 2 h through liquid-phase sintering and viscous sintering process. With BLMT glass increasing, the main phase of composites changed from $Li_2ZnTi_3O_8$ to $LaBO_3$ phase crystallized from glass. Nevertheless, the rutile phase was observed in composites with ≥10 wt% glass, which could adjust the temperature coefficient of resonant frequency (τ_f) to near-zero owing to the opposite τ_f value to other phases. Simultaneously relative permittivity (ε_r) and quality factor (Q×f) could be controlled by varying the content of $Li_2ZnTi_3O_8$ ceramic and BLMT glass. The composite with 20 wt% glass exhibited excellent dielectric properties: ε_r = 22.7, Q × f = 19,900 GHz, and τ_f = 0.28 ppm/°C. In addition, the good chemical compatibility between the composite with 5 wt% glass and Ag electrode made it as a potential candidate for LTCC technology.

1. Introduction

With the recent rapid development of the Tactile Internet (5th generation wireless systems), the Industrial Internet, Internet of Things, electronic warfare, satellite broadcasting and intelligent transport systems, the new advanced integration, packaging and interconnection technology is being strongly required to realize the microwave components (filter, resonator, antenna, capacitor, etc.) with high-miniaturization, high-reliability, multifunctional performance and usable at higher frequency range [1,2]. Low-temperature co-fired ceramic (LTCC) technology is turn out to be the upmost approach which widely used for multilayer circuit from fabrication to integrate, as well as build the different types of passive components and conductor into the ceramic [2,3]. To be applicable to the LTCC technology, the LTCC materials not only should possess an appropriate relative permittivity (ε_r, high for miniaturization and low for fast signal transmission), a high quality factor (Q × f), a near-zero temperature coefficient of resonant frequency (τ_f) but also can co-fired with little conductor loss, low electrical resistance at high frequencies and cost-effective Ag inner electrode (the melting point 961 °C) below 900 °C [1–3].

Nowadays, there are three dominant methods widely applied for simultaneously achieving the densification temperature of LTCC materials below 900 °C and possessing the excellent dielectric properties. The first approach is based on the glass-ceramic or filled glass-ceramic composites such as CaO–B_2O_3–SiO_2 glass-ceramic system from Ferro and lead borosilicate glass/Al_2O_3 system of Dupont [4,5], in which crystallized glass matrix acts as a main constituent (greater than 50 vol%) and/or fillers (Al_2O_3, SiO_2, mullite, cordierite) can modulate the dielectric properties, sintering process, mechanical strength and coefficient of thermal expansion (CTE) etc. [6–9]. The second approach is to lower the sintering temperature of present microwave dielectric ceramic through adding an optimal amount of the sintering additive by virtue of liquid-phase sintering mechanism, for instance B_2O_3, BaCu(B_2O_5), BaO-B_2O_3-ZnO glass [10–12].The last approach is developing and searching for new microwave dielectric ceramic systems with intrinsic low sintering temperature (so-called free-glass LTCC material) based on the low-melting oxide like TeO_2-based compounds, MoO_3-based compounds, V_2O_5-based compounds and Bi_2O_3-based compounds, etc [2,13–18]. However, many problems still exist in free-glass LTCC material, such as expensive and toxic raw materials, chemical incompatibility with Ag electrodes and large τ_f values, which is a huge barrier for them to be further applied in LTCC [2,16,19,20]. Hence, seeking for new suitable glass-ceramic system and lowering the sintering temperature of present ceramic are best choice for achieving the

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https://doi.org/10.1016/j.jeurceramsoc.2018.03.053
Received 9 January 2018; Received in revised form 29 March 2018; Accepted 30 March 2018
0955-2219/

cost-effective commercially available LTCC materials.

Recently, the dielectric ceramics in the Li_2O–ZnO–TiO_2 ternary system have drawn more attention due to its good microwave dielectric properties and the excellent chemical compatibility with Ag inner electrodes. And among them, $Li_2ZnTi_3O_8$ ceramic has excellent microwave dielectric properties with middle-relative permittivity (25.6), excellent quality factor (72,000 GHz) and negative temperature coefficient of resonant frequency (−11.2 ppm/°C) [21,22]. Although $Li_2ZnTi_3O_8$ ceramic could be completely densified at 1075 °C without sintering additives, it is a requisite to lower the sintering temperature to below 900 °C for being co-fired with Ag electrode. In order to reducing the sintering temperature, many work has been done by adding low-melting glasses or compounds, such as B_2O_3, Bi_2O_3, ZnO–B_2O_3–SiO_2 glass and ZnO–La_2O_3–B_2O_3 glass etc [10,23–25]. However, these sintering aids often bring about the deterioration τ_f value, for instance −19.5 ppm/°C for Bi_2O_3 and −13.4 ppm/°C for ZnO–La_2O_3–B_2O_3 glass. On other the hand, the above-mentioned work have focused on lowering temperature sintering below 900 °C in the presence of an optimal amount of liquid phase without any designed phase formation to modulate microwave dielectric properties. Many work shows that glass plus ceramic is a favorable method to improve dielectric properties for the fabrication of low-temperature co-fired ceramics [26,27]. Wang et al reported that the LTCC materials base on BaO-B_2O_3-SiO_2/$BaTiO_3$ system could be densified at 900 °C and relative permittivity was effectively adjustable from 5 to 30 by changing the mass percent of $BaTiO_3$ from 60 to 90. We also reported similar work that BBZ/$BaTi_4O_9$ composites sintered at 925 °C and as BBZ glass increased from 5 to 30 wt%, the ε_r and τ_f values decreased from 33 to 25 and from +25.44 to −3.19 ppm/°C, respectively. Therefore, if there is a glass that possess low Tg and Tm for lowering sintering temperature of $Li_2ZnTi_3O_8$ ceramic and crystallization phase for adjusting relative permittivity and τ_f values, the microwave dielectric properties of the final LTCC materials could be improved by varying the content of glass. It can be found from our previous work that B_2O_3-La_2O_3-MgO-TiO_2 (BLMT) glass is proved to be a good candidate duo to its low transformation temperature (644 °C) and great potential for LTCC applications [28,29].In addition, the crystal phases formed of the BLMT glass including $LaBO_3$ (ε_r = 12.5, Q × f = 76,000 GHz) and TiO_2 (ε_r = 108, Q × f = 44,000 GHz, τ_f = +456 ppm/°C) shows optimum dielectric properties. The major concern of this paper is to thoroughly investigate sintering behavior, crystallization, microstructures and dielectric properties of BLMT glass-$Li_2ZnTi_3O_8$ composite ceramics, and to develop some adjustable middle relative permittivity material systems sintered at 900 °C for LTCC through mixing designed $Li_2ZnTi_3O_8$ and B_2O_3-La_2O_3-MgO-TiO_2 glass.

2. Experimental

$Li_2ZnTi_3O_8$ phase was prepared by the solid-state-reaction method. Stoichiometry of Li_2CO_3, ZnO and TiO_2 (99.9%) were weighted and mixed in a Nylon tank using ethyl alcohol and ZrO_2 balls as media by planetary ball mill for 2 h. The mixture was then dried and calcined at 900 °C for 8 h to form $Li_2ZnTi_3O_8$ phase. The BLMT glass with the molar composition of 42.9B_2O_3-17.1La_2O_3-25.7MgO-14.3TiO_2 was prepared by a conventional glass fabrication process. The glass batch about 300 g was melted in a platinum crucible at 1350 °C for 2 h, and then the melts were quenched in water. The quenched glass was planetary-milled in aluminum jar with ethyl alcohol and ZrO_2 balls for 2 h. After being dried and screened through a 200-mesh sieve, the BLMT glass powder was obtained. Last, the BLMT glass powder and calcined $Li_2ZnTi_3O_8$ powder were weighed with the ratio of x BLMT-(100-x) $Li_2ZnTi_3O_8$ (2.5≤ × ≤80wt%) and planetary-milled with ZrO_2 balls and ethyl alcohol for 2 h. After drying, the mixture was granulated by adding 8 wt% poly(vinyl butyral) (PVB) solution for getting the uniformity particle size and good fluidity power. Preformed pellets of 15 mm in diameter and 8 mm in height were obtained from the powder using a cylindrical steel mold, and then were pressed at 2 MPa by hydraulic pressing, followed by sintering between 500 °C and 920 °C for 2 h in air at a heating rate of 5 °C/min.

The diff ;erential thermal analyzer (DTA) curve of the glass and composite powders was collected in a computerized system (DSC 404 C, Netzsch Instruments, Germany) at a heating rate of 10 °C/min from room temperature to 1100 °C. The crystalline phase present in sintered samples was identified by X-ray diff ;raction analysis (XRD, D8 ADVANCE, Bruker, Germany) using a Cu/Kα radiation, and was further analyzed by energy dispersive spectroscopy (EDS, Magellan 400, FEI Company, USA) and element-distribution mapping (EDM). The microstructure characteristics of the sintered samples was observed by field emission scanning electron microscope (FESEM, Magellan 400, FEI Company, USA). The sintering process was measured with 18 × 5.0 × 5.0 cm^3 "green" samples by using a horizontal-loading dilatometer with alumina rams and boats (DIL 402 C, Netzsch Instruments, Germany) with a heating rate of 10 °C/min. The bulk density of sintered samples was measured applying the Archimedes method. The relative permittivity and tan δ (dielectric loss) of the samples with the diameter of 12 mm and the height of 6 mm were collected by the Hakki-Coleman dielectric resonator method in the TE011 mode using an Agilent E8363A PNA series network analyzer. The Q value were calculated from the value in the light of the Q = 1/tan δ. The τ_f value was measured over the range from 25 to 85 °C heating through the temperature test cabinet (VTL7003, Vötsch, Germany), and was calculated by following equation:

$$\tau_f = {f_{85} - f_{25}}\Big/{60 \times f_{25}} \times 10^6 (ppm/°C) \quad (1)$$

where f_{85} and f_{25} represent the resonant frequencies at 85 °C and 25 °C, respectively.

3. Results and discussion

3.1. Sintering behavior

On the basis of previous studies [6–9,12,26–29],there may be some physical and chemical changes during the sintering process of the glass/ceramic LTCC system, such as the glass transition, devitrification of glass, the melting of phases or glass and reactions between glass and ceramic. In order to find the physical and chemical changes of BLMT-$Li_2ZnTi_3O_8$ composites during sintering process, the DTA curves of BLMT-$Li_2ZnTi_3O_8$ composites with different BLMT glass and pure BLMT glass are measured at a heating rate of 10 °C/min, as shown in Fig. 1. It

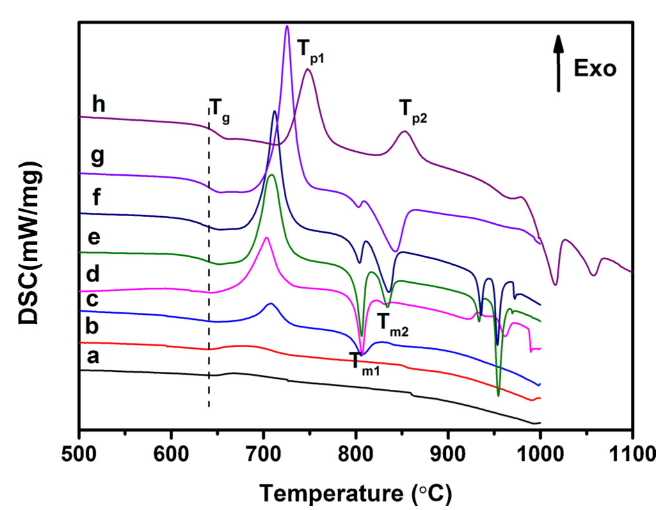

Fig. 1. DTA curves of the BLMT-$Li_2ZnTi_3O_8$ composites with different content of BLMT glass: a) 5, b) 10, c) 20, d) 40, e) 60, f) 70, g) 80 wt% and h) BLMT glass at a heating rate of 10 °C/min.