

Phase Evolution and Dielectric Properties of MgTiO₃-CaTiO₃-Based Ceramic Sintered with Lithium Borosilicate Glass for Application to Low Temperature Co-Fired Ceramics

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Effects on phase evolution caused by the addition of a new sintering agent, lithium borosilicate, $Li_2O \cdot B_2O_3 \cdot SiO_2$ (LBS) glass to 0.9MgTiO₃-0.1CaTiO₃ ceramic and resultant dielectric properties were investigated. The added LBS glass, a liquid phase sintering agent, significantly lowered the densification temperature from 1300° to about 950°C, while yielding decomposition of MgTiO₃ into MgTi₂O₅ and Mg₂TiO₄. At the same time, the by-products of the decomposition reaction, MgO and TiO₂, were dissolved into the glass network. Such phase evolution partly compensated the influence of deleterious glass addition so that the specimen demonstrated fairly good apparent dielectric properties.

I. Introduction

L ow-TEMPERATURE co-fired ceramic (LTCC) technology has received much attention because of the benefits of package miniature, reduced cost, and suitable high radio frequency (RF) applications to wireless local area networks (LAN) and mobile microwave communication module parts such as bluetooth, resonator, phase shifter, and duplexer, etc.¹ MgTiO₃–CaTiO₃ is a well-known ceramic material system for LTCC technology because of its appropriate dielectric constant (*k*) for microwave dielectric applications, high quality factor ($Q \times f$), and high temperature-stability (τ_f). Above all, the dielectric properties of MgTiO₃–CaTiO₃ can be tailored by controlling the molar ratio of each constituent, i.e., illmenite-structured MgTiO₃ (k = 17, $Q \times f = 160\,000$ GHz, $\tau_f = -45$ ppm/°C) and perovskite-structured CaTiO₃ (k = 170, $Q \times f = 3600$ GHz, $\tau_f = 800$ ppm/°C).^{2,3}

For LTCC applications, the addition of a glass to the MgTiO₃-CaTiO₃ ceramic composition is required to lower the sintering temperature; however, this addition inevitably sacrifices dielectric properties. Thus, in studying the influence of a sintering agent, the issues regarding the lowering of the densification temperature and the resultant dielectric properties are important. In a previous work by Yamamoto *et al.*,⁴ a 7 mol% addition of V₂O₅ to 0.95MgTiO₃-0.05CaTiO₃ lowered the sintering temperature from about 1300° to about 1000°C while displaying significant deterioration of dielectric properties.

For the case when 5-10 mol% B₂O₃ was added in their work, modification of the dielectric properties was minimal, while the required sintering temperature was as high as 1200°C. Jantunen et al.^{5,6} have also investigated the effect of the addition of several borosilicate glasses $RO-B_2O_3-SiO_2$ (R = Zn, Ba) to the MgTiO₃-CaTiO₃ system. In their work, as high as 70 wt% glass phase in the ceramic was required to lower the effective sintering temperature to 900°C. Therefore, efforts to investigate appropriate sintering agent (glass system), which ensures suitable densification as well as appropriate dielectric properties, are of importance for LTCC technology. In the present work, as an extension to the previous borosilicate glass system,^{5,6} the feasibility of a new lithium borosilicate, $Li_2O \cdot B_2O_3 \cdot SiO_2$ (LBS) glass composition has been investigated as a sintering agent for the MgTiO₃-CaTiO₃ system. This work will demonstrate that the studied new sintering agent is capable of ensuring suitable densification as well as appropriate dielectric properties.

II. Experimental Procedure

The starting materials to individually prepare MgTiO₃ and CaTiO₃ compounds were MgO (High Purity Chemical Lab., Tokyo, Japan), TiO₂ (rutile, High Purity Chemical Lab.), and CaCO₃ (High Purity Chemical Lab.), all of which were 99.9% pure powders. An appropriate amount of starting powders were mixed and ball-milled in a polyethylene bottle with ZrO_2 balls for 24 h using ethanol (MgTiO₃) and distilled water (CaTiO₃) as medium. Each mixture was rapidly dried and calcined at 1100°C for 2 h.

The glass was prepared by mixing LBS with a weight percent ratio of 3:6:1 and melted at 900°C for 1 h in a platinum crucible. Samples were quenched in air and pulverized to pass 200 mesh sieve.[‡] The calcined MgTiO₃, CaTiO₃, and glass frits were mixed stoichiometrically to prepare $0.9MgTiO_3-0.1CaTiO_3$ (MCT) with varying weight percentages of LBS glass. Then, the mixture was ball-milled for 48 h and dried, granulated, and pressed at 1000 kg/cm³ to form pellets 8 mm in diameter and 3 mm in thickness. The pellets were sintered from 900° to 1050°C for 2 h at a heating rate of 5°C/min.

Shrinkage of the specimens during heating was measured using a horizontal-loading dilatomter with alumina rams and boats (model DIL 402C, Netzsch Instruments, Shelb/Byern, Germany). The crystal structure of sintered sample was investigated using X-ray powder diffraction (model M18XHF, Mac-

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[†]Through a separate dilatometric expansion analysis of the compacted LBS glass frits, glass transition temperature was about 230°C. The compacted LBS glass frits crystallized to $Li_2B_4O_7$ at about 500°C followed by melting at about 720°C.

science Instruments, Yokohama, Japan) in the 2 θ -range from 20° to 60°. Polished and thermally etched surfaces of sintered specimens were examined using field emission scanning electron microscopy (FESEM: model JSM-6330F, JEOL, Tokyo, Japan). Microwave dielectric properties of sintered samples were measured using a network analyzer (model HP8720C, Hewlett Packard, Palo Alto, CA) in a frequency range from 8 to 10 GHz. The $Q \times f$ was measured through the transmission cavity method using a Cu cavity and Teflon supporter.⁷ Permittivity (*k*) was measured using the post resonator method⁸ and the temperature coefficient of the resonant frequency (τ_f) was measured using an Invar cavity in a temperature range from 10° to 80°C.⁹

III. Results and Discussion

(1) Densification, Phase Evolution, and Microstructure

Figure 1 shows the change in density of MCT ceramic with varying amounts of LBS glass as a function of sintering temperature. Although the theoretical density for full densification is hard to determine because of the presence of LBS glass and complicated material reactions in the specimen (will be discussed later), relative density has been determined Fig. 1(b) by assuming no material reactions in order to roughly estimate the degree of densification. From Fig. 1, 950°C seems to be sufficient for the appropriate densification of 10 and 20 wt% glass-added



Fig. 1. Change in apparent density of $0.9MgTiO_3-0.1CaTiO_3$ (MCT) ceramic as a function of sintering temperature at various lithium borosilicate (LBS) glass addition levels.



Fig. 2. X-ray diffraction patterns of $0.9MgTiO_3-0.1CaTiO_3$ ceramic sintered with 20 wt% lithium borosilicate glass at varying temperatures. Unmarked peaks are from MgTiO_3. *, MgTi_2O_5; M, MgTiO_3; s, Mg_2TiO_4; c, CaTiO_3; T, TiO_2 (rutile); m, MgO; L, Li_2B_4O_7; and b, (Mg,Ti)_2(BO_3)O.

specimens. For the 5 wt% glass-added specimen, acceptable densification is achieved at above 1000°C. Considering that glass-free MCT specimen requires sintering temperatures above about 1300°C, the addition of LBS glass in this work significantly lowers the sintering temperature. In the cases of specimens with a relatively large amount of glass, e.g., 20 wt%, firing at overly high temperatures, seems to slightly lower the density, probably because the volatile species in the glass, such as lithium and boron oxides, increase porosity.

The phase evolution during the sintering of 20 wt% glassadded specimens has been investigated as a function of rising temperature using XRD and the result is shown in Fig. 2. In order to efficiently study the change in maximum peak intensities with rising temperature, the samples were pulled out from the furnace when the intended temperature was reached.[§] As seen in the figure, the decrease in peak intensities of MgTiO₃ (unmarked in Fig. 2) is apparent as temperature rises unlike the case of CaTiO₃ (denoted as c). In addition, various secondary phases such as MgTi₂O₅ (marked as *), Mg₂TiO₄ (marked as s), MgO (marked as m), and TiO_2 (marked as T) are observed. The increase in the peak intensity of secondary phases such as MgTi₂O₅ and Mg₂TiO₄ with the temperature is so apparent that, at 1000°C, MgTiO₃ (unmarked) is no longer the major phase: MgTi₂O₅ (marked as *) and Mg₂TiO₄ (marked as s) are the major phases.

From the decrease in XRD peak intensity of MgTiO₃ and increase in Mg_2TiO_4 with temperature, Mg_2TiO_4 is interpreted to form by the decomposition of MgTiO₃,

 $2MgTiO_3 = Mg_2TiO_4 + TiO_2$ (dissolved into LBS glass) (1)

In Fig. 2, the peak intensity of Mg_2TiO_4 (marked as s) monotonically increases with temperature while that of TiO₂ (marked as T), which increases up to 700°C, diminishes above 700°C. The peak intensity eventually disappears above 950°C. From this

 $^{{}^{\$}}$ Identifying the specimens held for 2 h at the firing temperatures showed almost fully grown peaks so that the change in peak intensities with rising temperature was less significant.



Fig. 3. X-ray diffraction patterns from $0.9MgTiO_3-0.1CaTiO_3$ (MCT) ceramic sintered with 5, 10, and 20 wt% lithium borosilicate (LBS) glass at 1000°C for 2 h. Unmarked peaks are from MgTiO_3. *, MgTi₂O₅; s, Mg₂TiO₄; m, MgO; and b, (Mg,Ti)₂(BO₃)O.

result, TiO_2 is interpreted as dissolving into the LBS glass as the temperature rises.

Similarly, MgTi₂O₅ forms via the reaction,

 $2MgTiO_3 = MgTi_2O_5 + MgO$ (partially dissolved into LBS glass) (2)

Although $MgTi_2O_5$ (marked as *) and MgO (marked as m) form simultaneously, in Fig. 2 the increase in the peak intensity of $MgTi_2O_5$ with temperature is drastic whereas that of MgO is moderate. This difference implies that MgO is also partially dissolved into the LBS glass as temperature increases.

Having shown the effect of temperature on the phase evolution in Fig. 2, the effect of glass addition on the phase evolution at a constant temperature, i.e., 1000° C, is shown in Fig. 3. In order to allow enough reaction time between the glass and the MCT ceramic, samples were held for 2 h at 1000° C. In Fig. 3, the peak intensities of MgTiO₃ decrease with glass addition. At the same time, the peak intensities of MgTi₂O₅ and Mg₂TiO₄ increase with the addition of LBS glass: eventually they are more predominant over the MgTiO₃ phase in 20 wt% glass-added specimen. This result indicates that the decomposition of MgTiO₃ is fostered not only by the increase in temperature (Fig. 2) but also by the increase in glass addition (Fig. 3).

Figure 4 shows a SEM micrograph of polished specimens sintered at 950°C for 2 h with varying amounts of LBS glass. As shown in this figure, the 5 wt% specimen yields apparent formation of pores as consistent with the trend in density (Fig. 1). The increased addition of glass to 10 wt% results in an enhanced densification with the growth of grains, which is attributed to liquid phase sintering by the low-temperature-softening LBS glass. In a separate work, the LBS glass showed a drastic softening at about 700°C in a thermal shrinkage measurement. The glass addition as high as 20 wt% yields further growth of grains. Based on energy dispersive spectroscopy (EDS) (not shown), grains in 20 wt% specimen (Fig. 3(c)) mostly consist of MgTi₂O₅ (marked as "a") and Mg₂TiO₄ (marked as "b") grains with a minor volume of CaTiO₃ (marked as "c"), LBS glass (marked as "d"),[¶] and undecomposed MgTiO₃ (marked as "e"). These microstructural features are in accordance with the XRD obser-



Fig. 4. Scanning electron micrographs of sintered $0.9MgTiO_3-0.1Ca-TiO_3$ (MCT) ceramic at 950°C for 2 h with varying amounts of lithium borosilicate (LBS) glass: (a) 5, (b) 10, and (c) 20 wt%.

vation. In summary, the addition of LBS glass into MCT ceramic results in an improved densification (Fig. 1), decomposition of MgTiO₃ into the secondary phases (Figs. 2 and 3), and grain growth (Fig. 4).

(2) Microwave Dielectric Properties

Microwave dielectric properties of the studied specimens with varying amounts of LBS glass are shown in Fig. 5 as a function of sintering temperature. For the interpretation of the results, the reference material MCT and the secondary phases $MgTi_2O_5$ and Mg_2TiO_4 have been prepared separately and their dielectric properties are shown in Table I.

In Fig. 5(a), the permittivity of the glass-added specimens such as 10 and 20 wt% samples show decreased values from the MCT reference, in proportional to the amount of the added glass. This decrease seems to be natural as the permittivity of the

[•]The elongated ones were rich in silicon in EDS unlike any other grain shapes, indicating the LBS glass region: it is possibly localized during thermal etching for sample characterization.





Fig. 5. Microwave dielectric properties of $0.9MgTiO_3-0.1CaTiO_3$ (MCT) ceramic as a function of sintering temperature for varying lithium borosilicate (LBS) glass additions. (a) relative dielectric constant, k, (b) quality factor, $Q \times f$, and (c) temperature coefficient of resonant frequency, τ_{f} . The reference sample MCT (denoted as star) was sintered at 1300°C for 2 h.

Table I. Microwave Dielectric Properties of $MgTi_2O_5$ and Mg_2TiO_3

	Sintering condition	k	$Q \times f$	$\tau_{\rm f}$
MgTi ₂ O ₅	1500°C, 2 h	17.4	47 000	-66
Mg ₂ TiO ₃	1300°C, 2 h	14.4	55000	-54

LBS glass ($k = 7.97^{10}$) is lower than that of MCT (k = 23). For the case of 5 wt% specimen, especially when sintered at temperatures lower than 1000°C, the permittivity is even lower than the 10 and 20 wt% specimens although the glass addition was minimal. The presence of pores (k = 1) in this specimen because of the poor densification at low temperatures (Figs. 1 and 4(a)) is interpreted to yield such behavior.

Regarding the formation of the secondary phases during the densification, the presence of the phases such as Mg_2TiO_3 and $MgTi_2O_5$ does not seem to much alter the permittivity of the overall specimen since their permittivity values (Table I) are similar to the range of the overall values, i.e., 13–17 (Fig. 5(a)). The dissolved byproduct TiO₂ and MgO by Eqs. (1) and (2) into the LBS glass is anticipated to have increased the permittivity of the glass itself. This increase is the result of these oxides behaving as if their permittivities were 25.5 and 14.0, respectively,¹¹ once they are dissolved in the glass. These values are much higher than the LBS glass itself (7.97). After all, the eventual permittivity values of the studied specimens are 13–17, which are in the intermediate range between the values of MCT ceramic (23) and LBS glass itself (7.97).

The change in the $Q \times f$ of the specimens with varying amounts of LBS glass is shown in Fig. 5(b) as a function of sintering temperature. The decrease of the $Q \times f$ of the 5 wt% specimen at temperatures below 1000°C is again correlated with the poor densification of the specimen. For the case of well-sintered specimens at above 1000°C, a decrease in the $Q \times f$ from the MCT reference is apparent with the glass addition, although the additions more than 10 wt% up to 20 wt% did not yield further decrease. The reason why no further decrease resulted can be explained by the fact that the formation of the secondary phases such as MgTi₂O₅ and Mg₂TiO₄ is enhanced by the further addition of the LBS glass (Fig. 3). As seen in Table I, the $Q \times f$ of such secondary phases are fairly high, e.g., 47000-55000 GHz, even higher than the MCT (42800 GHz). Thus, although the 10-20 wt% addition of glass itself would tend to decrease the $Q \times f$, its enhancement of the decomposition of MCT to MgTi₂O₅ and Mg₂TiO₄ (Fig. 2) is interpreted to increase the $Q \times f$; thereby, the overall $Q \times f$ is compensated.

Figure 5(c) shows the temperature coefficient of the resonance frequency for specimens with varying LBS glass. In the figure, all the glass-added samples show fairly diminished τ_f from that of MCT ceramic ($\tau_f = 40 \text{ ppm/}^\circ\text{C}$). This decrease is associated with the fact that the τ_f of appearing (forming) compounds MgTi₂O₅ ($\tau_f = -66 \text{ ppm/}^\circ\text{C}$) and Mg₂TiO₄ ($\tau_f = -54 \text{ ppm/}^\circ\text{C}$) are more negative than the disappearing (decomposing) compound MgTiO₃ ($\tau_f = 40 \text{ ppm/}^\circ\text{C}$) by the glass addition. However, the contribution of the MgO- and TiO₂-dissolution into the LBS glass to the τ_f of the specimen is not clear at this moment.

Although the decomposition of MgTiO₃ because of glass addition decreases τ_f in general, the detailed trends with temperature and glass addition, as shown in Fig. 5(c), require interpretation. For the case when 5 wt% glass is added, the τ_f decreases at temperatures below 1000°C, which occurs simultaneously with the poor densification of the samples in this temperature range. For the well-sintered specimens at temperatures above about 1000°C, increase in glass addition from 5 to 10 wt% decreases the τ_f from about 13 to roughly about 0 ppm/°C, which, as mentioned above, is believed to be associated with the more enhanced formation of the secondary phases, MgTi₂O₅ and Mg₂TiO₄ having highly negative values.

The specimens with 10 and 20 wt% glass additions are welldensified throughout the temperature range shown in Fig. 5(c). Comparing these specimens, the increase in glass addition from 10 to 20 wt% does not necessarily diminish τ_f correspondingly at temperatures between 950° and 1000°C. This phenomenon is hardly interpretable because the enhanced decomposition of MgTiO₃ and formation of MgTi₂O₅ and Mg₂TiO₄ with increased glass addition should have lowered τ_f correspondingly at 950°-1000°C. Such behavior can only be interpreted by assuming that the change in the composition of the LBS glass because of the dissolution of MgO and TiO₂ tend to increase τ_f value, inhibiting the corresponding decrease in τ_{f} ." Such a role of MgO- and TiO₂-dissolution into LBS glass is further supported by the fact that the 20 wt% glass added specimen shows greatly increased τ_f at 1050°C. Since the increased temperature enhances the decomposition of MgTiO₃ (the source for lowering τ_f), the plausible source for such a drastic increase in τ_f at 1050°C can only be assigned to the change in glass composition because of the dissolution of MgO and TiO_2 . A separate work is under way to further confirm this proposition. In summary, at high temperature and high glass addition conditions, there is a tendency that the contribution from the formation of MgTi₂O₅ and Mg₂TiO₄ phases (which decreases τ_f) is compensated or overwhelmed by the change in glass composition because of the dissolution of MgO and TiO₂ (which is interpreted to increase τ_f).

From above, the studied LBS glass system is shown to ensure the densification and decomposition of MCT ceramic at a fairly

^{II}Although the physical origin is not clear, dissolution of crystalline TiO₂, having the most high permittivity (k = 100) among common oxides for glass network, results in higher effective permittivity (k = 25) than any other commonly dissolved oxides in glass: TiO₂ dissolution increases the k of the glass as if the k of TiO₂ in glass were 25¹¹. Similarly, the very high τ_r of crystalline TiO₂ (400 ppm/°C) may also increase the τ_r of the glass system when it is dissolved.

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low temperature. The LBS glass-added specimen yields fairly good resultant dielectric properties for the application of the studied material to LTCC technology. The 10 wt% LBS glass-added specimen fired at 950°C demonstrated a permittivity of 19.1, a $Q \times f$ of 13000 GHz, and a τ_f of -1.3 ppm/°C.

IV. Conclusions

The effects of LBS glass addition to MCT ceramic on densification and phase evolution, as well as the resultant dielectric properties, were investigated. The glass addition apparently improved the densification of the specimen via liquid phase sintering. During the firing process, decomposition of MgTiO₃ to MgTi₂O₅ and Mg₂TiO₄ was apparent, yielding dissolvable MgO and TiO₂, respectively, into the LBS glass. Such phenomenon was further enhanced as either the temperature or glass addition increased. Permittivity of the specimen decreased with the addition of the low-permittivity glass, as qualitatively consistent with the rule of mixture. The glass-assisted decomposed products, either crystalline phases such as MgTi₂O₅ and Mg₂TiO₄, or the dissolved products MgO and TiO2, did not much alter the overall permittivity value. The $Q \times f$ of the specimen also decreased because of the addition of low- $Q \times f$ glass. However, an overly high addition, e.g., 20 wt%, did not decrease the factor correspondingly, because of the enhanced formation of the MgTi₂O₅ and Mg₂TiO₄ having very high $Q \times f$. For the case of the temperature coefficient of resonance frequency, τ_f , the decomposition products MgTi₂O₅ and Mg₂TiO₄ decreased the $\tau_{\rm f}$, while the change in glass composition because of the dissolution of MgO and TiO₂ was interpreted to be a source to increase the τ_f . Thus, an overly high addition of glass, e.g., 20 wt%, does not necessarily decrease the τ_f ; in fact, the τ_f can even be increased. The investigated new sintering agent, lithium borosilicate glass, was capable of ensuring suitable densification as well as fairly good apparent dielectric properties: the 10 wt% LBS glass-added specimen fired at 950°C for 2 h demonstrated a permittivity of 19.1, a $Q \times f$ of 13000 GHz, and a τ_f of $-1.3 \text{ ppm}/^\circ\text{C}$.

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