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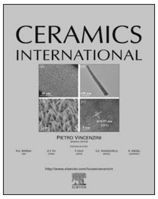

$Li_2ZnTi_3O_8$ based High κ LTCC tapes for improved thermal management in hybrid circuit applications

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ABSTRACT

A low temperature co-fired ceramic based on $Li_2ZnTi_3O_8$ (LZT), that possess auspicious thermal and dielectric properties is reported. In order to achieve the low sintering temperature suitable for LTCC applications (875 °C), 1 wt% of 20:Li_2O-20: MgO-20: ZnO-20:B_2O_3-20: SiO_2 (LMZBS) glass was added to LZT ceramics. The post-milled powder had an average particle size of 450 nm with an effective surface area of 0.812 m^2g^{-1}. A well dispersed tape casting slurry was prepared using xylene/ethanol mixture as solvent and fish oil as dispersant. The crystal structure and microstructure of the tapes were analyzed through XRD and scanning electron microscopy (SEM). The microwave dielectric properties of the green as well as sintered tapes were measured at different frequencies (5, 10 and 15 GHz). The $Li_2ZnTi_3O_8$+1 wt% LMZBS has shown excellent thermal conductivity of 5.8 W/mK, thermal expansivity (11.97 ppm/°C) closer to silver electrode, low temperature coefficient of dielectric constant (−29 ppm/°C) and ultralow dielectric losses (tanδ~10^{-4}).

1. Introduction

The size reduction trend of hand held electronic devices have now grown into newer dimensions with the advent of hybrid circuit concept, which is realized by embedding passive components at the intermediate layers, giving ample room to mount active components on the surface of the multilayer structure. In this direction, low temperature co-fired ceramic (LTCC) technology has attracted much attention because of its ease of design and functional benefits due to excellent electrical performance, partly contributed by enabling highly conductive electrode metals like Ag, Cu, Au etc [1–3]. For an ideal material to be qualified for LTCC applications, besides lower sintering temperature (< 950 °C), it should possess low dielectric constant ($\varepsilon_r < 10$), low dielectric loss (tanδ < 10^{-3}), tolerable coefficient of thermal expansivity (CTE) with respect to electrodes (< 20 ppm/°C) and high thermal conductivity (> 10 W/mK). Surprisingly enough, most of the commercial LTCC substrate possesses CTE close to silicon (< 5 ppm/°C), which can exert thermal stress on passive components due to the former's higher thermal expansivities (> 15 ppm/°C). Secondly, achieving high thermal conductivity is also harder to realize, since most of the ceramics have lower thermal conductivities, which gets further lowered with the addition of glasses. Nonetheless, any material that qualifies to show a thermal conductivity above 5 W/mK is really appreciable since they can partly eliminate thermal vias in certain specific LTCC applications.

Lowering the sintering temperature without deteriorating the dielectric properties is the principal hurdle towards the goal of developing a successful LTCC material. In general, plenty of techniques are available to lower the sintering temperature of ceramic materials such as addition of glasses and low melting oxides as sintering aids, chemical processing, using smaller particles as the starting materials and so for [4]. Recent works suggest that, the use of a proper low loss and low temperature melting glass as a sintering aid, is the most suitable approach in this direction [5,6]. It was reported that multicomponent glasses are more effective than single component glasses in the aspect of possessing better dielectric properties. The selection of a suitable sintering aids is of prime importance, because in some cases the addition of an improper glass may deteriorate the microwave dielectric properties besides aggravating the grain growth, which permits some ions from glassy phase to substitute at the matrix lattice and form satellite phases [7].

Commercial LTCC materials in general, are found to possess low dielectric constants ($\varepsilon_r < 10$), which pose little freedom to microelectronic circuit designers. However, certain specific applications such as microwave filters demand high dielectric constant LTCC tapes as substrates in hybrid circuits. It should be noted that non ferroelectric, high dielectric constant, but low loss LTCC substrates are advantageous since they have smaller levels of cross talk. Interestingly, there is a

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surprising scarcity of literature on high dielectric constant LTCC materials except a few studies like Zhou et al. who developed a $Bi_2Mo_2O_9$ based LTCC material with high dielectric constant [8]. Recently a few high dielectric constant compositions of ultra-low temperature co-fired ceramics (ULTCC) based on $(1-x)BiVO_4$-$xTiO_2$ (x=0.4, 0.50, 0.55 and 0.60) were also reported [9]. Other than these isolated research and development reports, LTCC tapes with high dielectric constant ($\varepsilon_r > 20$) are not at all available in the commercial market. The present paper is a candid attempt in this direction to develop a novel LTCC substrate possessing $\varepsilon_r > 21$ in the sintered form, along with a combination of low dielectric loss and interesting thermal and mechanical characteristics. This kind of LTCC materials can also serve as a buffer layer between piezoelectric laminates (a passive component) and low loss dielectric laminates (a signal processing component), in periodic multilayer structures.

Recently, a resurged interest was generated on the spinel structured $Li_2ZnTi_3O_8$ based ceramic system because of their comparatively low sintering temperature (1075 °C) and excellent dielectric properties [10–12]. Blasse *et al.* in 1963 reported $Li_2ZnTi_3O_8$ for the first time. Later, its stoichiometry and crystal structure have been investigated by Hernandez *et al.* [9,12] In 2010 Sumesh *et al.* reported the microwave dielectric properties of $Li_2ZnTi_3O_8$ sintered at 1075 °C for the first time (ε_r=25.6, $Q_u$xf=72000 GHz and τ_f=−11.2 ppm/°C) [12]. Huang *et al.* investigated the effect of Mg and Co doping on the microwave dielectric properties of $Li_2ZnTi_3O_8$. They obtained high Q factor for the compositions $Li_2(Zn_{0.94}Mg_{0.06})Ti_3O_8$ ($Q_u$xf=150000 GHz) and $Li_2(Zn_{0.92}Co_{0.08})Ti_3O_8$ ($Q_u$xf=140000 GHz) [13]. Subsequently, a lot of research work was carried out on different LTCC compositions involving $Li_2ZnTi_3O_8$ [14,15]. Recently, Sumesh and Sebastian reported the microwave dielectric properties of $Li_2ZnTi_3O_8$+1 wt% LMZBS glass composite [16]. The bulk ceramic composite sintered at 925 °C has a dielectric constant of 24.3, $Q_u$xf=58000 GHz with a τ_f of −11 ppm/°C. Besides, the said composite is chemically compatible with silver electrode material. In the present study, we have employed a non aqueous based tape casting technique, in order to develop $Li_2ZnTi_3O_8$+1 wt% LMZBS (LZT+LMZBS) glass composite as a candidate material for high κ LTCC applications. The structural, microstructural, thermal, dielectric and mechanical properties of the newly developed LTCC tape sintered at 875 °C were analyzed. In comparison with the commercial LTCC products, the new LTCC material has a higher coefficient of linear expansivity (CTE) and thermal conductivity, that can complement to enhance their reliability.

2. Experimental

2.1. Preparation of LZT+LMZBS glass composite

$Li_2ZnTi_3O_8$ (LZT) was synthesized by solid state ceramic route using high purity Li_2CO_3 (99%), ZnO (99.9%), and TiO_2 (99.8%) from Aldrich (St. Louis. MO, USA) as the starting materials. Stoichiometric amounts of all these chemicals were ball milled together in ethanol medium using yttria stabilized zirconia balls for 24 h. The slurry was then dried overnight in a hot air oven at a temperature of 100 °C and was calcined at a temperature of 900 °C in a high temperature furnace with a dwell time of 4 h. In order to bring down the sintering temperature of LZT, 1 wt% LMZBS glass (20:Li_2O 20: MgO 20: ZnO, 20:B_2O_3, 20: SiO_2) was added to it. Prior to this, LMZBS glass powder was prepared from high-purity chemicals of B_2O_3 (99%, Sigma-Aldrich), Li_2CO_3, SiO_2 (99.6%, Sigma-Aldrich), ZnO and $(MgCO_3)_4.Mg(OH)_2{\cdot}5H_2O$ (99.9% Sigma-Aldrich) using the splash quenching method and then made into fine powder. The ceramic powder was then added together with 1 wt% LMZBS and ball milled in ethanol medium for 24 h for homogenous mixing of the ceramic and glass powders, for further reduction in the particle size. The phase purity of the as prepared LZT+LMZBS was studied by powder X- ray diffraction using Ni filtered Cu *Kα* radiation (PANalytical X′pert PRO diffractometer, Almelo, Netherlands). The average particle size was characterized by dynamic light scattering (Zetasizer Nanoseries: ZEN 3600, Malvern, Worcestershire, UK) and the BET surface area of LZT+LMZBS powder was estimated using surface area analyzer (Gemini 2375, Micromeritics, Norcross, USA). The CTE of the LZT+LMZBS were analyzed using a thermo mechanical analyzer (TMA SS7300, SII Nano Technology Inc, Northridge, CA, USA) respectively. The linear thermal expansion coefficient (α_l) was calculated in the temperature range of $T_1 < T < T_2$, by the following equation.

$$\alpha_l = \frac{L_2 - L_1}{L_1(T_2 - T_1)} \tag{1}$$

where L_1 and L_2 are the lengths of the specimen at temperature T_1 and T_2 respectively. The thermal conductivity of the sintered ceramic of LZT+LMZBS was directly measured by a xenon flash technique using laser flash thermal properties analyzer (FlashLine2000, Anter Corporation, Pittsburgh, USA) where the relevant portion of a suitably shaped ceramic specimen (thickness=2.72 mm and diameter=12.67 mm) is heated locally using an IR flash gun. The specific heat of the sample can be calculated by assuming that the energy absorbed by the sample and a standard reference sample are the same and is given by,

$$C_{sample} = \frac{(mC\Delta T)_{ref}}{(m\Delta T)_{sample}} \tag{2}$$

Thermal diffusivity (*D*) is calculated by the instrument by measuring t_{50} (half rise time), time for the back face temperature to reach 50% of its maximum value and the relationship between *D* and t_{50} is given by the famous Parker relation as [17],

$$D = \frac{0.139a^2}{t_{50}} \tag{3}$$

where a is the thickness of the sample. From the measured value of *D*, C and known value of density (ρ), the thermal conductivity *K* can be calculated by the below equation,

$$K = DC\rho \tag{4}$$

2.2. Preparation of LZT+LMZBS tape

For a uniform and homogenous tape preparation, the viscosity of the slurry should be optimized to yield maximum colloidal stability. Initially, sedimentation stability studies were conducted by keeping the powder loading constant at 50 wt% and varied the amount of dispersant. Here, fish oil (Arjuna Natural Extracts, Kerala, India) was used as the dispersant. The slurry preparation was done in two stages; in the first stage, the powder is mixed with dispersant and xylene/ethanol (50:50) solvent system and was ball milled for one day. In the second stage it was added with polymeric binder (poly vinyl butyral, (PVB) (Sigma–Aldrich)) and two types of plasticizers, benzyl butyl phthalate (Sigma–Aldrich) and poly ethylene glycol (Sigma–Aldrich), were added to provide strength and flexibility to the green tape. A few drops of cyclohexanone (Sigma–Aldrich) was used as the homogenizer. The dispersant was optimized by measuring the viscosity of the slurry in the first stage by varying the concentration of fish oil from 0.5 to 2 wt%. The viscosity measurements were carried out by using a rheometer (Brookfield, R/S Plus, MA, USA). The slurry with an optimal balance of the filler, solvents, dispersants and plasticizers was casted into thin ceramic tapes of approximate thickness 50 µm using a tape casting machine (Keko equipment, Zuzemberk, Slovenia) on a silicon coated Mylar® film, employing double doctor blade technique [18]. The thermal decomposition profile of the green tape was examined using thermo gravimetric analyzer, TG (Perkin Elmer, Waltham, USA). The dried green tapes were cut and thermolaminated (14 layers) at a temperature of 70 °C under a pressure of 5 MPa for 15 min. The hot