

EFFECTS OF DENSIFICATION MISMATCH ON STRESS
DEVELOPMENT DURING COFIRING AG-BASED MULTILAYER
CERAMIC LAMINATES

BY

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ABSTRACT

Stress and camber developments during cofiring a bi-layer Ag/ BaTi₄O₉+ZnO-B₂O₃ glass (BTZB) laminate are caused by the densification rate mismatch between Ag and BTZB layers. A small amount of TiO₂, 1.22-3.67 vol%, is added into Ag paste to reduce the densification rate mismatch between Ag and BTZB layers, which results in a smaller sintering mismatch stress generated and defect-free multilayer Ag/BTZB laminates. The camber development during cofiring the bi-layer Ag/BTZB laminate measured experimentally is in good agreement with that calculated by using the linear shrinkage rate difference between Ag+3.67 vol% TiO₂ and BTZB laminates.

I. INTRODUCTION

Rapid development of wireless communication requires multilayer ceramic devices with broad bandwidth and low insertion loss at high frequencies, and high-degree integration of different functions of components to reduce dimension [1-2]. To meet the above requirements, low-temperature cofired ceramics (LTCC), which evolves from high-temperature cofired ceramics (HTCC) produced mainly by multilayer alumina laminates with Mo or W as internal metallization fired at 1600°C [3], is developed by cofiring with high-electrical-conductivity metallization, such as Ag, Cu and Au. Since those metals with low electrical resistance have a low melting point of around 1000°C (Table I [4]), the sintering temperatures of multilayer LTCC devices need to be controlled below 1000°C. Moreover, since Cu easily oxidizes during cofiring, and Au is too costly for commodity products, Ag becomes the most favorable choice to produce multilayer LTCC devices massively, and the sintering temperatures must be controlled less than 900°C.

A. Dielectric Materials of LTCC

The loss of multilayer ceramic devices at high frequencies, which corresponds to the reciprocal value of quality factor (Q_{total}), relates to the loss of dielectric ($1/Q_c$) and metal ($1/Q_m$) by $1/Q_{\text{total}} = 1/Q_c + 1/Q_m$ [4]. Therefore, to produce low-loss multilayer ceramic devices for wireless communication, ceramic materials need to have a low dielectric loss and conductor metals to have a low electrical resistance at high frequencies. Desirable dielectric materials, which need to be cofirable and chemically compatible with Ag, should have a broad range of dielectric constants with a low dielectric loss at high frequencies. Dielectric materials with a high dielectric constant are used for embedded capacitors to reduce dimension of devices, and dielectric with a low dielectric constant for integrated inductors to reduce the loss of multilayer ceramic devices. Several approaches to prepare dielectric materials for LTCC including glass + ceramics (multiphase ceramics), glass-ceramics (crystallizable glass) and low-fire crystalline compounds have been taken [5-14]. Typical compositions and dielectric properties of commercially available dielectric materials for LTCC are listed in Table II [15]. For the glass + ceramic approach, a mixture

of low-softening-point glass acting as a sintering additive, and the ceramic fillers adjusting the physical properties of the resulting composites is prepared. The properties of the final composite are determined by the ratio of glass to ceramic filler, and the individual properties of the mixtures. The borosilicate glass + alumina system developed by Fujitsu and lead-borosilicate glass + alumina by DuPont are two of the typical systems [16,17]. Due to its processing robustness and simplicity to fine-tune the physical properties of fired multiphase composites, this approach is preferably used in the commercially available LTCC systems, and also chosen in this study. In the case of glass-ceramic systems, a crystallizable glass is used, e.g., crystallizable cordierite by IBM and crystallizable $\text{CaO-B}_2\text{O}_3\text{-SiO}_2$ glass by Ferro [18,19]. The degree of crystallization that occurs during firing is the predominant factor controlling the properties of the final products. Therefore, to optimize the processing parameters, a thorough and systematic understanding of the crystallization kinetics and mechanism of glass-ceramic systems are required. One of most important advantages of the glass-ceramic approach is to have a low dielectric loss due to a small amount of residual glass left. However, since the total amount of crystalline phases formed during firing is not easy to control precisely, the dielectric constant of final products varies when the initial powder sizes or processing conditions change. This reduces the accuracy of microwave circuit design for LTCC devices. For the approach of low-fire crystalline compounds, low-fire crystalline oxides without adding low-softening-point glasses such as TeO_2 -based, MoO_3 -based and WO_3 -based compounds, which can be densified at 600-800°C and exhibit promising microwave properties, are used [12-14]. Concern to this approach is the low densification temperatures, which are too close to that required for binder burnout. This might result in poor densification and high dielectric loss due to an excessive amount of residual carbon existing in the fired devices.

B. Modules and manufacturing process of LTCC

A typical multilayer LTCC module for wireless communication is schematically shown in Fig. 1 [20], where discrete devices including large-value capacitors, inductors and resistors, surface acoustic wave (SAW) filters and power amplifier (PA) are mounted on top surface by a reflow process. Moreover, low-value capacitors, inductors and resistors, filters and transmission lines are embedded inside of ceramic laminates. Vias are used to

connect between layers. Figure 2 shows a typical manufacturing process for multilayer LTCC devices [21]. Ceramic powders and organic vehicle including solvents, binders, dispersants and plasticizers are mixed uniformly by ball milling to prepare slurries. The slurry is then cast on a polyester film to form thin green tapes. Vias on green tapes are formed by mechanical punching or laser ablating. Circuits on green sheets and via filling are made by screen printing conductor pastes. After drying, the green tapes are stacked in sequence, then laminated by applying heat and pressure to fabricate multilayer laminates. The singulated parts are fired slowly ($1\text{-}2^{\circ}\text{C}/\text{min}$) below $400\text{-}500^{\circ}\text{C}$ in a continuous furnace to ensure the completion of binder removal. After binder burnout, the laminates are then fired at a higher heating rate ($5\text{-}10^{\circ}\text{C}/\text{min}$) to densification temperatures ($\sim 900^{\circ}\text{C}$). To reduce the possibility to form cofiring defects, the densification mismatch between dielectric and conductor metals need to be minimized. Ni and Au films, which are used for post-fired assembly, are electrolessly plated on the surface metallization of densified LTCC modules (Fig. 1). For LTCC components such as filters, the densified parts are terminated with conductor paste, which also requires another firing to ensure strong adhesion between dielectric and termination paste. Ni and Sn, which are used for surface mounted devices to connect to printed circuit boards, are electrolytically plated in aqueous solutions.

Table I. Electrical Resistance and Melting Point of Conductor Metals [4]

Metal	Electrical resistance ($\mu\Omega\cdot\text{cm}$)	Melting point ($^{\circ}\text{C}$)
Ag	1.6	960
Au	2.3	1063
Cu	1.7	1083
Mo	5.8	2610
Ni	6.9	1455
W	5.5	3410

Table II. Dielectric Constant (k) and Quality Factor (Q) of Commercially Available LTCC Systems [15]

Suppliers	Glasses	Ceramic Fillers	k	Q
Alcoa	Borosilicate Glass	SiO_2	3.9-4.2	330
Asahi Glass	$\text{Ba-Al}_2\text{O}_3\text{-SiO}_2\text{-B}_2\text{O}_3$	Al_2O_3	7.4	-
Corning	Crystallizable Glass	Crystalline Cordierite	5.2	-
DuPont	Lead-borosilicate	Al_2O_3	7.8	250
Ferro	$\text{CaO-B}_2\text{O}_3\text{-SiO}_2$	-	5.9	500
Fujitsu	Borosilicate Glass	Al_2O_3 , SiO_2	4.9	-
Heraeus	$\text{CaO-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$	Al_2O_3 -	7.8	450 (1MHz)
Hitachi	Pb-alumina-boro-silicate	Al_2O_3 , CaZrO_3	9-12	300-1000
IBM	$\text{Li}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$	β -spodumene	5.0-6.5	-
IBM	$\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$	Crystalline Cordierite	5.2-5.7	-
Kyocera	Pb-borosilicate Glass	Al_2O_3 , SiO_2	7.9	500 (2GHz)
Kyocera	ZnO- borosilicate	Al_2O_3 , SiO_2	5.0	800 (10GHz)
Matsushita	PbO-borosilicate	Al_2O_3	7.8	500 (1 MHz)
Matsushita	$\text{Na}_2\text{O-CaO-alumino-silicate}$	Al_2O_3	7.4	-
Murata	$\text{BaO-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-CaO-SiO}_2$	-	6.1	300 (5GHz)
NTK	Ca-Al-borosilicate	Al_2O_3	7.6	330 (3GHz)
NEC	Borosilicate Glass	Al_2O_3	6.0	300 (1MHz)
NEC	Pb-borosilicate	Al_2O_3 , SiO_2	7.8	300 (1MHz)
Taiyo Yuden	$\text{Al}_2\text{O}_3\text{-CaO-SiO}_2\text{-ZrO}_2\text{-MgO-B}_2\text{O}_3$	-	6.7	1000
Taiyo Yuden	$\text{Al}_2\text{O}_3\text{-SiO}_2\text{-ZrO}_2\text{-MgO}$	-	7.3	500
TDK	SrO-borosilicate	Al_2O_3	7.0-7.4	400

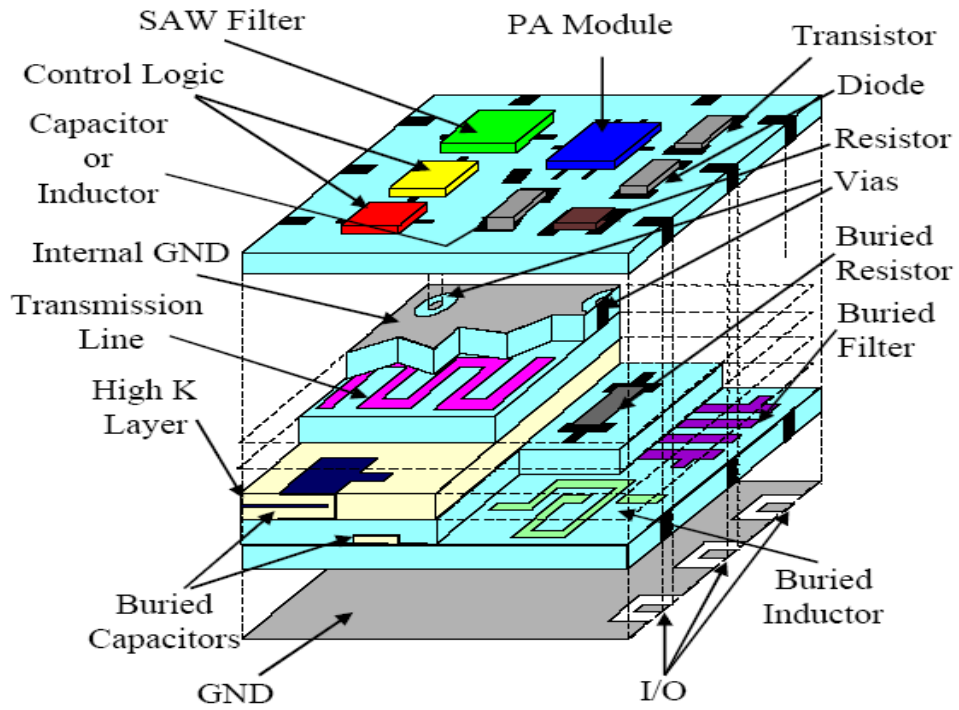


Figure 1. Typical multilayer LTCC modules. SAW: surface acoustic wave filter; PA: power amplifier; GND: ground; I/O: Input/ Output [20].

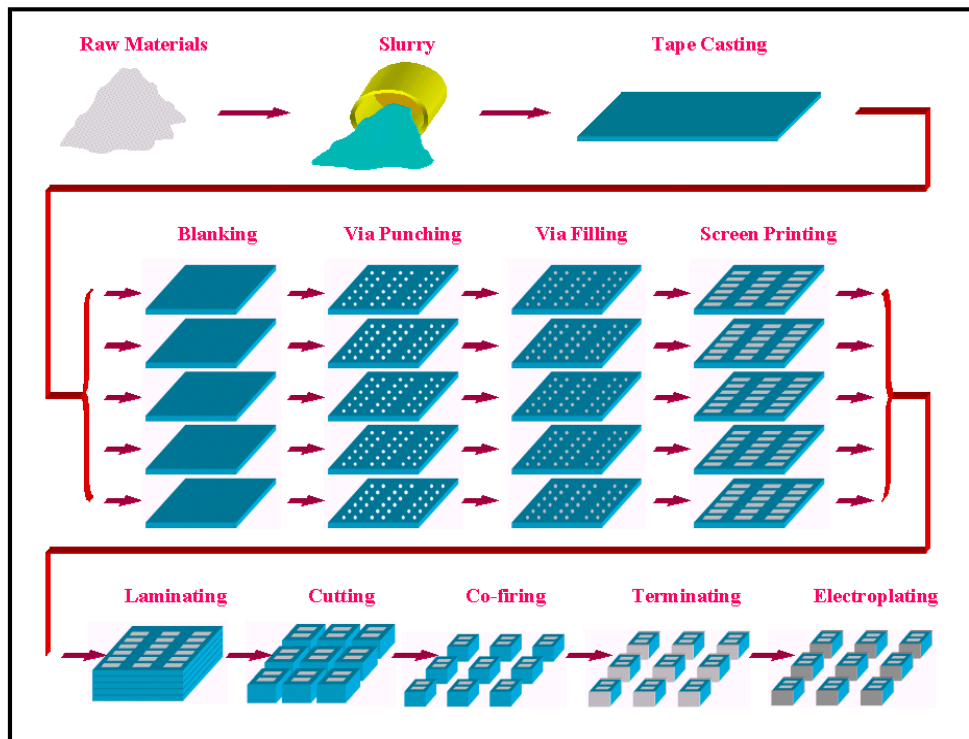


Figure 2. Typical manufacturing process of LTCC devices [21].

C. Motivation of this study

To produce defect-free multilayer LTCC devices, densification mismatch between conductor metal and ceramic dielectric, which could generate undesirable defects including delamination and cracks in the fired devices, need to be thoroughly understood. Camber development during cofiring bi-layer mixed materials is mainly caused by their linear shrinkage rate difference, and reduced by increasing their thickness ratio. The calculated results of camber development during cofiring bi-layer mixed materials, based upon a viscous model using their shrinkage rate difference, are close to those measured experimentally [22-24]. Moreover, sintering mismatch stresses generated during cofiring mixed materials can be reduced by minimizing their densification mismatch. Absence of cofiring defects is observed if the sintering potential of the mixed materials, which is the driving force of sintering, is greater than that of sintering mismatch stress [25-28].

In this study, a glass + ceramic dielectric system with $\text{BaTi}_4\text{O}_9 + 15\text{vol}\% \text{ZnO-B}_2\text{O}_3$ glass (BTZB), which has a dielectric constant of ~ 30 and Q value > 1000 at 15 GHz, is chosen. The BTZB can be densified at $875\text{-}900^\circ\text{C}$ and the pure Ag paste, densified at $550\text{-}600^\circ\text{C}$. With the addition of $1.22\text{-}3.67 \text{ vol}\% \text{TiO}_2$, the densification temperature of Ag paste is increased to $850\text{-}900^\circ\text{C}$. Effects of TiO_2 content added into Ag pastes on camber and stress development during cofiring a bi-layer Ag/BTZB laminate are investigated. The effect of thermal expansion mismatch on the camber and stress development is disregarded in the stress analysis because the thermal expansion coefficient mismatch is relatively small compared with densification mismatch between Ag and BTZB. Linear shrinkage data is measured by a thermal mechanical analyzer, which is then used to calculate the shrinkage rate difference. Camber development of the bi-layer Ag/BTZB laminates during cofiring is in-situ recorded by an optical system. The camber data is used to calculate the sintering mismatch stress generated during cofiring, which is also compared with that obtained using the linear shrinkage rate difference from dilatometric data.

II. LITERATURE REVIEW

A. Constitutive equations for a porous viscous material under sintering

The sintering process of a porous material has been initially described as viscoelastic, at which a combination of elastic springs and viscous dashpots has been proposed to characterize its mechanical response under densification [29-32]. However, since the viscoelastic treatment is too unnecessarily complicated and the densification strain is much larger than elastic strain, the deformation strain during sintering primarily comes from viscous flow or creep of porous compacts. Therefore, a linearly viscous constitutive relationship, which is similar to that for diffusional creep with a linear relation between stress and strain rate, is sufficient to describe the mechanical response of a sintering compact [33]. For an isotropic porous material, its sintering behavior under the influence of an external uniaxial stress is related to the uniaxial strain rate, and porous uniaxial viscosity by the following constitutive equations [34-36]:

$$\begin{aligned}\dot{\epsilon}_X &= \dot{\epsilon}_f + \frac{1}{E_p} [\sigma_X - \nu_p(\sigma_Y + \sigma_Z)] \\ \dot{\epsilon}_Y &= \dot{\epsilon}_f + \frac{1}{E_p} [\sigma_Y - \nu_p(\sigma_X + \sigma_Z)] \\ \dot{\epsilon}_Z &= \dot{\epsilon}_f + \frac{1}{E_p} [\sigma_Z - \nu_p(\sigma_X + \sigma_Y)]\end{aligned}\tag{1}$$

where $\dot{\epsilon}_i$ is the strain rate under a uniaxial stress (σ_i) in the i direction, $\dot{\epsilon}_f$ is the free strain rate, σ_i is the uniaxial stress, E_p is the porous uniaxial viscosity, and ν_p is the viscous Poisson's ratio. The viscous Poisson's ratio of porous compacts (ν_p), which is related to the relative sintered density (ρ) by

$$\nu_p = \frac{1}{2} \left(\frac{\rho}{3-2\rho} \right)^{\frac{1}{2}}\tag{2}$$

that varies in the range of 0.28-0.5 for $\rho=0.6-1.0$ [34-36]. Since the uniaxial strain rate of a sintering body under load should include the free strain rate caused by densification, it must be subtracted prior to the determination of porous uniaxial viscosity (Eq. (1)). For example, if the load is applied in the Z direction (σ_Z) only, i.e., $\sigma_X = \sigma_Y = 0$, the porous uniaxial viscosity (E_p) can be calculated by

$$E_p = \frac{\sigma_z}{\dot{\epsilon}_z - \dot{\epsilon}_f} \quad (3)$$

Sinter-forging and bending creep have been proposed to measure the viscosity of glasses, ceramic-filled glasses and polycrystalline ceramics [37-40]. However, the bending creep test is not suitable for porous compacts during densification. Sinter-forging tests are generally conducted under a constant load, which easily develops anisotropic microstructure during firing. This can result in larger measured porous viscosities. To solve this problem, a cyclic load, which minimizes the possibility in forming anisotropic microstructure during firing, is applied by using a loading dilatometry during isothermal sintering of porous compacts [41,42]. Results on ceramic-filled glass systems show that the porous uniaxial viscosities measured by the cyclic load (Eq. (3)) are always smaller than those obtained by constant load. More isotropic microstructure developed during cyclic load has been identified to be the root cause [42]. At a given densification, moreover, the porous uniaxial viscosity decreases with increasing temperature due to microstructural softening or enhancing atomic migration kinetics. The porous uniaxial viscosity increases with increasing densification during isothermal sintering due to increasing strength of a sintering body [28,41,42].

The free strain rate ($\dot{\epsilon}_f$) is related to sintering potential or sintering stress (Σ), which is an apparent driving force of densification. The sintering potential is a hydrostatic compressive stress to reduce the volume of the sintering body. If a hydrostatic tensile stress equal to the sintering potential ($\sigma_x = \sigma_y = \sigma_z = -\Sigma$) is applied to each direction, the shrinkage stops and the linear strain rate becomes zero ($\dot{\epsilon}_x = \dot{\epsilon}_y = \dot{\epsilon}_z = 0$) during sintering. According to Eq. (1), the sintering potential (Σ) is related to free strain rate ($\dot{\epsilon}_f$) by

$$\Sigma = \frac{E_p}{1-\nu_p} \dot{\epsilon}_f \quad (4)$$

It should be noted that the sintering potential in Eq. (4) is not a real stress. It is an equivalent hydrostatic stress which could yield the same densification rate as that achieved by the sintering driving force of porous compacts, i.e., the difference between total surface energy

and total grain boundary energy. Therefore, if the mismatch tensile stress generated during cofiring mixed materials is greater than the sintering potential of each constituent material, the possibility in forming cofiring defects including cracks or delamination becomes higher. The magnitude of sintering potentials is in the range of 100-400 kPa for low-fire borosilicate glass + alumina, and 400-600 kPa for a polycrystalline $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$ dielectric [43,44].

B. In-plain tensile stress generated by densification mismatch during cofiring mixed materials

It was demonstrated previously that a viscous model could describe the camber development during cofiring of a two-layer metal/ceramic laminate and its root cause was mainly their linear shrinkage rate mismatch [22-28]. The linear shrinkage rate mismatch between layers can result in mismatch stress during firing, and the layer that sinters more rapidly is more susceptible to form cofiring defects such as cracks and warpage/delamination [26-28]. Another source of mismatch stress is the thermal expansion mismatch between materials, which takes place during cooling when the densified layers are brittle. Since the densification mismatch strains are much larger than those of thermal expansion mismatch strain, the mismatch stress originated from the thermal expansion mismatch is ignored in this analysis [26,27].

A sintering mismatch stress (σ_{Metal}^{AVG}), which is an average biaxial stress in the metal layer and resulted from the linear shrinkage rate mismatch between metal and ceramics during cofiring a bi-layer metal/ceramic laminate, can be described by [26,27, 34-36]:

$$\sigma_{Metal}^{AVG} = \left[\frac{m^4 + mn}{n^2 + 2mn(2m^2 + 3m + 2) + m^4} \right] \hat{\sigma}_{Metal} \quad (5)$$

where m is the thickness ratio ($m = h_{metal}/h_{ceramics}$) between metal and ceramics, n is the viscosity ratio between metal and ceramics (Eq. (6)), and $\hat{\sigma}_{Metal}$ is the nominal viscous mismatch stress (Eqs. (7) and (8)). The thickness ratio (m) is determined by measuring the thickness of metal and ceramic layer in the multilayer laminate fired at different temperatures. The viscosity ratio (n) between metal and ceramics is described by

$$n = \left[\frac{E_p^{Metal}}{1-\nu_p^{Metal}} \right] \left[\frac{1-\nu_p^{Ceramics}}{E_p^{Ceramics}} \right] \quad (6)$$

where E_p^{Metal} and $E_p^{Ceramics}$ are the uniaxial viscosities, and ν_p^{Metal} and $\nu_p^{Ceramics}$, the viscous Poisson's ratio of porous metal and ceramics, respectively. The nominal viscous mismatch stress in the metal layer ($\hat{\sigma}_{Metal}$) in Eq. (5) is related to the linear strain rate difference between ceramics and metal ($\Delta\dot{\epsilon}_{Ceramics-Metal}$) by [26,27, 34-36]

$$\hat{\sigma}_{Metal}^{\Delta\dot{\epsilon}} = \frac{E_p^{Metal}}{1-\nu_p^{Metal}} \Delta\dot{\epsilon}_{Ceramics-Metal} \quad (7)$$

The nominal viscous mismatch stress in the metal layer ($\hat{\sigma}_{Metal}^{\Delta\dot{\epsilon}}$) can then be calculated by Eq. (7) using the data of the linear shrinkage rate difference and the porous uniaxial viscosities. With the data of the calculated $\hat{\sigma}_{Metal}$, m and n , the average sintering mismatch stress in the metal layer (σ_{Metal}^{AVG}) can be determined as a function of temperature by Eq. (5).

The nominal viscous mismatch stress in the metal layer ($\hat{\sigma}_{Metal}$) can also be calculated by camber rate in the following [26,27, 34-36]

$$\hat{\sigma}_{Metal}^{\kappa} = \left[\frac{m^4 n^2 + 2mn(2m^2 + 3m + 2) + 1}{6(m+1)^2 mn} \right] E_p^{Metal} \kappa \quad (8)$$

where κ is the normalized camber rate. Incorporating the data of porous uniaxial viscosity, the normalized camber rate, n and m into Eq. (8), the nominal viscous mismatch stress in the metal layer ($\hat{\sigma}_{Metal}^{\kappa}$) can be calculated. Combining the above nominal viscous mismatch stress ($\hat{\sigma}_{Metal}^{\kappa}$) data into Eq. (5), the average sintering mismatch stress in the metal layer (σ_{Metal}^{AVG}) as a function of temperature is determined.

It is interesting to note that the above calculations in Eq. (5) only represent the average sintering mismatch stress across the metal layer. However, it has been shown that the stress distribution inside multilayer laminate is not uniform. Finite element analysis [45] shows that the sintering mismatch stress increases from the top surface of the metal layer to the interface of asymmetric metal/ceramics laminate, where the largest stress

always exists if there is sintering incompatibility present. The largest sintering mismatch stress (σ_{Metal}^{Max}), which is located at the interface of metal/ceramic laminate, can be calculated by [26,27]

$$\sigma_{Metal}^{Max} = \left[\frac{m^4 n (4m+3) + 1}{m^4 n^2 + 2mn(2m^2 + 3m + 2) + 1} \right] \hat{\sigma}_{Metal} \quad (9)$$

Results on alumina/zirconia hybrid laminates show that cofiring defects including cracks and de-bonding are formed if the densification rate mismatch between layers is significant [26,27]. The extent in forming cofiring defects can be minimized by decreasing mismatch stress during sintering. This can be accomplished by using slower heating rate to relax the mismatch stress, or mixing alumina in zirconia to minimize the densification rate mismatch between layers.

C. Effects of densification mismatch on camber development

Since the porous metal and ceramics do not behave elastically during sintering, their response to stresses are characterized by the linearly viscous constitutive equations in Eq. (1). The linearly viscous equations (Eq. (1)) are similar to the linearly elastic constitutive equations caused by the thermal expansion mismatch between metal and ceramics with

- (1) Strain replaced by strain rates
- (2) Elastic modulus by porous uniaxial viscosity
- (3) Poisson's ratio by porous Poisson's ratio.

Since the linear shrinkage rate difference between metal and ceramics has been identified to be the major cause to develop camber during cofiring a two-layer metal/ceramic laminate, the camber rate can be calculated by Eq. (10). This is analogous to the modified Stoney equation and derived on the basis of the linearly viscous constitutive relationship in Eq. (1) [46,47].

$$\dot{\kappa}_{\Delta \dot{\epsilon}} = \frac{-6h_{Metal}}{h_{Ceramics}^2} \frac{1-\nu_p^{Ceramics}}{1-\nu_p^{Metal}} \frac{E_p^{Metal}}{E_p^{Ceramics}} \Delta \dot{\epsilon}_{Ceramics-Metal} \quad (10)$$

With the porous uniaxial viscosity (E_p^{Metal} and $E_p^{Ceramics}$), the calculated viscous

Poisson's ratio of porous metal and ceramics (ν_p^{Metal} and $\nu_p^{Ceramics}$), the thicknesses of metal (h_{metal}) and ceramics ($h_{ceramics}$), and the linear strain rate difference between ceramic and metal ($\Delta\dot{\epsilon}_{Ceramics-Metal}$), the camber rate can be calculated by Eq. (10). Results of cofiring Ni/BaTiO₃ laminates show that the densification rate mismatch between Ni and BaTiO₃ is the root cause for the generation of camber during cofiring [24]. At a given thickness of Ni electrode, both the camber and camber rate increase with a decrease in the squared thickness of the BaTiO₃ dielectric layer. Mathematical analyses of camber development based upon the linearly viscous model (Eq. (10)) are consistent with those measured. Similar results were also reported in the low-fire Ag/glass-ceramic and Au/glass + ceramic systems [22,23, 46].

III. EXPERIMENTAL PROCEDURE

A. Sample Preparation

The as-received BaTi₄O₉+15vol% ZnO-B₂O₃ glass (BTZB) powder (Fuji Titanium, Tokyo, Japan) had a median size of 0.5-1 μm (Horiba LA 910, Japan) and a specific area of 3-5 m²/g. The samples used in this study were prepared by tape casting, stacking, and laminating processes. The slurry, which was prepared by mixing the BTZB powder with a commercial non-aqueous organic vehicle containing binder and plasticizers, was cast on a Mylar carrier (DuPont, DE, Taiwan) using a continuous tape caster. The slurry contained 20 vol% BTZB powder, 60 vol% solvent and 20 vol% binder + plasticizers. Tape drying was carried out isothermally at 60°C. The green tapes, which had a thickness of 30 μm , were stored in a dry box with a controlled temperature and relative humidity of water at 25°C and 50%, respectively. The lamination condition used in this study was 18 MPa (2610.7 Psi) at 80°C for 5 min. The relative green density of the pressed laminates was determined dimensionally and in the range of 55%-58%. The BTZB laminates with a dimension of 3.7mm x2.9mm x2.0mm were prepared for linear shrinkage strain measurements. Similar processes were used to fabricate Ag laminates of pure Ag, Ag+1.22 vol% (0.5 wt%)TiO₂, and Ag+3.67 vol% (1.5 wt%)TiO₂. The TiO₂ was prepared by thermally oxidizing C₃₂H₆₈O₄Ti (Alfa Aesar, Ward Hill, MA), which was mixed into the Ag paste by using a three-roller mill. The Ag films, which were prepared by lamination at 14 MPa at 70°C for 5 min, had a relative green density in the range of 45-50%.

B. Linear Shrinkage and Uniaxial Viscosity Measurements

The linear shrinkage of BTZB and silver laminates were measured by a thermal mechanical analyzer (TMA, Seiko, Chiba, Japan). The binder removal was conducted at a heating rate of 3.5°C/min from room temperature to 500°C in air. After binder burnout, the samples were fired at a heating rate of 5°C/min to 900°C and held at 900°C for 2 h. The same firing profile was used for uniaxial viscosity (E_p) measurements, under cyclic loading.

C. Camber Measurements

For the camber studies, samples were prepared by screen printing Ag paste with a thickness of 10-12 μm onto a single sheet of BTZB green tape. The bi-layer Ag/BTZB laminates with a thickness ratio of 1/4 were sectioned to a size of 8x1 mm with the top layer completely covered with silver paste. Firing was performed at a heating rate of 3.5°C/min from room temperature to 500°C and a heating rate of 5°C/min from 500°C to 900°C then held at 900°C for 2 h in a tube furnace. Camber development during co-firing was recorded continuously by taking photographs using a camera system setup at the end of the tube furnace. Cambers (curvatures) were determined by measuring bending curvature of the samples on magnified photographs taken at different temperatures and times. Multilayer Ag/BTZB laminates were prepared by screen printing Ag paste onto a single sheet of BTZB green tape and dried isothermally at 70°C for 15 minutes. This process was repeated until the thickness ratio of Ag/BTZB is 1/4 and 1/1. The multilayer Ag/BTZB laminates were then sectioned to have a dimension of 3.7x2.9x0.3 mm³. The microstructure of densified Ag/BTZB laminates samples were examined by a scanning electron microscope (JSM-IT100, JEOL, Tokyo, Japan).

IV. RESULTS

A. Linear Strain Measurements

Linear strain curves of BTZB, pure Ag, and Ag doped with 1.22-3.67 vol% (0.5-1.5 wt%) TiO_2 are shown in Fig. 3(A). The linear strain (ϵ) is calculated by $(L_o - L(t))/L_o$ where L_o is the initial length, and $L(t)$ is the length of samples at time, t . The densification temperatures for pure Ag are in the range of 300-600°C, which are much lower than those of BTZB, 800-900°C. To minimize the above densification mismatch, a small amount of TiO_2 , 1.22-3.67 vol% (0.5-1.5 wt%), is added into Ag to slow down its densification. The densification temperatures of Ag are increased up to 625-825°C with 1.22 vol% (0.5 wt%) TiO_2 present; however, slight increase in densification temperatures to 650-850°C is observed when the TiO_2 content is increased further to 3.67 vol% (1.5 wt%). Moreover, the total linear shrinkages of Ag with 1.22-3.67 vol% TiO_2 are slightly larger than that of pure Ag, but close to that of BTZB. The above observations are confirmed with the results of linear strain rate in Fig. 3(B), which are obtained by taking the derivative of the linear strain curves in Fig. 3(A). The shrinkage rate data measured at 200-300°C in Fig. 3(B) are related to the burnout of organic added in the Ag pastes and BTZB green tapes. It is also found that all of the shrinkage rate curves exhibit a maximum value, i.e., 450°C for pure Ag, ~850°C for the Ag with 1.22-3.67 vol% TiO_2 , and 880°C for BTZB. The above results clearly indicate that the addition of small amount of TiO_2 into Ag paste shifts its shrinkage curve to higher temperatures, which significantly reduces the linear shrinkage rate mismatch with BTZB.

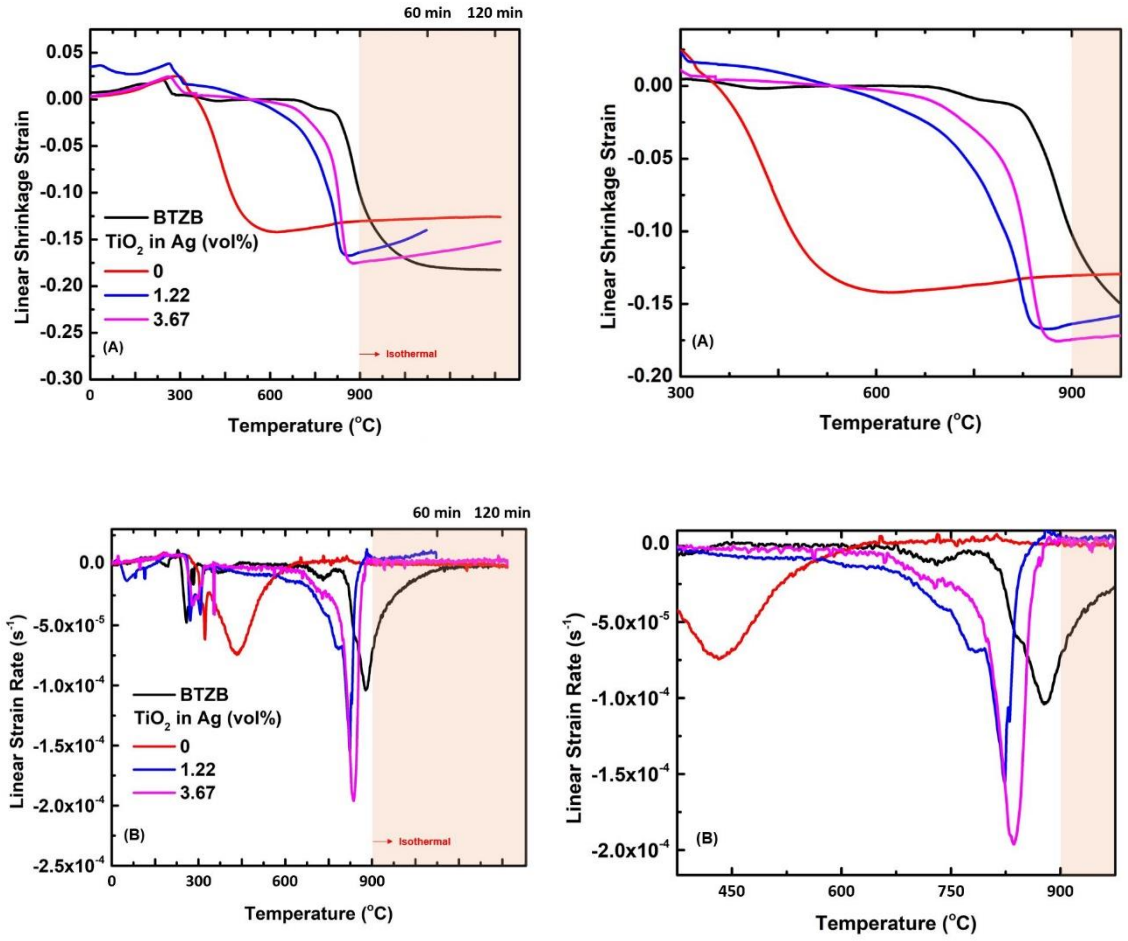


Figure 3. (A) Linear shrinkage strain (B) strain rate profiles of unconstrained BTZB dielectric and Ag paste doped with different TiO₂ contents, fired at a heating rate of 3.5K/min to 500°C and 5K/min to 900°C. The samples were then fired isothermally at 900°C for 120 min.

Since the results in Figs. 3(A) and 3(B) show insignificant difference in shrinkage behavior for the Ag pastes with 1.22-3.67 vol% TiO_2 , the following analyses will focus on the Ag pastes with and without 3.67 vol% TiO_2 . The linear strain rate difference between BTZB and Ag laminates ($\Delta\dot{\epsilon}_{\text{BTZB-Ag}}$) is shown in Fig 4. It is found that for pure Ag, the linear strain rate difference between BTZB and Ag exhibits two peaks, the first one with positive values located at 300-600°C and the second one with negative values at temperature above 700°C. For the Ag sample with 3.67 vol% TiO_2 , however, the first one with positive values shifts to 650-850°C, and the second with negative values moves to temperatures above 850°C. Insignificant shrinkage rate difference is observed after firing at 900°C for 60-120min, where the densification of BTZB apparently stops. Results in Fig 4 further show that the temperatures range to observe significant shrinkage rate difference between BTZB and Ag is 300-900°C, which is much broader than that Ag with 3.67 vol% TiO_2 , 650-900°C. The above results are further verified with microstructural examination in Fig. 5, where dense and uniform microstructure is found at 550-600°C for pure Ag (Figs. 5(C)-(D)), 850-900°C for Ag+3.67 vol% TiO_2 (Figs. 6(B)-(C)), and 900°C for 90 min for BTZB (Fig. 7(D)).

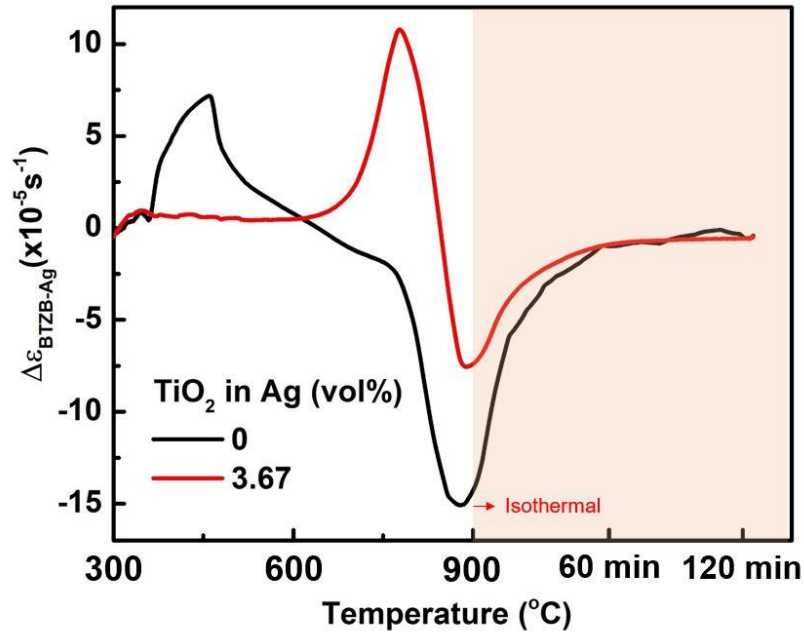


Figure 4. Effect of TiO_2 content added in Ag paste on linear shrinkage rate difference between Ag and BTZB ($\Delta\dot{\epsilon}_{\text{BTZB-Ag}}$).

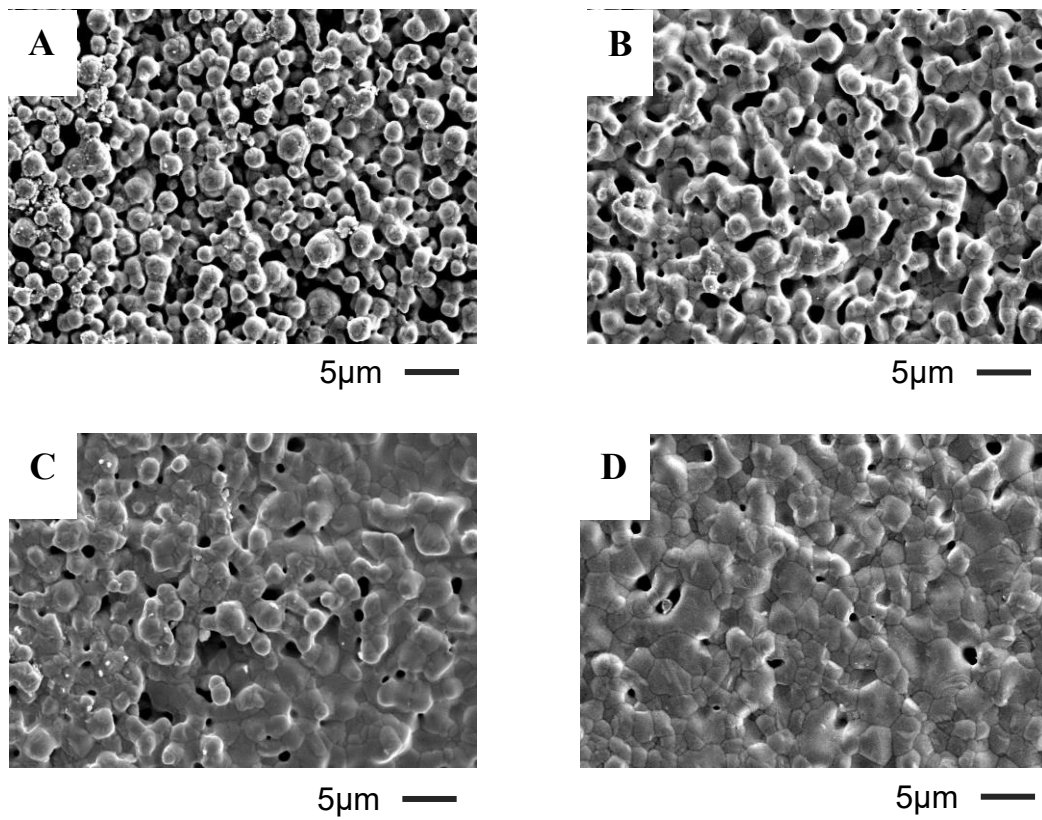


Figure 5. Surface microstructure of pure Ag fired freely at (A)400, (B)500, (C) 550 and (D) 600°C.

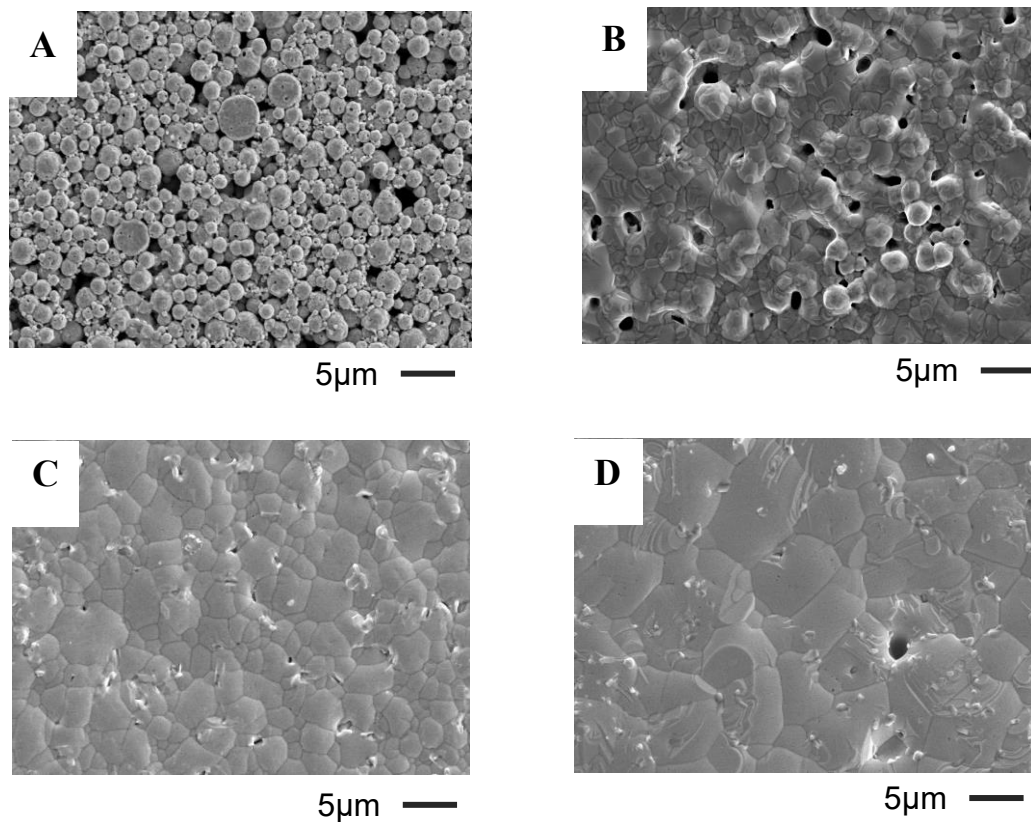


Figure 6. Surface microstructure of Ag+3.67 vol% TiO₂ fired freely at (A)800, (B)850, (C) 900 and (D) 900°C for 60 min.

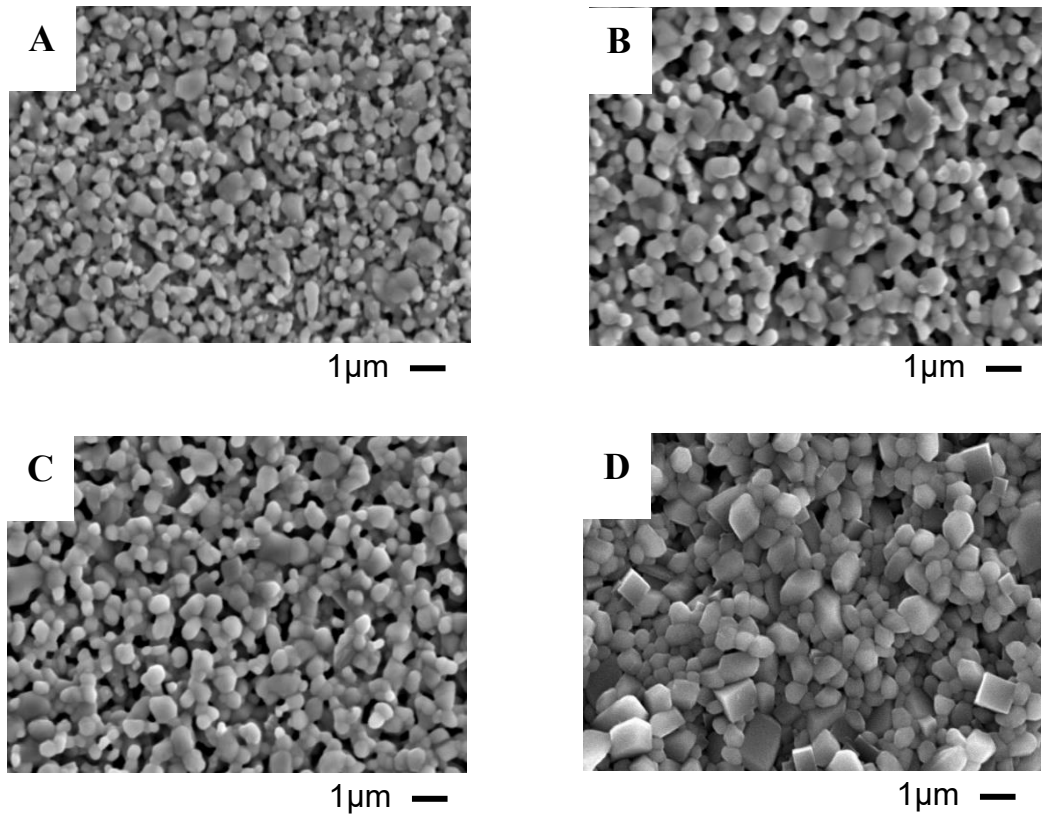


Figure 7. Surface microstructure of BTZB fired freely at (A) 800, (B) 850, (C) 900 and (D) 900°C for 90 min.

Results in Fig. 8 show that the addition of TiO_2 slows down not only densification (Figs. 3 and 4) but also grain growth of Ag during firing at 900°C. Insignificant grain growth of BTZB during firing at 900°C for 90-360 min is noticed. It is believed that the added TiO_2 particles act as constrained sites to the densification and grain boundary migration of Ag during firing because no mutual dissolution between TiO_2 and Ag is noticed and reported previously.

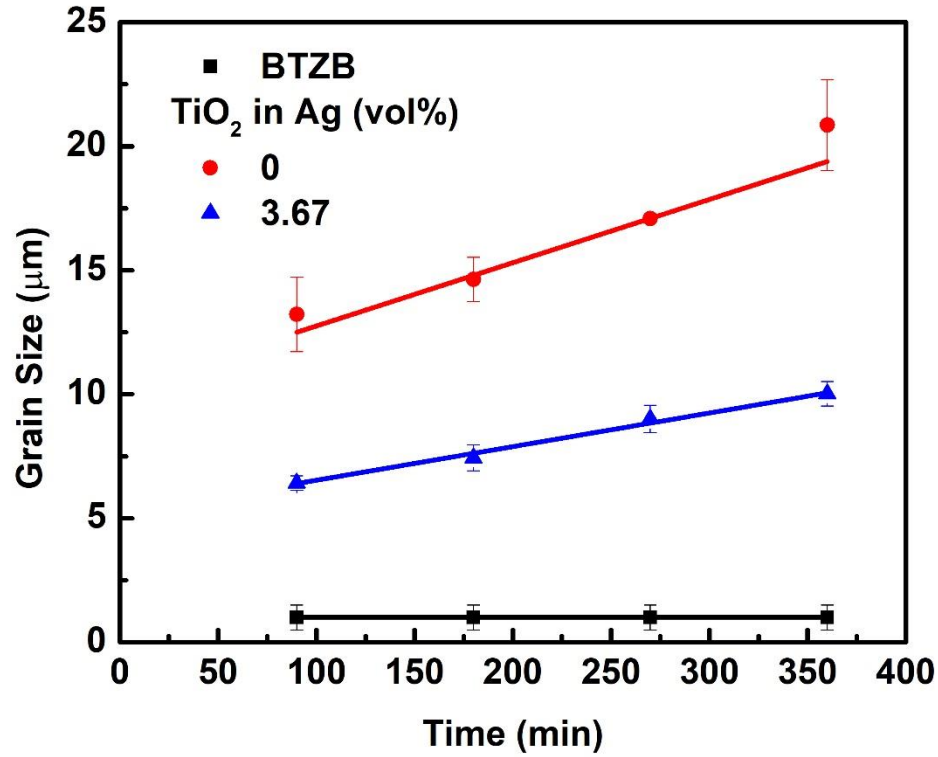


Figure 8. Effect of TiO₂ content added in Ag paste on grain size of Ag fired at 900°C for 90-360 min. Grain sizes of BTZB are also given for comparison.

B. Camber Measurements

Camber development at different temperatures for the bi-layer Ag/BTZB laminates with a thickness ratio of 1/4 ($h_{Ag}/h_{BTZB} = 1/4$), where the Ag is on the top side, is shown in Fig. 9. For all samples investigated, the laminate starts flat and then cambers toward the silver side because the shrinkage of Ag with different amounts of TiO₂ occurs more rapidly than that of BTZB. The curvature continues increasing up to 900°C (Fig. 9(C)), but decreases when firing extends up to 900°C for 20 min (Fig. 9(D)). During the soaking period at 900°C, the laminate exhibits flat initially (Fig. 9(E)), and then cambers toward the BTZB side (Figs. 9(F)-(G)) when the shrinkage of BTZB becomes evident.

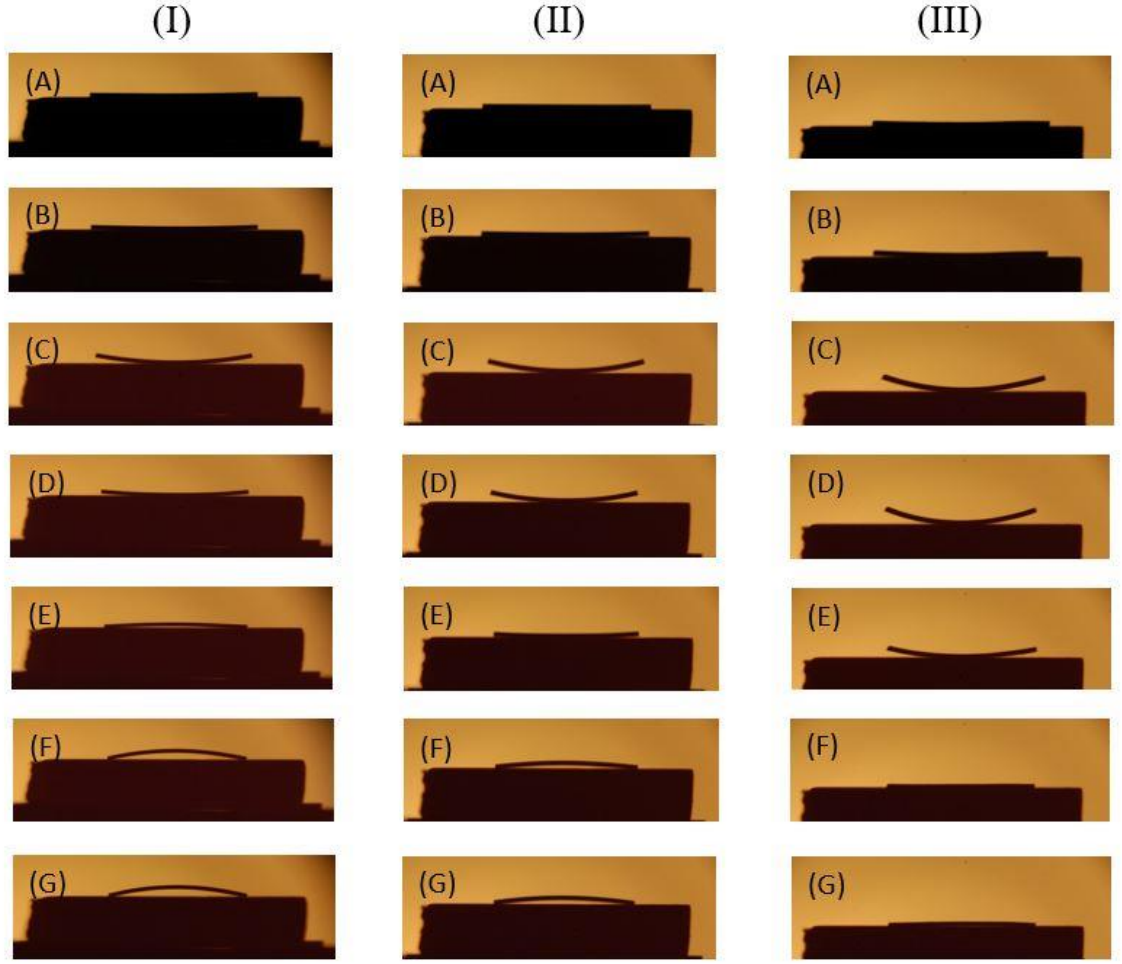


Figure 9. Photos of camber development for the bi-layer pure Ag/BTZB laminate with a $m=h_{Ag}/h_{BTZB}=1/4$ at (I) Pure Ag/BTZB (II) Ag + 1.22 vol% TiO_2 /BTZB (III) Ag + 3.67 vol% TiO_2 /BTZB (A) 500, (B) 850, (C) 900, (D) 900°C for 20 min, (E) 900°C for 30min, (F) 900°C for 60 min and (G) 900°C for 120 min.

The curvature (k') data are normalized by the total thickness of laminate ($h_{Ag}+h_{BTZB}$) as

$$k' = \frac{h_{Ag}+h_{BTZB}}{r} \quad (11)$$

where r is the radius of curvature. A positive curvature is defined when the sample cambers toward the Ag side. Moreover, the positive curvature implies that the Ag layer is under in-plane compressive stress, and the BTZB layer under in-plane tensile stress during cofiring. The sign of stress in different layers is reversed when the curvature becomes negative.

Figure 10(A) summarizes the normalized curvature data as a function of temperature. For all Ag samples with different amounts of TiO₂ investigated, a similar trend of curvature development is observed, i.e., a positive camber observed at 750-900°C, reaching a maximum at 900°C for 10-20 min, and then decreasing with increasing soaking period at 900°C. At a given temperature, moreover, a larger positive camber with more TiO₂ in Ag is observed. However, a larger negative camber is observed for the Ag samples with less amount of TiO₂ during isothermal firing at 900°C. Figure 10(B) shows the normalized camber rate ($\dot{k}$) as a function of temperature, which is obtained by taking the derivative of the curves in Fig. 10(A). For all Ag compositions investigated, the positive camber rate increases initially, goes through a maximum at 800-825°C, and then decreases with increasing temperature. As firing continues, the camber rate is insignificant at 860-875°C, and then becomes negative as firing continues. It reaches a maximum when fired isothermally at 900°C for 10-20 min, and reaches negligible again at 900°C for 60-90 min. The microstructure of the interface between Ag and BTZB is shown in Fig. 11 using the Ag film with 3.67 vol% TiO₂ as an example. No separation between Ag and BTZB is observed even though a significant camber is developed. Both Ag and BTZB layers adhere strongly, without cofiring defects such as cracks and delamination formed at the interface.

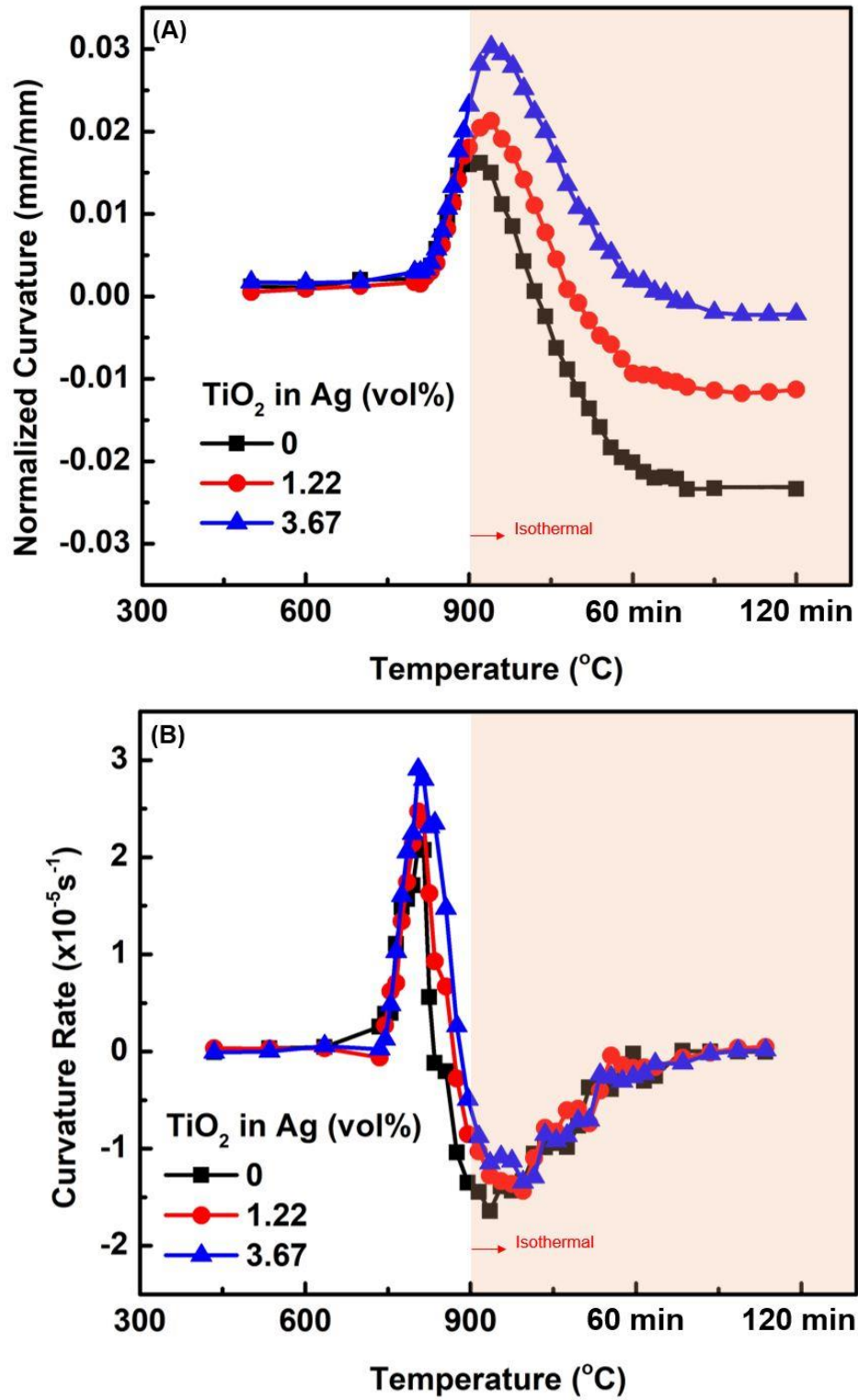


Figure 10. Effect of TiO_2 content added in Ag paste on (A) normalized curvature (B) normalized curvature rate as a function of temperature for the bi-layer Ag/BTZB laminates with $m=h_{\text{Ag}}/h_{\text{BTZB}}=1/4$.

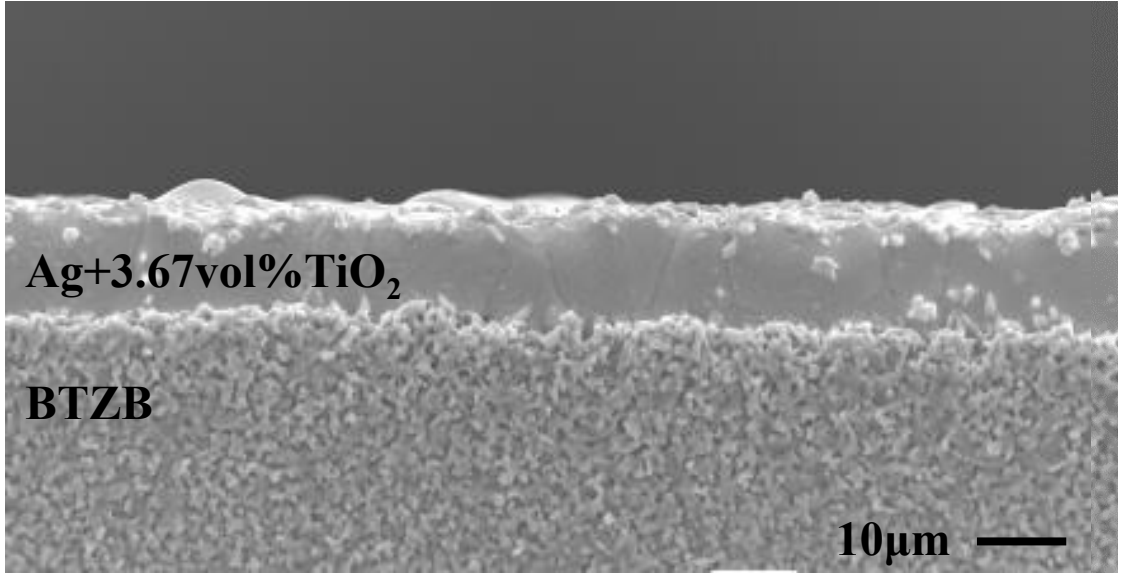


Figure 11. SEM micrograph for the interfacial area between Ag and BTZB in the bi-layer Ag+3.67 vol% TiO₂/BTZB laminate fired at 900°C for 120 min.

C. Uniaxial Viscosity Measurements

To prevent any anisotropic microstructures from forming in the X-Y plane during sintering, cyclic loading at different temperatures were applied on Ag and BTZB laminates with a dimension of 3.7x2.9x2.0 mm³. For all samples investigated, the load was applied for 4 min uniaxially in the z-direction. The strain rate under load was collected at 60, 90, and 120 sec after the load was applied. To further prevent anisotropic microstructure development during sintering, the interval between each load was at least 20 min apart. As shown in Fig 12, the uniaxial viscosity was determined by calculating the slope of the best fit line according to Eq. (3). As the applied pressure and temperature increase so does the strain rate, but as the samples reach densification temperature, strain rate decreases. Figure 13 shows results of uniaxial viscosity of BTZB (E_p^{BTZB}), and Ag (E_p^{Ag}) with different TiO₂ contents, which are determined by a cyclic loading TMA [25-28, 40, 41]. The uniaxial viscosity decreases with increasing temperature at a given density due to microstructural softening but increases with increasing densification at a given temperature due to an increase in mechanical strength.

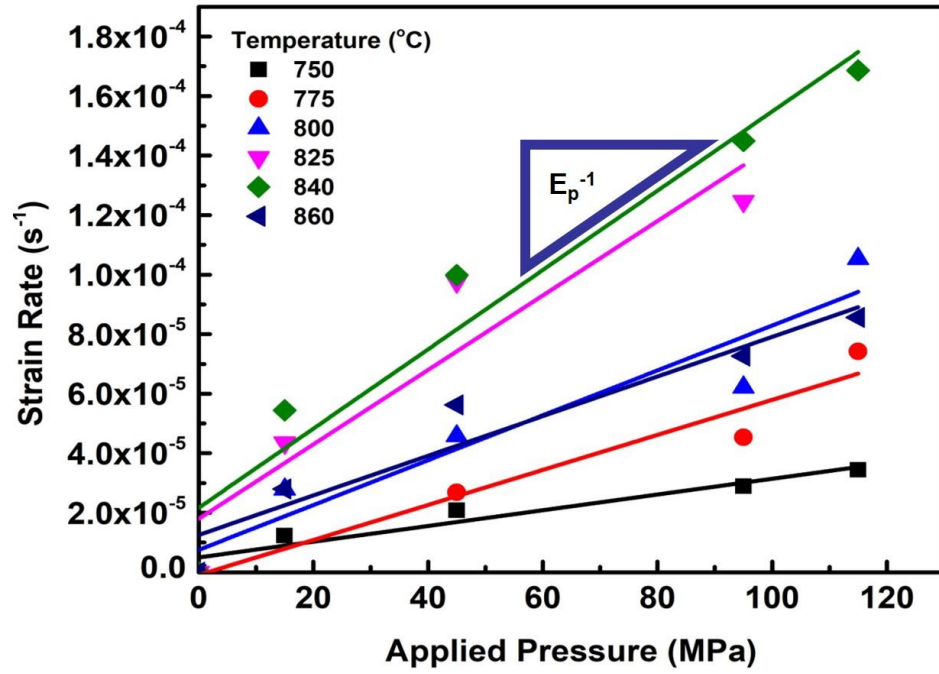


Figure 12. Effect of applied pressure on strain rate of a porous BTZB dielectric at different temperatures.

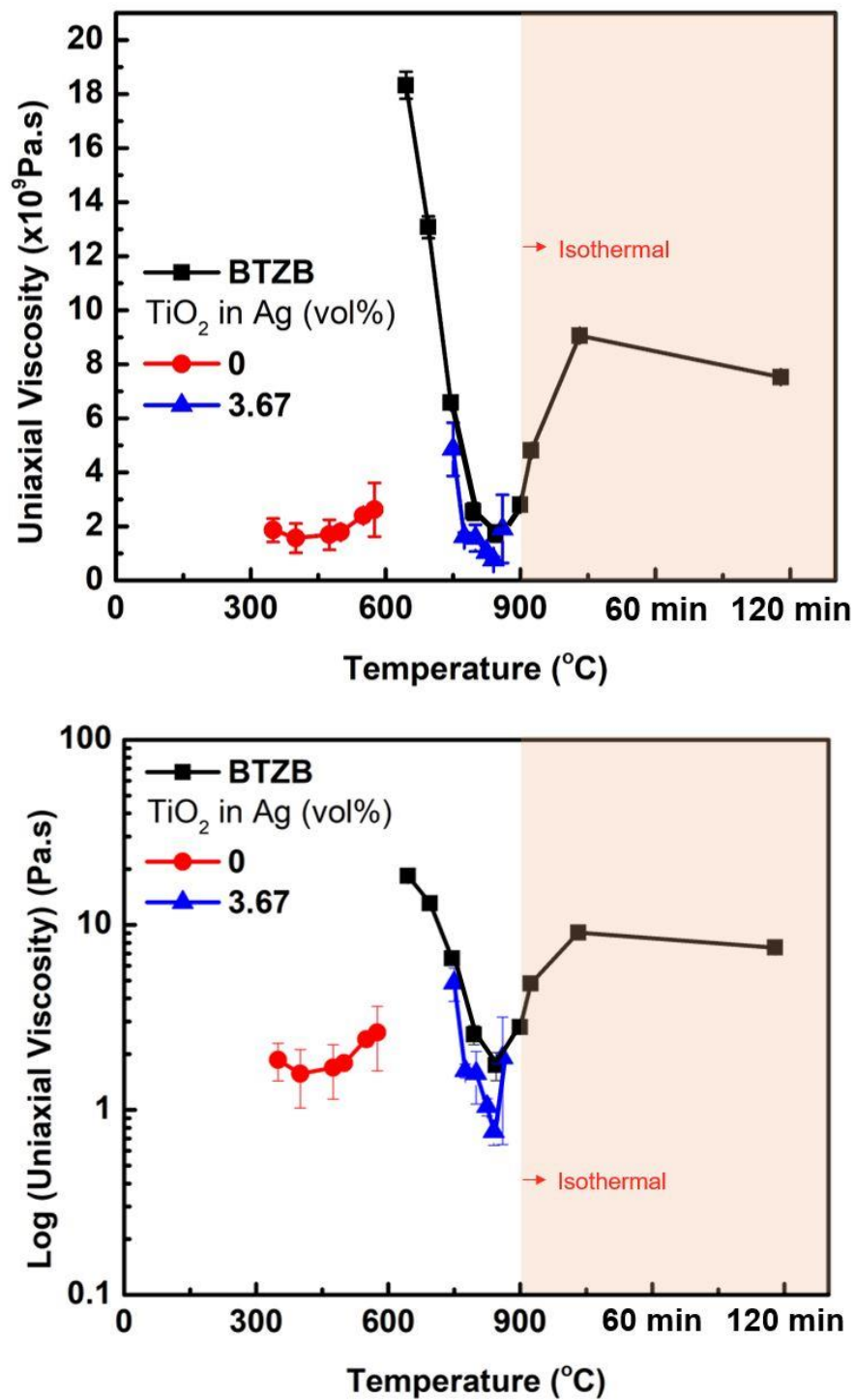


Figure 13. Porous uniaxial viscosity (E_p) of Ag, Ag+3.67 vol% TiO_2 and BTZB as a function of temperature, fired at a heating rate of 5K /min in air.

V. DISCUSSION

It has been reported that a sintering mismatch stress is generated when the densification mismatch exists during cofiring mixed materials [25-28]. Moreover, cofiring defects are formed if the above mismatch stress is greater than that of sintering potential, which is an apparent driving force of densification. The sintering potential (Σ) is related to the uniaxial viscosity (E_p), viscous Poisson's ratio (ν_p) and linear shrinkage strain rate ($\dot{\epsilon}_f$) as shown in Eq. (4) [34-36]. The viscous Poisson's ratio of Ag (ν_p^{Ag}) and BTZB (ν_p^{BTZB}), which is related to the relative sintered density (ρ) by Eq (2), varies in the range of 0.28-0.5 for $\rho=0.6-1.0$ [34-36]. TMA data (Fig. 3(A)) of linear shrinkage measured in the three directions of laminates are used to calculate the relative sintered densities of Ag and BTZB as a function of temperature. With linear shrinkage strain rate data in Fig. 3, the sintering potentials of Ag with different amounts of TiO_2 and BTZB as a function of temperature are calculated, as shown in Figs. 14 and 15, respectively. It is found that the maximum value of sintering potential is -1.2, -3.7 and -2.0 MPa for pure Ag, Ag+3.67 vol% TiO_2 and BTZB, respectively.

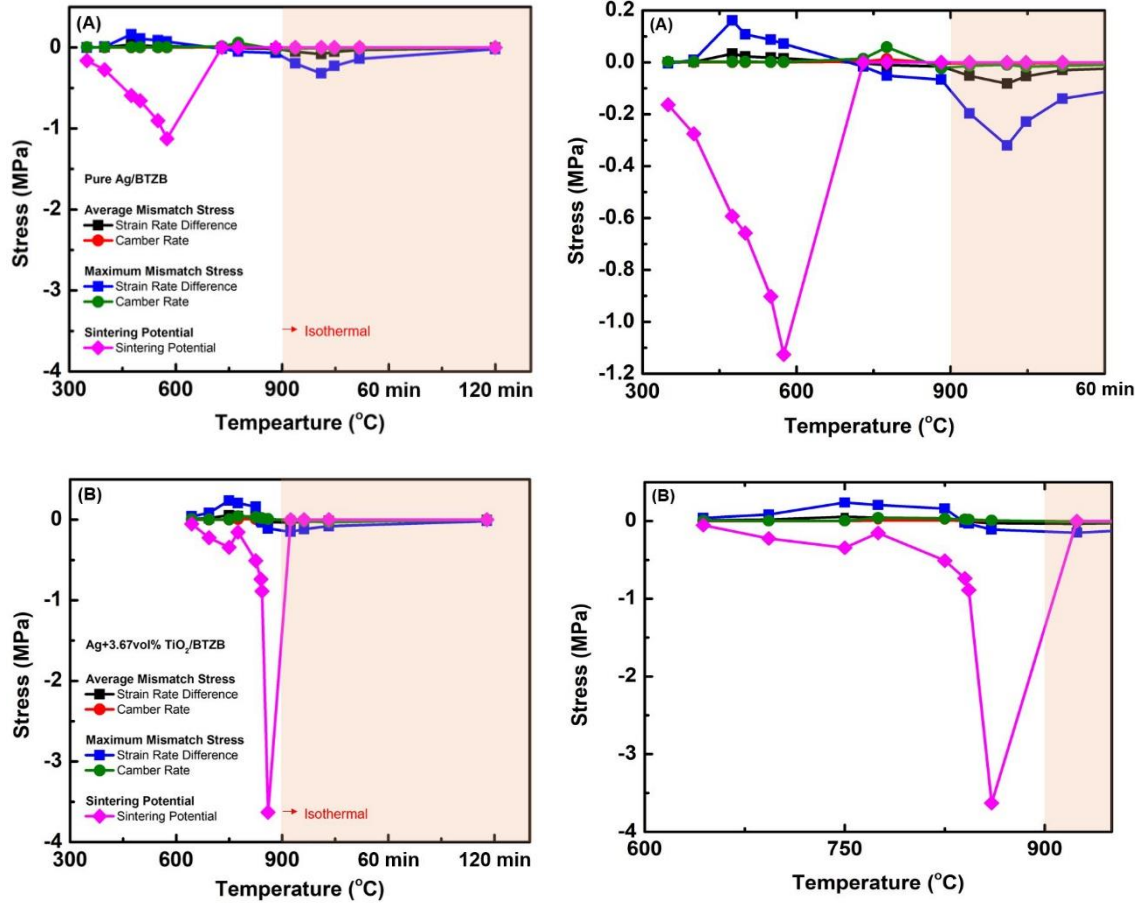


Figure 14. Average (σ_{Ag}^{AVG}) and maximum (σ_{Ag}^{Max}) sintering mismatch stress for the bi-layer (A) pure Ag/BTZB and (B) Ag+3.67 vol% TiO₂/BTZB laminate as a function of temperature calculated by linear strain rate difference ($\Delta\dot{\epsilon}_{BTZB-Ag}$) from TMA data in Fig. 4, and normalized curvature rate data ($\dot{k}$) in Fig. 10. Sintering potential of Ag (Σ_{Ag}) and Ag+3.67 vol% TiO₂ calculated by Eq. (4) is also given for comparison.

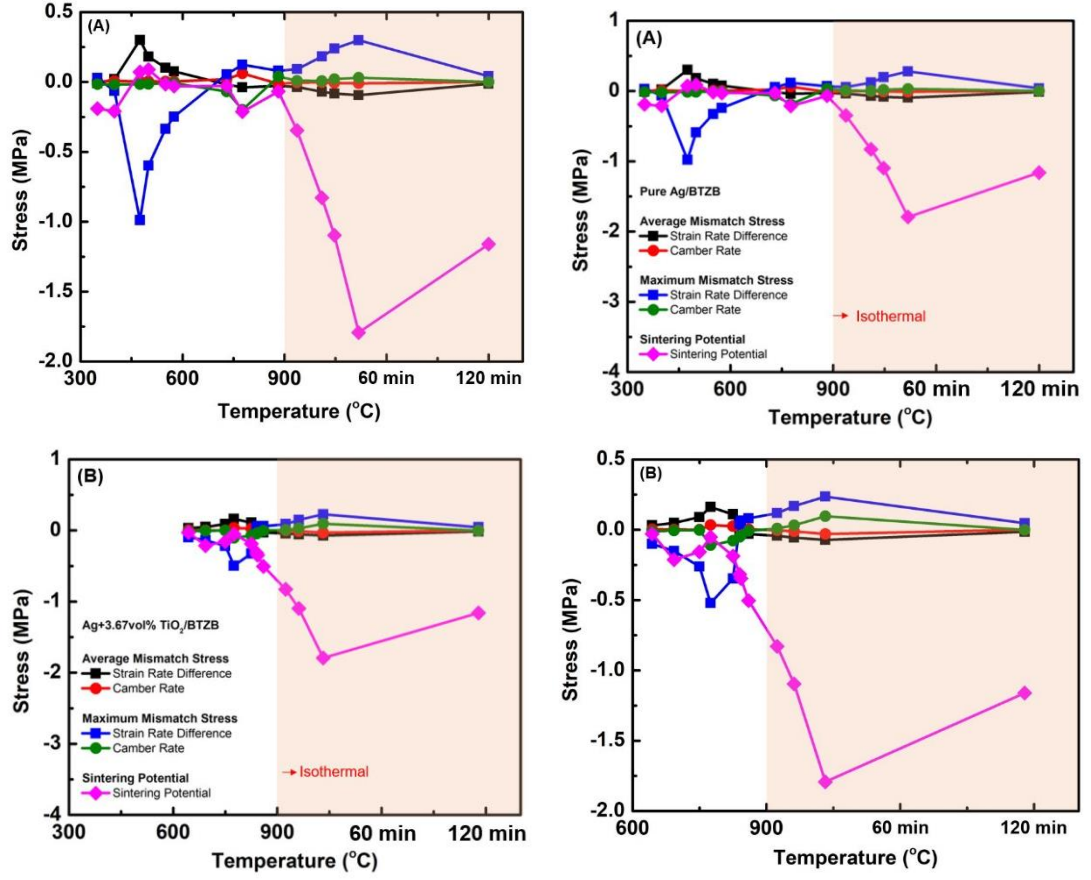


Figure 15. Average (σ_{BTZB}^{AVG}) and maximum (σ_{BTZB}^{Max}) sintering mismatch stress for the bi-layer (A) pure Ag/BTZB and (B) Ag+3.67 vol% TiO₂/BTZB laminate as a function of temperature calculated by linear strain rate difference ($\Delta\dot{\epsilon}_{BTZB-Ag}$) from TMA data in Fig. 4, and normalized curvature rate data ($\dot{k}$) in Fig. 10. Sintering potential of BTZB (Σ_{BTZB}) calculated by Eq. (4) is also given for comparison.

The average sintering mismatch stress in the Ag layer (σ_{Ag}^{AVG}), which is caused by the linear shrinkage rate mismatch between Ag and BTZB layers, can be calculated by Eq. (5) where n is the viscosity ratio between Ag and BTZB calculated by Eq. (6) and $\hat{\sigma}_{Ag}$ is the nominal viscous mismatch stress by Eqs. (7) and (8) [25-28]. By measuring the thickness of Ag and BTZB in the bi-layer laminate, the thickness (m) is 0.25 ± 0.02 for the initial thickness ratio and remains relatively unchanged during sintering. The nominal viscous mismatch stress in the Ag layer ($\hat{\sigma}_{Ag}^{A\dot{\epsilon}}$) in Eq. (7) is related to the linear strain rate difference between BTZB and Ag ($\Delta\dot{\epsilon}_{BTZB-Ag}$) (Fig. 4), uniaxial viscosity of Ag (E_p^{Ag}) in Fig. 13, and viscous Poisson's ratio of Ag (ν_p^{Ag}). With the data of the calculated $\hat{\sigma}_{Ag}^{A\dot{\epsilon}}$, m and n , the average sintering mismatch stress in the Ag layer with different TiO₂ contents (σ_{Ag}^{AVG}) can be determined as a function of temperature by Eq. (5), as shown in Fig. 14(A) for pure Ag/BTZB, and Fig. 14(B) for Ag+3.67 vol% TiO₂/BTZB laminates. The average sintering mismatch stress in the Ag layer (σ_{Ag}^{AVG}) varies in the range of ± 0.1 MPa for Ag/BTZB (Fig. 14(A)) and ± 0.03 MPa for Ag+3.67 vol% TiO₂ (Fig. 14(B)) at 300-900°C.

The camber rate data in Fig. 10 can also be used to calculate the nominal viscous mismatch stress in the Ag layer ($\hat{\sigma}_{Ag}^{\kappa}$) by Eq. (8) [25-28]. Incorporating the data of uniaxial viscosity (E_p^{Ag}) in Fig. 13, the normalized camber rate in Fig. 10, n and m into Eq. (8), the nominal viscous mismatch stress in the Ag layer ($\hat{\sigma}_{Ag}^{\kappa}$) can be calculated. Combining the above nominal viscous mismatch stress ($\hat{\sigma}_{Ag}^{\kappa}$) data into Eq. (5), the average sintering mismatch stress in the Ag layer (σ_{Ag}^{AVG}) as a function of temperature is calculated, as shown in Fig. 14. For all compositions and temperatures investigated, the average sintering mismatch stress in the Ag layer (σ_{Ag}^{AVG}) varies in the range of ± 0.05 MPa for Ag/BTZB (Fig. 14(A)) and ± 0.03 MPa for Ag+3.67 vol% TiO₂ (Fig. 14(B)) at 300-900°C. Since the stress distribution inside multilayer laminate is not uniform, the sintering mismatch stress increases from the top surface of the Ag layer to the interface of asymmetric Ag/BTZB laminate [45]. In other words, the largest stress always exists at the boundary of Ag/BTZB if there is sintering incompatibility present. The largest sintering mismatch stress (σ_{Ag}^{Max}), which is located at the interface of Ag/BTZB laminate, can be calculated by Eq. (9) [25-28]. The largest sintering mismatch stress results, which are calculated using the nominal

stress obtained by Eqs. (7) and (8), exhibit similar trend as those obtained for average mismatch stresses in Fig. 16. The maximum stresses always have 0.1-0.2 MPa larger than those of average sintering mismatch stresses. Results in Fig. 16 further show that the sintering potentials of pure Ag and Ag+3.67 vol% TiO₂ are much larger than those of maximum stresses, indicating that the full densification of Ag films can still be achieved with BTZB layer present during cofiring.

Similar calculations are also performed for the BTZB layer, with a slight change in the largest sintering mismatch stress (σ_{BTZB}^{Max}) calculated by [26,27]

$$\sigma_{BTZB}^{Max} = \left[\frac{m^4 n - m(3m+2)}{m^4 n^2 + 2mn(2m^2 + 3m + 2) + 1} \right] \hat{\sigma}_{BTZB} \quad (12)$$

and the results are shown in Fig. 17. Under most of conditions, the sintering potential of BTZB is much larger than those of mismatch stresses except the pure Ag sample at 300-600°C calculated by the linear shrinkage strain rate difference (Fig. 17(A)). This suggests cofiring defects such as cracks or de-lamination be formed during cofiring multilayer Ag/BTZB laminates. Figures 18(A) and (B) show microstructure of multilayer Ag/BTZB laminates with a thickness ratio of Ag/BTZB=1/4. For both Ag and Ag+3.67 vol% TiO₂, no cofiring defects are found. Detailed examination of the results in Fig. 15 reveals that the mismatch stress of BTZB calculated by the linear shrinkage strain rate difference are larger than those calculated by the camber results, especially for the pure Ag sample. Since the former is obtained under free sintering of Ag and BTZB layers by TMA, and the latter, under cofiring of bi-layer Ag/BTZB laminates. The difference might be resulted from the constrained sintering of Ag induced by BTZB layer during cofiring, which is evidenced by microstructural examination of pure Ag (Figs. 17(A)-(D)) and Ag+3.67 vol% (Figs. 18(A)-(D)) on the bi-layer Ag/BTZB laminates. Figure 17 clearly indicates that the full densification temperatures of pure Ag have been increased from 550-600°C (Fig. (3)) under free sintering to 800-900°C ((Figs. 17(A)-(D)) under cofiring bi-layer Ag/BTZB laminates. For the Ag+3.67 vol% TiO₂ sample, however, slight increase in the full densification temperatures from 850-900°C under free sintering (Figs. 6) to 900°C for 0-60 min under cofiring of bi-layer Ag/BTZB laminates (Figs. 18(A)-(D)). The above observations are also confirmed with camber rate results, which can be verified by Eq. (10) [46, 47]. With

the uniaxial viscosity (E_p^{Ag} and E_p^{BTZB}) results in Fig. 13, the calculated viscous Poisson's ratio of porous Ag and BTZB (ν_p^{Ag} and ν_p^{BTZB}), and the thicknesses of Ag (h_{Ag}) and BTZB (h_{BTZB}), the camber rate can be calculated by Eq. (10) and the results are shown in Fig. 19. For the laminates with pure Ag, the first calculated peak located at 400-500°C is much smaller than that observed at 800-850°C. It is believed that the above phenomenon is caused by constrained sintering of Ag induced by BTZB layer due to significant densification mismatch. For the bi-layer laminate with Ag+3.67 vol%TiO₂, the calculated camber rate results agree well with those observed because the densification mismatch between Ag+3.67 vol% TiO₂ and BTZB is minimal, resulting in a much less constrained sintering effect of Ag+3.67 vol% TiO₂ by the BTZB layer. To further confirm the above arguments, the thickness ratio between Ag and BTZB layers has been increased up to the unity in fabricating multilayer Ag/BTZB laminates. Delamination between Ag and BTZB, and separation in the BTZB layer are clearly observed in the multilayer laminate of Ag/BTZB (Fig. 20(A)), however, defect-free in the multilayer laminate of Ag+3.67 vol% TiO₂/BTZB (Fig. 20(B)) is still found. It is understood that the thick Ag layers not be fully constrained by the BTZB layers, inducing a larger in-plane sintering mismatch tensile stress which causes the poorly densified BTZB layers from delamination during cofiring at 300-600°C.

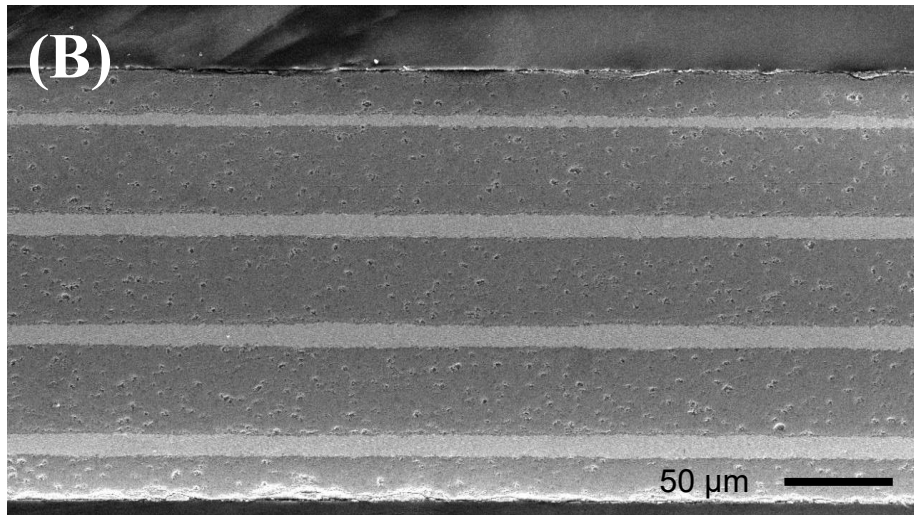
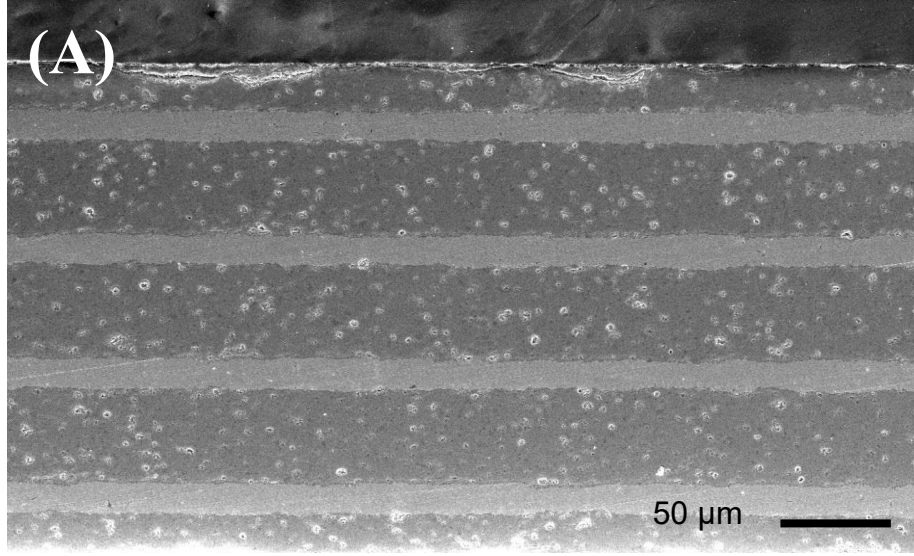


Figure 16. SEM micrographs for the multilayer (A) Ag/BTZB and (B) Ag+3.67 vol% TiO₂/BTZB laminate with $m=h_{Ag}/h_{BTZB}=1/4$ fired at 900°C for 120 min.

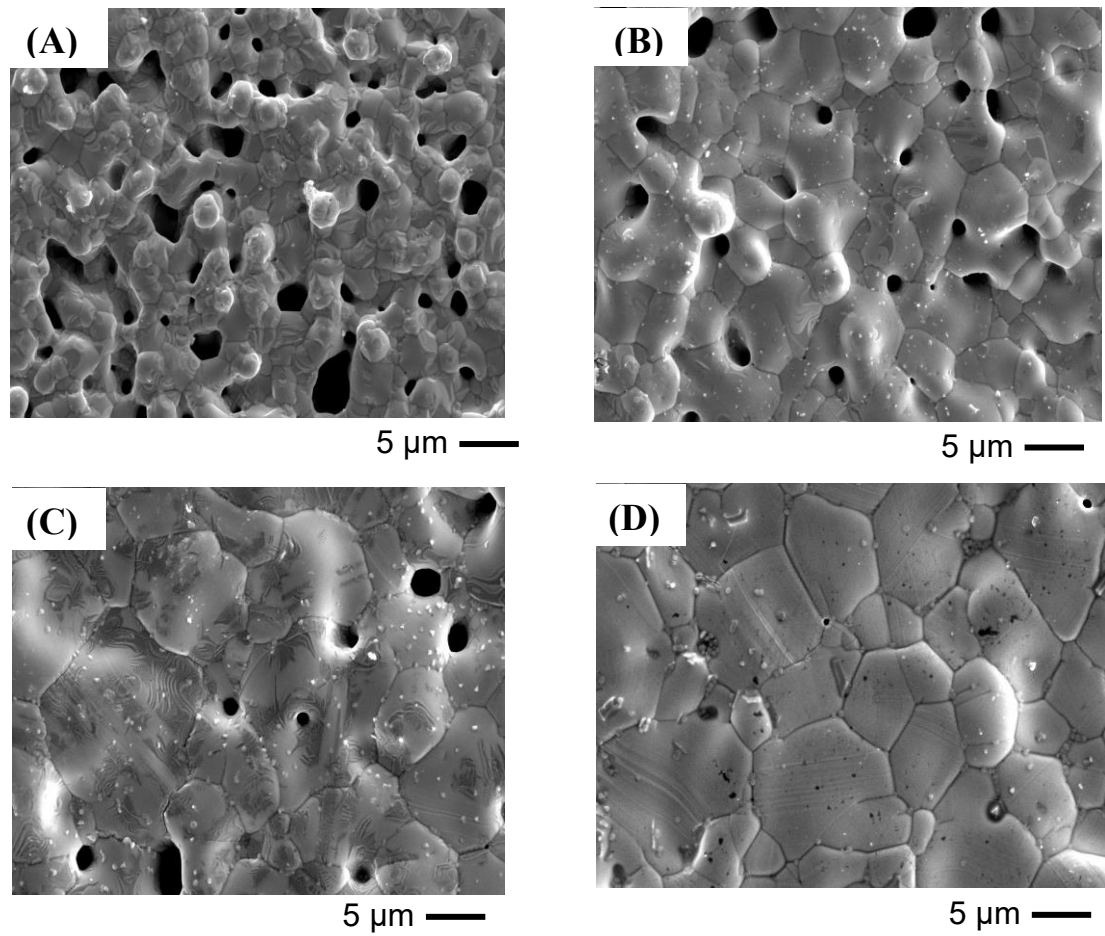


Figure 17. Microstructure of Ag in the bi-layer Ag/BTZB laminate fired at (A)750, (B)800, (C) 850 and (D) 900°C.

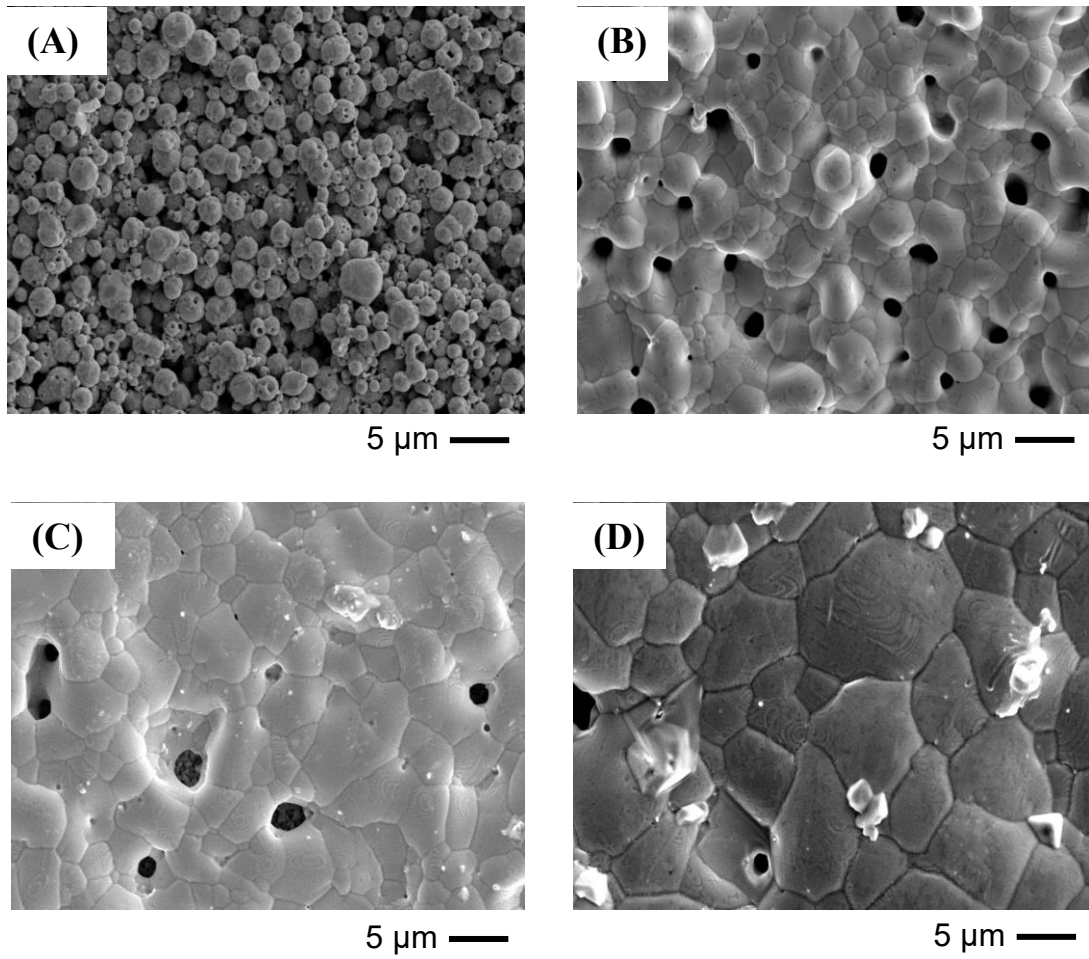


Figure 18. Microstructure of Ag in the bi-layer Ag+3.67 vol% TiO₂/BTZB laminate fired at (A)800, (B)850, (C) 900 and (D) 900°C for 60 min.

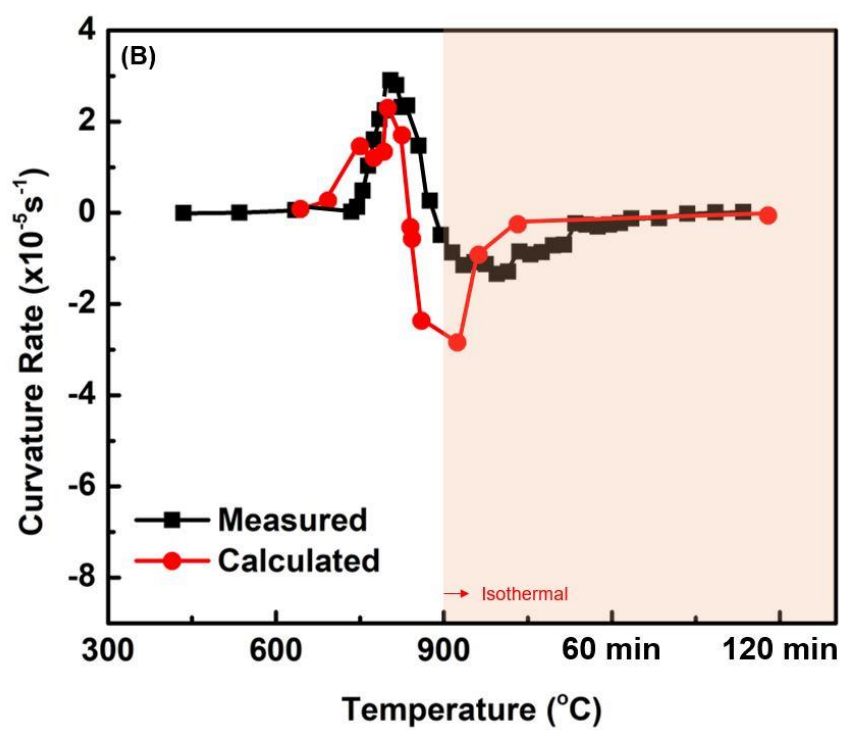
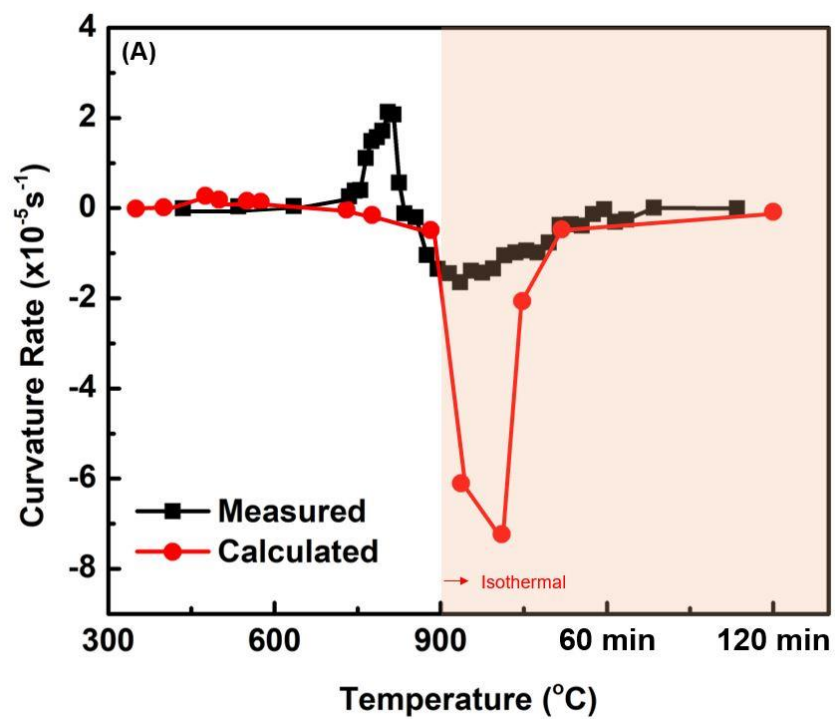


Figure 19. Measured and calculated camber rates as a function of temperature and time for the bi-layer (A) Ag/BTZB, and (B) Ag+3.67 vol% TiO₂/BTZB laminate.

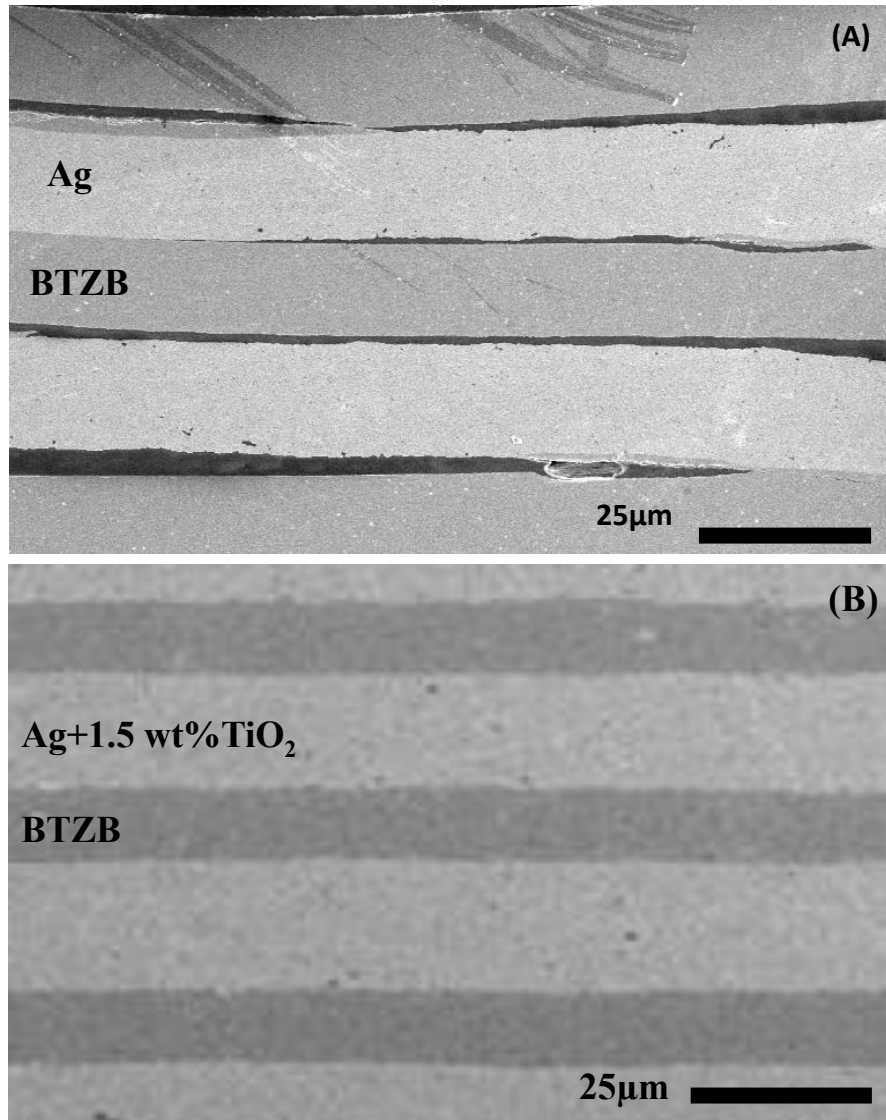


Figure 20. SEM micrographs for the multilayer (A) Ag/BTZB and (B) Ag+3.67 vol% TiO₂/BTZB laminate with $m=h_{Ag}/h_{BTZB}=1/1$ fired at 900°C for 120 min.

VI. SUMMARY AND CONCLUSIONS

Densification rate mismatch between Ag paste and $\text{BaTi}_4\text{O}_9+15 \text{ vol\% ZnO-B}_2\text{O}_3$ glass (BTZB) dielectric tape has been identified as the root cause of camber and stress development during cofiring a bi-layer Ag/BTZB laminate. To minimize the above densification rate mismatch during cofiring, the Ag paste is mixed with 1.22-3.67 vol% TiO_2 . With linear shrinkage of Ag paste and BTZB tape, the camber development during cofiring the bi-layer Ag/BTZB laminate can be calculated, which exhibits good agreement with those observed experimentally. For all Ag compositions investigated, no cofiring defects such as delamination or cracks are found in the multilayer structure of Ag/BTZB laminates with a thickness ratio of $\text{Ag/BTZB}=1/4$. For the pure Ag paste, however, delamination is observed when the thickness ratio of Ag/BTZB is increased to unity. This is due to the fact that free sintering becomes more significant for a thicker Ag layer at low temperatures, generating an in-plane sintering mismatch tensile stress in the BTZB layer greater than that of sintering potential.

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