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Role of lithium borosilicate glass in the decomposition of $MgTiO_3$-based dielectric ceramic during sintering

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Abstract

The decomposition behaviour of $0.9MgTiO_3$–$0.1CaTiO_3$ dielectric ceramic during a liquid phase sintering by lithium borosilicate (LBS) glass was studied. The decompositions of $MgTiO_3$ into $MgTi_2O_5$ and Mg_2TiO_4 were apparent during the sintering although the reactions are thermodynamically unfavourable in glass-free compositions. The role of the LBS glass in favouring the decomposition reaction was investigated in terms of the thermodynamic activity of the reaction product in the glass. The decomposition reactions were not necessarily harmful because of the high dielectric performance of the decomposition products, $MgTi_2O_5$ (17.4 permittivity; 47,000 GHz quality factor) and Mg_2TiO_4 (14.4 and 55,000 GHz, respectively).

Keywords: A. Ceramics; D. Dielectric properties

1. Introduction

$MgTiO_3$–$CaTiO_3$ is a well-known ceramic material in low temperature co-fired ceramic (LTCC) technology [1–3]. The addition of glass to the $MgTiO_3$–$CaTiO_3$ ceramic composition is a convenient means for lowering the sintering temperature from about 1350 °C. As the glass addition degrades the dielectric properties as well, the development of a suitable glass system for the low temperature sintering has to be carried under the constraint of minimizing the degradation of the dielectric properties. Thus, it is prerequisite to understand the material reactions during the sintering process under the presence of glass, because these reactions influence the densification process as well as the resultant dielectric properties.

In the present study, the decomposition reaction of $0.9MgTiO_3$–$0.1CaTiO_3$ (MCT) ceramic was investigated during the sintering process under the presence of a new sintering agent glass system, lithium borosilicate (LBS) glass. This composition is an extension to previously studied borosilicate glasses RO–B_2O_3–SiO_2 ($R = Zn$, Ba) [4–6]. This work will demonstrate that the decomposition of $MgTiO_3$ is thermodynamically unfavourable, but it can take place under the presence of LBS glass ($2MgTiO_3 = Mg_2TiO_4 + TiO_2$ and $2MgTiO_3 = MgTi_2O_5 + MgO$). The role of glass in favouring the decomposition reactions has been investigated in terms of thermodynamic

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activities of MgO and TiO_2 in glass. It is also reported that the decomposition reaction is not necessarily harmful because of the high dielectric performance of the decomposition products $MgTi_2O_5$ and Mg_2TiO_4.

2. Experimental procedure

Stoichiometric amounts of MgO (High Purity Chemical Lab., Japan), TiO_2 (rutile, High Purity Chemical Lab.), and $CaCO_3$ (High Purity Chemical Lab.) powders (all were 99.9% pure) were mixed, ball-milled, dried, and calcined at 1100 °C for 2 h to prepare either $MgTiO_3$ or $CaTiO_3$ compounds. Li_2O, B_2O_3, and SiO_2 powders (LBS) were mixed with a weight percent ratio of 3:6:1 and melted at 900 °C for 1 h in a platinum crucible, followed by quenching and pulverization to pass 200 mesh sieve. To prepare $0.9MgTiO_3$–$0.1CaTiO_3$ (MCT) ceramic, the calcined $MgTiO_3$, $CaTiO_3$, and glass frits were mixed stoichiometrically, ball-milled for 48 h, dried, granulated, and pressed at 98 MPa to form pellets with 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 dilatometer with alumina rams and boats (model DIL402C, Netzsch Instruments, Germany). The crystal structure of the sintered sample was investigated using X-ray powder diffraction (model M18XHF, Macscience Instruments, Japan) in the 2θ range from 20 to 60°. The polished and thermal etched surfaces of sintered specimens were examined using field emission scanning electron microscopy (FESEM: model JSM-6330F, JEOL, Japan). The microwave dielectric properties of the sintered samples were measured using a network analyzer (model HP8720C, Hewlett Packard, USA) in a frequency range of 8–10 GHz. The quality factor ($Q \times f$) was measured through the transmission cavity method using a Cu cavity and Teflon supporter [7]. The relative dielectric constant (k) was measured using the post resonator method [8] and the temperature coefficient of the resonant frequency (T_f) was measured using a Invar cavity in a temperature range of 10–80 °C [9].

3. Results and discussion

3.1. Densification

Fig. 1 shows the shrinkage behaviour of the as-pressed specimens with varying LBS glass as a function of rising temperature. Also, the behaviour of as-pressed LBS glass frit itself is included in Fig. 1 as a reference. The LBS glass shows a higher rate of shrinkage from about 230 °C, i.e., the glass transition temperature of LBS glass. As the temperature increases to about 500 °C, another high-shrinkage-rate region (500–540 °C) appears, which results from the devitrification of the LBS glass. As seen in Fig. 2,[1] the LBS glass is crystallized into the $Li_2B_4O_7$ compound from approximately 500 °C, which may increase the density of the specimen, yielding enhanced shrinkage from approximately 500 °C as shown in Fig. 1. From about 720 °C, the LBS specimen shows excessive shrinkage, due to the initiation of the melting of the $Li_2B_4O_7$ crystals, which melt completely at about 840 °C as seen in the figure.

According to Fig. 1, a good densification of $0.9MgTiO_3$–$0.1CaTiO_3$ ceramic requires a firing temperature above approximately 1300 °C. The increased addition of LBS glass decreases the densification temperature due to the role of the low-melting compound $Li_2B_4O_7$. This decrease demonstrates the capability of the new LBS glass composition as a liquid phase sintering agent for $MgTiO_3$–$CaTiO_3$ based ceramics. As the addition of LBS glass increases to as high as 20 wt.% (Fig. 1), the shrinkage behaviour of the specimen roughly shows the trend of LBS itself at temperatures below approximately 650 °C. However, in the 650–700° C range, additional shrinkage occurs in the 20 wt.% LBS-added specimen, possibly due to the decomposition of $MgTiO_3$ which will be discussed in the next section.

The measured apparent densities of sintered specimens with varying amounts of LBS glass are shown in Table 1.[2] Although the increase in firing temperature certainly increases the density, in the cases of specimens with relatively large amounts of glass, e.g., 10 and 20 wt.%, firing at overly high temperatures (e.g., 1050 °C for the 10 wt.%

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[1] The samples in Fig. 2 were air quenched as the temperature reached the target point.

[2] Relative density is hard to determine due to the complicated material reactions described in the next section.

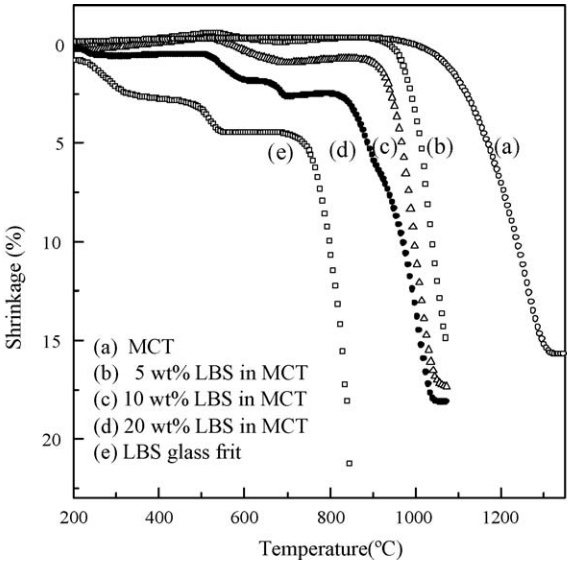


Fig. 1. Shrinkage behaviour of $0.9MgTiO_3$–$0.1CaTiO_3$ ceramic with varying amounts of LBS glass.

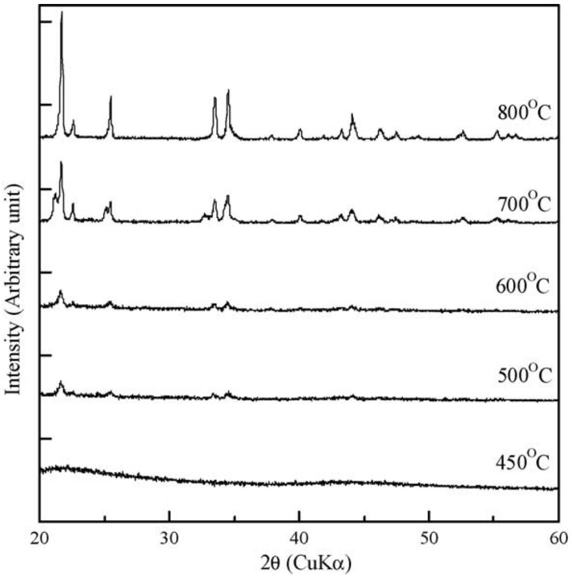


Fig. 2. XRD patterns from lithium borosilicate glass itself heat-treated at varying temperatures. All the peaks are from $Li_2B_4O_7$.

Table 1
Densities of specimens with varying amounts of LBS sintered at different temperatures (g/cm^3)

LBS addition (wt.%)	900 °C	950 °C	1000 °C	1050 °C
5	2.163	2.646	3.436	3.679
10	2.225	3.383	3.552	3.487
20	2.528	3.304	3.259	3.154

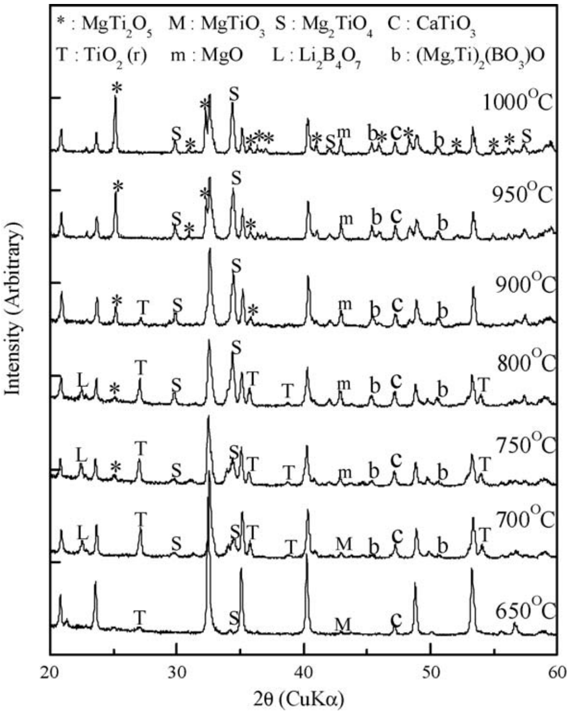


Fig. 3. XRD patterns from 0.9MgTiO$_3$–0.1CaTiO$_3$ ceramic sintered with 20 wt.% LBS glass at varying temperatures. The unmarked peaks are from MgTiO$_3$.

specimen and 1000–1050 °C for the 20 wt.% specimen) slightly lowers the density. This decrease probably occurs because the volatization of light species in the glass, such as lithium and boron oxides, increase porosity.

3.2. Decomposition of MgTiO$_3$

In order to investigate the material reactions during the elevation of temperatures, the 20 wt.% LBS glass-added specimens were removed from the furnace during heating (5 °C/min) at varying temperatures for XRD analysis; the results are shown in Fig. 3. As can be seen in the figure, the decrease in the peak intensity of MgTiO$_3$ (unmarked in Fig. 3) is apparent with the formation of various secondary phases such as MgTi$_2$O$_5$ (marked as *), Mg$_2$TiO$_4$ (marked as S), MgO (marked as m), and TiO$_2$ (marked as T). Of the secondary phases, the growth of MgTi$_2$O$_5$ and Mg$_2$TiO$_4$ with the temperature is very significant. Since the decrease in the XRD peak intensity of MgTiO$_3$ (unmarked) and the increase in Mg$_2$TiO$_4$ (marked as S) take place simultaneously, MgTiO$_3$ is interpreted as decomposing into Mg$_2$TiO$_4$ via the material reaction,

$$2\mathrm{MgTiO_3} = \mathrm{Mg_2TiO_4} + \mathrm{TiO_2} \tag{1}$$

In relation to the reaction (1), it is interesting to note that the peak intensity of TiO$_2$ (denoted as T) increases up to 700 °C, while it diminishes at temperatures above 700 °C. However, that of Mg$_2$TiO$_4$ (denoted as S) monotonically increases, as aforementioned. From this phenomenon, TiO$_2$ is interpreted as dissolving into the LBS glass as the temperature increases to above approximately 700 °C.

As for the formation of MgTi$_2$O$_5$ (marked as *), it also forms by another decomposition reaction,

$$2\mathrm{MgTiO_3} = \mathrm{MgTi_2O_5} + \mathrm{MgO} \tag{2}$$

Once MgTi$_2$O$_5$ (marked as *) and MgO (marked as m) appear at approximately 750 °C in Fig. 3, the peak intensity of MgTi$_2$O$_5$ grows continually with temperature. However, that of MgO does not increase correspondingly, especially

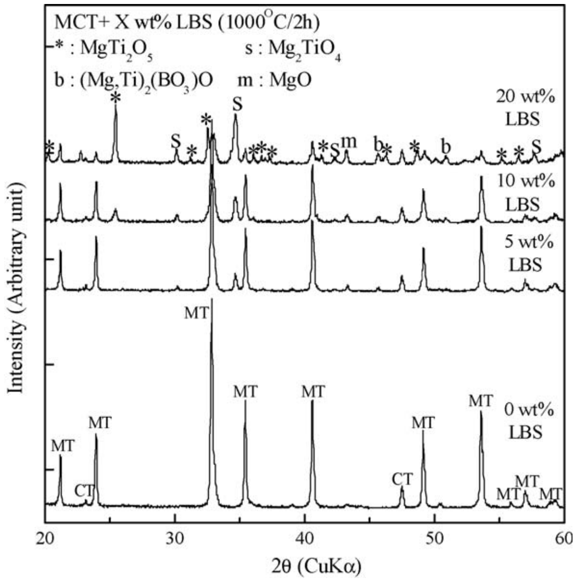


Fig. 4. XRD patterns from reference $0.9MgTiO_3$–$0.1CaTiO_3$ ceramic (sintered at 1300 °C for 2 h) and $0.9MgTiO_3$–$0.1CaTiO_3$ ceramic sintered with 5, 10, and 20 wt.% LBS glass at 1000 °C for 2 h. MT ($MgTiO_3$) and CT ($CaTiO_3$) symbols are intentionally unmarked in the upper patterns for clarity.

at above 850 °C. From such a limited increase in the peak intensity of MgO, it is also believed to have partially dissolved into the LBS glass.

In addition to the investigation of the effect of temperature on the material reaction as discussed above, the degree of material reaction is shown in Fig. 4 as a function of glass addition at 1000 °C. For such purpose, the samples were held for 2 h at 1000 °C to allow sufficient reaction time. Included in Fig. 4 is the LBS glass-free MCT ceramic, separately densified at 1300 °C for 2 h as a reference. Similar to the effect of temperature (Fig. 3), the increased addition of LBS glass is shown to facilitate the decomposition reactions (1) and (2): the peak intensity of $MgTiO_3$ decreases but those of $MgTi_2O_5$ and Mg_2TiO_4 increase with the addition of LBS glass.

However, as apparent in Fig. 4, such decompositions are not observed in the glass-free MCT ceramic composition fired at 1300 °C. In order to check the thermodynamic feasibility of the decomposition of $MgTiO_3$ itself, Gibbs free energy change of the reactions (1) and (2) are plotted as a function of reaction temperature in Fig. 5, using thermodynamic data shown in Barin [10]. In Fig. 5, the Gibbs free energy change of both reactions are positive in the range of densification temperature: the decompositions of $MgTiO_3$ itself are thermodynamically unfavourable, as consistent with the XRD peak intensity of the MCT reference shown in Fig. 4.

However, the decomposition reactions actually took place under the presence of the LBS glass. The Gibbs free energy change (roughly in the range of 16–24 kJ/mol in Fig. 4) for the two reactions is only slightly positive considering the fact that the Gibbs free energy of formation (ΔG_f) for the compounds involved in the reactions is highly negative: from 626.85 to 1126.85 °C, ΔG_f for $MgTiO_3$, $MgTi_2O_5$, Mg_2TiO_4, MgO, and TiO_2, are −1308.779 to −1158.464, −2089.79 to −1855.102, −1815.309 to −1610.318, −504.255 to −442.919, and −780.233 to −691.634 kJ/mol, respectively [10]. Thus, the appropriate lowering of the activity of the reaction product would render the Gibbs free energy change for the overall reaction to be negative, in light of the following thermodynamic relations for reaction Eqs. (1) and (2),

$$\Delta G = \Delta G^\circ + RT\ln\frac{a_{Mg_2TiO_4}\,a_{TiO_2}}{a_{MgTiO_3}} = \Delta G^\circ + RT\ln a_{TiO_2} \tag{3}$$

$$\Delta G = \Delta G^\circ + RT\ln\frac{a_{MgTi_2O_5}\,a_{MgO}}{a_{MgTiO_3}} = \Delta G^\circ + RT\ln a_{MgO} \tag{4}$$

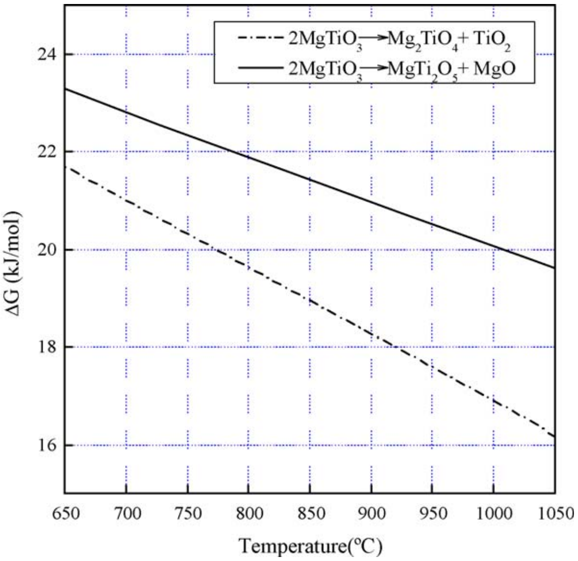


Fig. 5. Gibbs free energy change for the decomposition reactions as a function of reaction temperature.

where G is Gibbs free energy, a is activity, T is temperature, R is gas constant, and superscript ° denotes standard state. In Eqs. (3) and (4), the activity of $MgTiO_3$, $MgTi_2O_5$, and Mg_2TiO_4 was assumed to be in unity as they are pure condensed phases present in the reaction system. However, the activity (effective mole fraction) of TiO_2 and MgO acts as a variable as these oxides are observed to disappear (dissolve into the LBS glass). Thus, the issue is then how much the activities of MgO and TiO_2 have to be lowered in order to render the Gibbs free energy change of the decomposition reactions to be negative. The required critical activities to favour the decomposition reactions are plotted in Fig. 6. As seen in Fig. 6, if the activities of MgO and TiO_2 are lowered to 0.049–0.168 and 0.060–0.230, respectively, within the temperature range 650–1050 °C, the decomposition reactions are thermodynamically favourable. LBS glass in this work is interpreted to take MgO and TiO_2 away from the reaction site (by admitting them into the glass network), and thereby may lower the activities (effective mole fractions) of MgO and TiO_2 from unity to such values as shown in Fig. 6. Thus, without the role of LBS glass to admit MgO and TiO_2 into the glass network, the decomposition reactions (1) and (2) would be unfavourable.

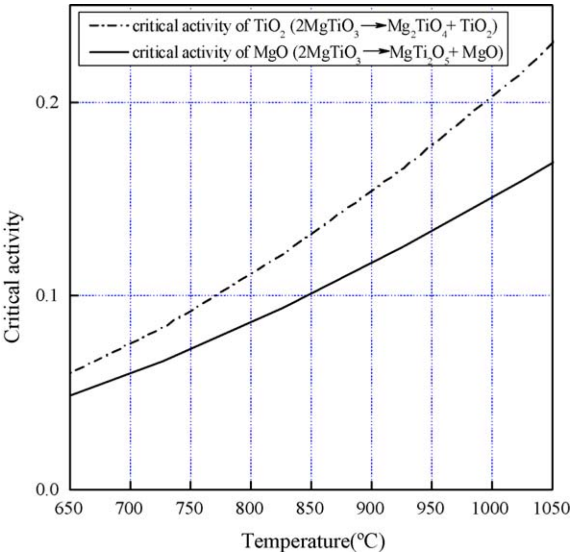
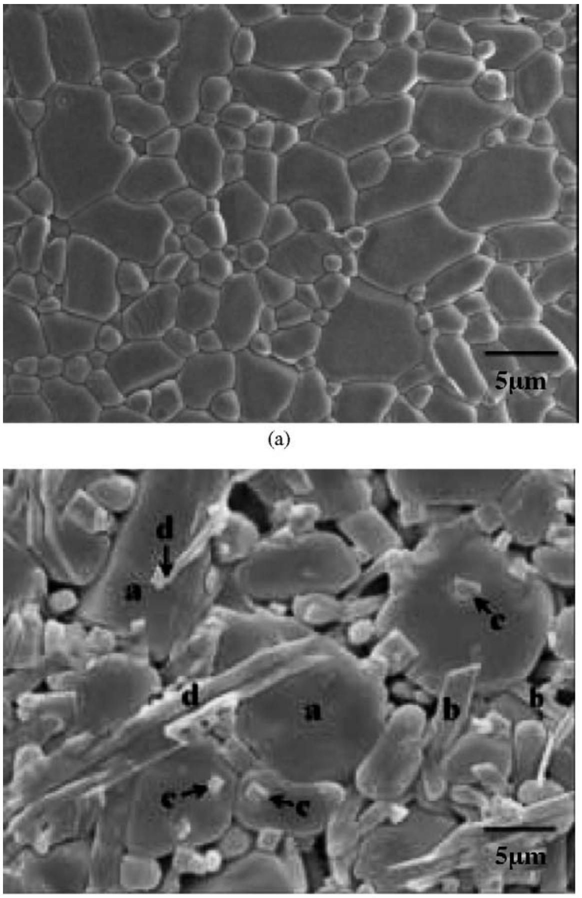


Fig. 6. Change in critical activity of MgO and TiO_2 required to favour the decomposition reactions as a function of reaction temperature.



(a)

(b)

Fig. 7. SEM micrograph of (a) $0.9MgTiO_3$–$0.1CaTiO_3$ reference ceramic (sintered at 1300 °C for 2 h) and (b) 20 wt.% LBS glass-added $0.9MgTiO_3$–$0.1CaTiO_3$ ceramic (sintered at 1000 °C for 2 h).

3.3. Microstructure and dielectric properties

Fig. 7(a) shows the thermally etched microstructure of the MCT reference ceramic fired at 1300 °C for 2 h. The relatively large grains are $MgTiO_3$ while the relatively smaller ones are either $MgTiO_3$ or $CaTiO_3$, based on energy dispersive spectroscopy (EDS) analysis (not shown). The thermally etched microstructure of the 20 wt.% LBS glass-added MCT ceramic fired at 1000 °C for 2 h is shown in Fig. 7(b). The large grains (larger than the undecomposed $MgTiO_3$ in Fig. 7(a)) marked as ‘a’ are $MgTi_2O_5$; and the small grains marked as ‘b’ are Mg_2TiO_4, based on the EDS results shown in Fig. 8. Consistent with the XRD results in Fig. 4(a), the $MgTi_2O_5$ and Mg_2TiO_4 grains take the majority of the volume in the specimen. The small grains having right-angled corners (marked as ‘c’) are shown to be $CaTiO_3$ (Fig. 8). Such grains are often embedded in the larger grains, e.g., $MgTi_2O_5$, which might have occurred during the significant growth of the $MgTi_2O_5$ grains. The needle-like area (marked as ‘d’) is rich in Mg, Ti, and Si, indicating that it is the LBS glass area.[3] Although it was difficult to identify individual undecomposed $MgTiO_3$ grains via EDS during the SEM observation, these grains are believed to take the shape of grains similar to small ones such as Mg_2TiO_4 (marked as ‘b’). In summary of the microstructural observation, decomposition products $MgTi_2O_5$ (large grains) and Mg_2TiO_4 (smaller ones) are major grains while the decomposition of $CaTiO_3$ is negligible, as consistent with the XRD results.

The sintered specimen, possessing decomposed $MgTi_2O_5$ and Mg_2TiO_4 grains with major crystalline phases, showed good dielectric properties: the 10 wt.% LBS glass-added sample fired at 950 °C for 2 h showed a permittivity

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[3] The needle shape may result from the thermal etching during the sample preparation for the SEM.

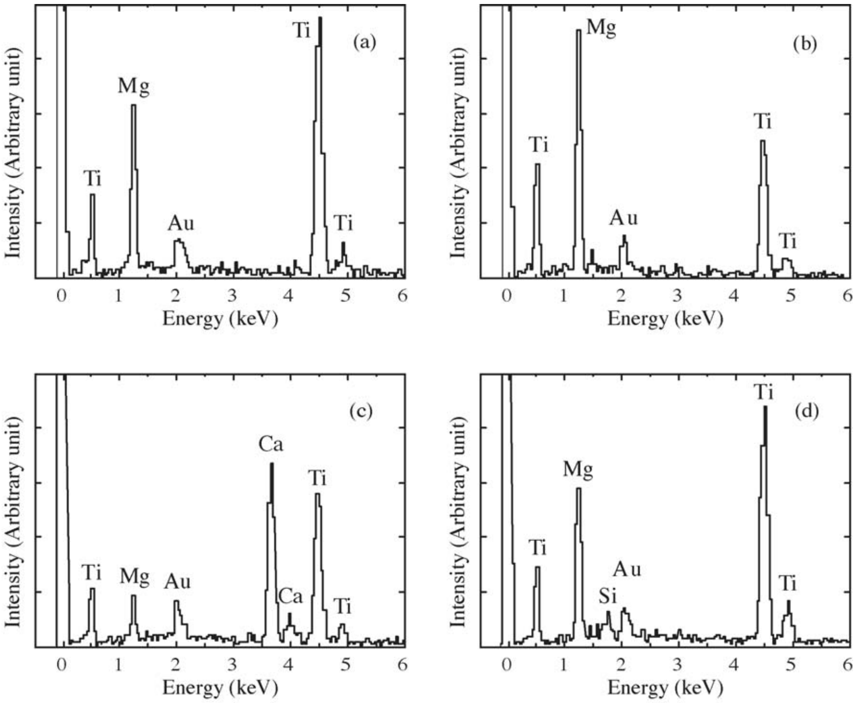

Fig. 8. EDS results from the areas marked in Fig. 7(b): marked as 'a' (a), 'b' (b), 'c' (c), and 'd' (d).

of 19.1, and a quality factor of 13,000 GHz, and a T_f of −1.3 ppm/°C. In order to investigate the role of the decomposed products, $MgTi_2O_5$ and Mg_2TiO_4, on the dielectric properties of the overall specimen, pure $MgTi_2O_5$ and Mg_2TiO_4 phases were prepared separately at 1500 °C for 2 h and 1300 °C for 2 h, respectively (Fig. 9). Although the major phases are $MgTi_2O_5$ and Mg_2TiO_4 (the permittivities are 17.4 and 14.4, respectively), there exists a very high permittivity phase $CaTiO_3$ (170) in the densified specimen (Figs. 3, 4, and 7); thus, the permittivity can be higher than 17.4. The quality factors of $MgTi_2O_5$ (47,000 GHz) and Mg_2TiO_4 (55,000 GHz) were superior to that of $0.9MgTiO_3$–

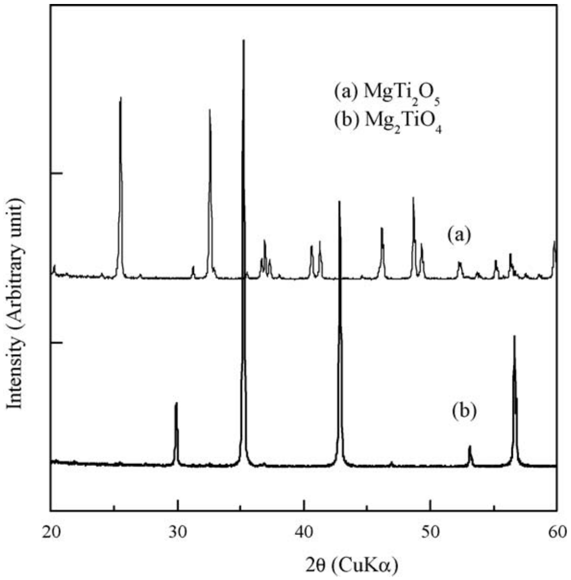

Fig. 9. XRD patterns from $MgTi_2O_5$ and Mg_2TiO_4 prepared at 1500 °C for 2 h and 1300 °C for 2 h.

$0.1CaTiO_3$ (MCT: 44,000 GHz), explaining the high quality factor (13,000 GHz) of the sintered specimen with the LBS glass. Hence, the decomposition reaction is not necessarily harmful because of the high dielectric performance of the decomposition products $MgTi_2O_5$ and Mg_2TiO_4.

4. Conclusions

The decomposition behaviour of $MgTiO_3$ based dielectric ceramic during a liquid phase sintering with lithium borosilicate glass has been investigated. The presence of the LBS glass results in the decomposition of $MgTiO_3$ via the reactions, $2MgTiO_3 = Mg_2TiO_4 + TiO_2$ and $2MgTiO_3 = MgTi_2O_5 + MgO$, although they are thermodynamically unfavourable in glass-free ceramic compositions. Through XRD results and thermodynamic analysis, the role of the LBS glass is revealed as adopting TiO_2 and MgO into the LBS glass network, thereby lowering the activity of TiO_2 and MgO, which, in turn, favours the decomposition reactions. The final microstructure of the MCT dielectric ceramic, after densification and decomposition reactions, revealed $MgTi_2O_4$ and Mg_2TiO_5 as major grains, which is consistent with the XRD results. The decomposition reactions were not necessarily harmful because of the high dielectric performance of the decomposition products, $MgTi_2O_5$ (17.4 permittivity; 47,000 GHz quality factor) and Mg_2TiO_4 (14.4 and 55,000 GHz, respectively).

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