

## Process and property characterization of La-Al-B-O/ $\text{Al}_2\text{O}_3$ glass ceramic composites

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A LAB glass with a composition of 10 mol%  $\text{La}_2\text{O}_3$  + 10 mol%  $\text{Al}_2\text{O}_3$  + 80%  $\text{B}_2\text{O}_3$  made into a composite with 30-50%  $\text{Al}_2\text{O}_3$  filler was prepared and investigated. Processing optimization and several engineering properties used for microwave substrates are reported, including densification, interaction with Ag electrodes, dielectric properties as a function of frequency, acid dissolution and microstructure. The glass ceramic composite, i.e. L30A, without lead and alkali, can be densified by two-step sintering to a density better than 99% with minimal glass residue. The densified composite does not react with Ag up to 950 °C in 1 h, and does not dissolve in an acid solution (pH=3.5) in 2 h. The dielectric constant and loss are in the range of 5.6-5.9 and  $1.4 \times 10^{-3}$ - $5.5 \times 10^{-3}$ , respectively. The coefficient of thermal expansion (CTE) and thermal conductivity of the composite are reported.

**Key words:** LAB, glass-ceramics, composite, microwave, dielectric, acid dissolution, CTE, thermal conductivity.

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### Introduction

Several low firing-temperature (< 1000 °C), lead-free glass-ceramic materials [1-13] have been studied for co-firing electronic applications. There are several critical issues relating to the applications of glass-ceramic substrates, as discussed in the literature [12, 13]. The primary issue is to consider the interaction between the glass-ceramic and an electrode, e.g. Ag, during sintering, as applying to low-temperature cofired ceramic (LTCC) laminated layers. The second issue is the value and variation of the density and microwave properties, such as the dielectric constant ( $k$ ), dielectric loss ( $\tan \delta$ ). When a glass is partially transformed into crystal phases, not only complete densification should be attained, but also suitable crystallization must be achieved after heat-treatment for a LTCC application. Otherwise, any glass-ceramic materials containing porosity or with a low degree of crystalline phases would result in relatively poor dielectric properties. However, the addition of a glass phase could greatly lower the sintering temperature of a ceramic filler, and benefit the densification of composite matrix. The last consideration relates to the evaporation of a low melting constituent, e.g.  $\text{B}_2\text{O}_3$ , during sintering, and dissolution of alkaline-based glass in aqueous solution.

Our previous studies [13, 14] have reported one La-Al-B-O (LAB) glass ceramic system. The processing

window of the LAB glasses was determined after having been melted at 1350 °C for 1 h in air. [13] Thermal analysis, wetting measurement showed that the initial shrinkage temperature of the LAB glasses could be as low as around 700 °C. [14] One glass composition (L2 glass) with a composition of  $\text{La}_2\text{O}_3$  10 mol%,  $\text{Al}_2\text{O}_3$  10 mol%,  $\text{B}_2\text{O}_3$  80 mol% showed the most suitable sintering and wetting behavior on an  $\text{Al}_2\text{O}_3$  surface. Therefore, it was chosen as the glass precursor in this study. Afterwards, two crystal phases, including equi-axed grains ( $\text{LaBO}_3$ ) and flaky crystals ( $\text{LaAl}_2\text{B}_3\text{O}_9$ ) were identified as being formed at temperatures between 750 °C to 950 °C. It was also reported that the compositions of the LAB glasses (L1-L5) showed little deviation, ca.  $\leq 3\%$  of  $\text{B}_2\text{O}_3$ , from the batched compositions. The reduction of  $\text{B}_2\text{O}_3$  was due to the evaporation during high-temperature (1350 °C) melting.

As a consequence, the objectives of the present work were set to clarify the properties for applications as a microwave substrate. We tended to rule out the uncertainty of Ag migration and its influence on the LAB- $\text{Al}_2\text{O}_3$  glass-ceramic (LAB-A) composites. Also, the dielectric constants at MHz ranges reduced with the formation of crystalline phases ( $\text{LaBO}_3$  and  $\text{LaAl}_2\text{B}_3\text{O}_9$ ). The reduction of the dielectric loss and dielectric constant would benefit applications at the higher frequency range. Finally, the dissolution of LAB glass and LAB/ $\text{Al}_2\text{O}_3$  glass-ceramic composite in acid solution was tested for the assurance of room temperature processing in contact with any acidic chemicals.

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## Experimental

### Materials and Preparation steps

L2 glass powder, prepared as in the previous report, [14] was mixed with various mass% of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> filler (A32, 99.5% pure,  $\alpha$ -phase, average size 1.04  $\mu$ m, Sumitomo Chemical Corp., Tokyo, Japan). The preparation of LAB/Al<sub>2</sub>O<sub>3</sub> green tape was started by a colloidal processing, followed by tape casting and drying. methyl ethyl ketone (MEK) and ethanol in azeotropic composition were used as a solvent mixture. The solid consisting of the slurry was controlled at 40 vol%. The mixture “L30A” means a L2 glass mixed with 30 mass% of Al<sub>2</sub>O<sub>3</sub> fillers.

One Ag paste (DuPont 6145, conductive paste, USA) was used and the microstructure is shown in Fig. 1. The viscosity of the paste was between 120-200 Pa·s, and the paste contained a few percent of glass particles.

The LAB glass, L30A bulk and L30A tape specimens with a thick Ag layer were binder-burn-out first, then sintered at various temperatures (750-1000 °C) for different holding periods. The heating rate was set in 5 °C/min or 10 °C/min, sintering in air and cooling in the furnace.

### Characterization

#### – Microstructural observation

The composite samples were mounted, cut, ground and polished along the interface Ag/glass ceramics. The samples were then coated with a thin layer of Au or carbon to improve electrical conductivity for microscopical observation. The morphologies of polished samples were analyzed by scanning electron microscopy (SEM, Philips XL30, Philips Co., USA) equipped with an X-ray energy dispersive spectroscopy (EDS,

DX-4, EDAX Co., USA) and field-emission SEM (Leo Instrument 1530, England).

#### – Thermal Analysis

The sintering behavior was measured by using a thermal mechanical analyzer (TMA, SETSYS TMA 16/18, SETRAM. Co., France).

#### – X-ray Diffraction Analysis

The phase identification of calcined glass samples and tapes was investigated by an X-ray diffractometer (Philips PW1830, Philips Instrument, Netherlands, XRD) using Cu K $\alpha$  radiation. The scan speed was 3°/min and each step was 0.04°.

#### – Measurement of Dielectric Properties

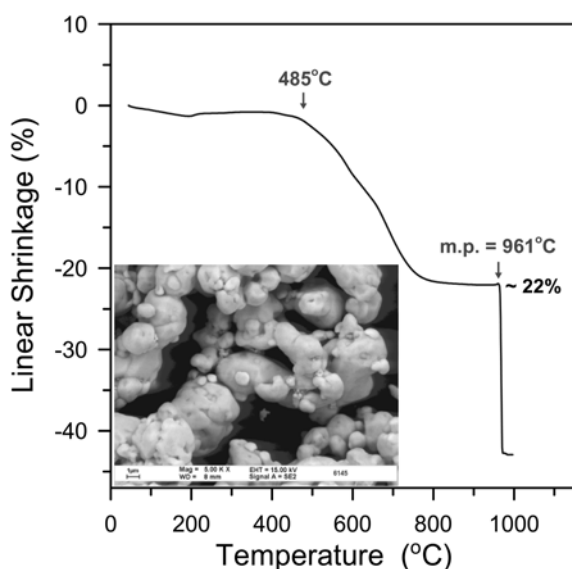
A RF impedance analyzer (HP-4291B RF impedance/material analyzer, Agilent, USA) was used to measure the dielectric characteristics of various specimens. Cylindrical rod sample with a thickness of 3.0 mm and a diameter of 10.0 mm was prepared for the measurements. The dielectric properties, including dielectric constant ( $\epsilon$ ) and dielectric loss ( $\tan \delta$ ) were measured at three frequency ranges, including 10 MHz, 100 MHz, and 1 GHz.

#### – Coefficient of Thermal Conductivity (CTE) and Thermal Conductivity

Bulk samples of the composition L30A, which had been prepared were sintered at 800 °C/1 h to 850 °C/10 min in air for the test of CTE. The CTE was measured between 25 °C-500 °C using a dilatometer (Model TA 2490, Netzsch Instruments, Paoli, PA). An instrument (Hot Disk AB, Bridge system, Sweden) was used to measure the thermal conductivity of the sintered samples. Cylindrical rod sample with a thickness of 5.0 mm and a diameter of 2.0 cm was placed between two parallel metal probes of Cu.

#### – Dissolving Test

This dissolution test of B<sub>2</sub>O<sub>3</sub> content from the sintered L2 glass and L30A samples (sintered at 800 °C/1 h and 850 °C/10 min) was conducted in de-ionized water and acid solution. The chip-like samples with a mass around 500 mg were immersed in 10 g de-ionized water (pH ~6.4), and aged for 24 h to 72 h at room temperature. After aging, the testing samples were dried for 4 h and measured for mass loss. The other test replaced the water bath by an acidic solution, which was diluted from an HCl solution (99%, EP grade, Showa Chemical Co., Japan) with de-ionized water to a concentration of 0.1 M and showed a pH value of ca. 3.5. The pH value of the solutions was measured by a pH-meter (MODEL SP-7, SENTEX, Taiwan).

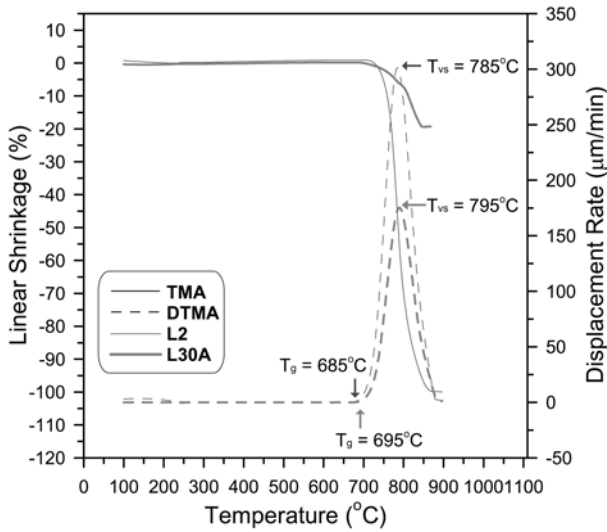


**Fig. 1.** Dilatometric sintering curves of the binder-burn-out Ag powder heat treated to 1000 °C and holding for 10 min in air. Inserted SEM image reveals the particle morphologies.

## Results and Discussion

### Optimal Densification

Previous data [14] showed that the amount of glass present in a LAB system was the primary control factor for the densification of LAB-A glass ceramics. A high



**Fig. 2.** TMA and DTMA curves of L2 glass and L30A glass-ceramic composite tested at a heating rate of 10°C/min. The sample was sintered under a 0.98 kPa compressive stress.

sintered density, > 98%, could be achieved for the formulation with 70 mass% L2 glass by sintering at 850 °C for 1 h. However, the microstructural characterization revealed that a small amount (~2%) of porosity was still retained in the matrix. Therefore, in order to reach better densification, the sintering of the L30A glass-ceramic composite needs to be optimized by modifying the sintering schedule.

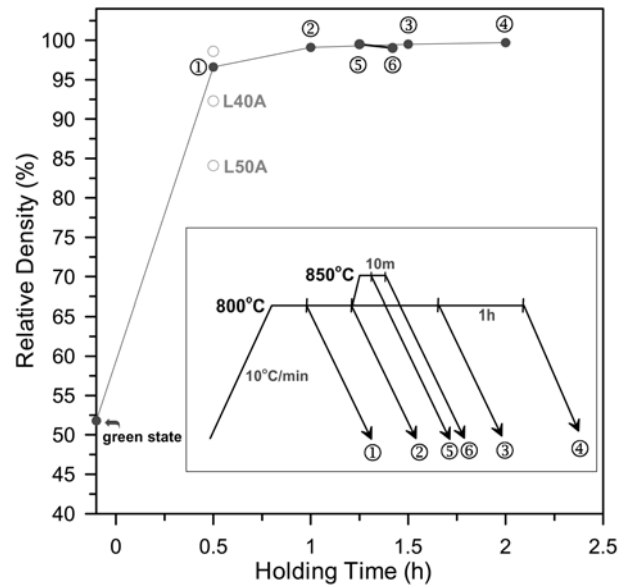
A detailed investigation by TMA for understanding the behavior of glass viscous flow has been conducted and the data are shown in Fig. 2. It is possible to sinter the glass composites without the growth of the crystalline phase within the temperature range between  $T_o$  (starting temperature of crystal growth) and  $T_g$  (glass transition temperature). It was noted the temperature difference ( $\Delta T$ ) was 100 °C for L2 glass and L30A composite. In addition, the onset temperature (685 °C) of  $T_g$  of a viscous L2 glass was close to that (695 °C) of the L30A. The  $T_g$  of L30A shifted about 10 °C to a higher temperature due to the  $Al_2O_3$  filler addition. The maximum sintering rate of the glass and the composites took place at the temperature ( $T_{vs}$ ) of 785 °C and 795 °C, respectively. Consequently, the optimal viscous sintering of L30A could be chosen at 800 °C.

The relative densities of the L30A composites from different heat-treatments are shown in Table 1 and Fig. 3. The bulk density data revealed that the L30A showed the best sinterability among these series. In comparison, the density was improved to 98.6% as sintering at 800 °C; namely, nearly no porosity was observed for the heat-treatment at 800 °C for 4 h.

As a consideration of devitrification of a dense matrix, the heat-treatment at 850 °C for 10 min, i.e. the condition “5” shown in Fig. 3, is the optimum schedule for L30A which is able to achieve 99.5% relative density. In addition, a longer heat-treatment at

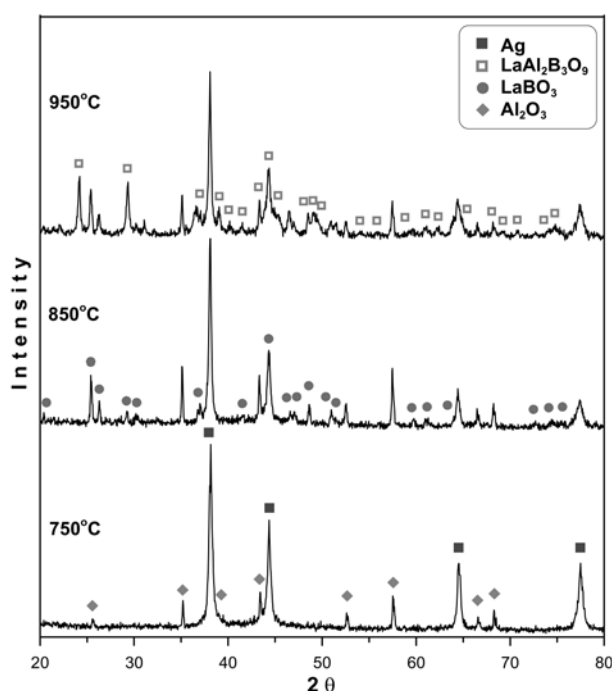
**Table 1.** Sintered and dielectric properties of various LAB/ $Al_2O_3$  and pure L2 glass samples tested at different frequency ranges

Specimen	Heat-Treatments	Bulk density (g/cm <sup>3</sup> )	k	$\tan \delta$ ( $1/Q$ , $\times 10^{-3}$ )	Testing frequency (MHz)
L2 Glass	—	3.45	6.78	10.3	10
			6.79	21.6	100
			6.69	26.1	1000
L30A	800 °C/1h	3.54 (98.6%)	6.08	3.8	10
			6.01	3.6	100
			5.83	5.9	1000
L40A	800 °C/1h	3.15 (86.3%)	5.51	6.7	10
			5.44	6.8	100
			5.06	9.4	1000
L50A	800 °C/1h	2.91 (78.6%)	4.09	11.8	10
			4.01	10.2	100
			3.53	16.2	1000
L30A	800 °C/1h-850 °C/10 min	3.56 (99.4%)	5.91	1.4	10
			5.82	3.2	100
			5.61	5.5	1000
L40A	800 °C/1h-850 °C/10 min	3.39 (92.8%)	5.03	4.5	10
			4.99	4.0	100
			4.78	8.8	1000
L50A	800 °C/1h-850 °C/10 min	3.04 (82.2%)	3.85	8.6	10
			3.94	9.8	100
			3.61	14.3	1000



**Fig. 3.** Relative density with respect to the holding time by different heat-treatments of LAB glass with 30 mass%  $Al_2O_3$  filler (L30A). Two comparable cases (L40A and L50A) are included. The sintering density (marked in “O” open circles) of three composites were directly sintered at 850 °C for 30 min.

850 °C, i.e. the condition “6”, shows a density lower than the previous cases (“3”, “4”, or “5”). Longer holding time at 850 °C for the composites causes



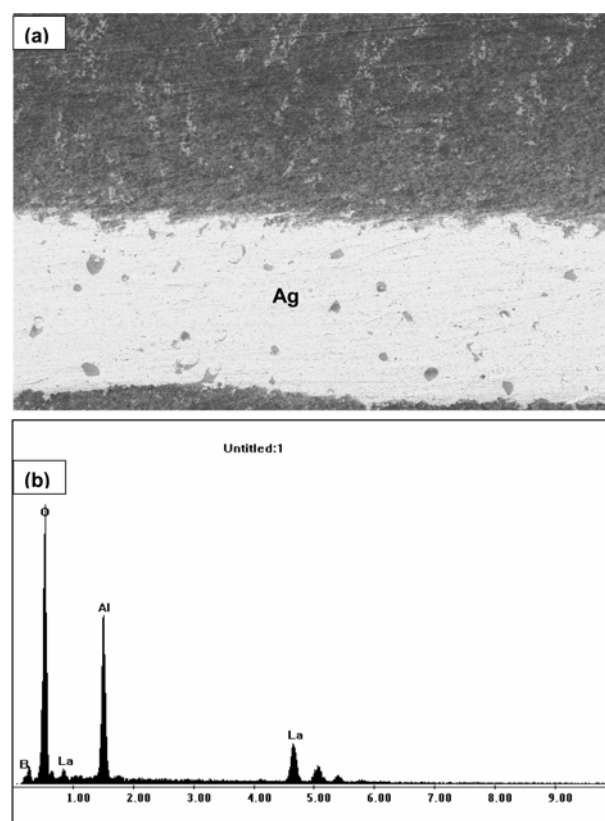
**Fig. 4.** XRD spectra of the L30A glass-ceramic composite (powder mixture) cofired with the Ag-paste at different temperatures for 1 h in air.

crystallization,<sup>\*1</sup> but impedes the densification. The heat-treatment “5” (800 °C/1 h-850 °C/10 min) with a crystallization for 10 min is sufficient and appropriate for the L30A glass-ceramic composite to reach full density and sufficient crystallization.

#### Cofiring of L30A and Ag Layer

The sintering behavior of a binder-burn-out (BBO) Ag powder was measured and shown in Fig. 1, which showed a starting point for sintering at about 485 °C, and had a linear shrinkage of about 22% on sintering to 800 °C. The inserted SEM image revealed the Ag powder after BBO step is pure Ag with a small amount of glass filler. The Ag powder had a bimodal size distribution.

In order to understand the reaction between L30A and Ag during sintering, the L30A/Ag powder mixture was heat-treated at 750 °C, 850 °C, and 950 °C, respectively, for 1 h. The XRD spectra (Fig. 4) showed that the L30A was in the original state at 750 °C, while an additional phase was identified to be the Ag (JCPD file, #04-0783). For the mixtures heated to 850 °C and 950 °C, except  $\text{LaBO}_3$  (850 °C) and  $\text{LaAl}_2\text{B}_3\text{O}_9$  (950 °C), no new compound was formed after the treatment. A cross-section of a laminate L30A-Ag composite is shown in Fig. 5(a). The microstructure appears with a Ag layer of about 20  $\mu\text{m}$ , and the interface between L30A (darker region) and Ag (the brightest layer).



**Fig. 5.** (a) SEM micrograph of L30A/Ag laminate layers and (b) EDS spectrum of the area 10  $\mu\text{m}$  next to the interface. The sample had been heat-treated at 850 °C for 30 min in air. The Ag layer had a thickness of ca. 20  $\mu\text{m}$ , and contained small amount of glass particles.

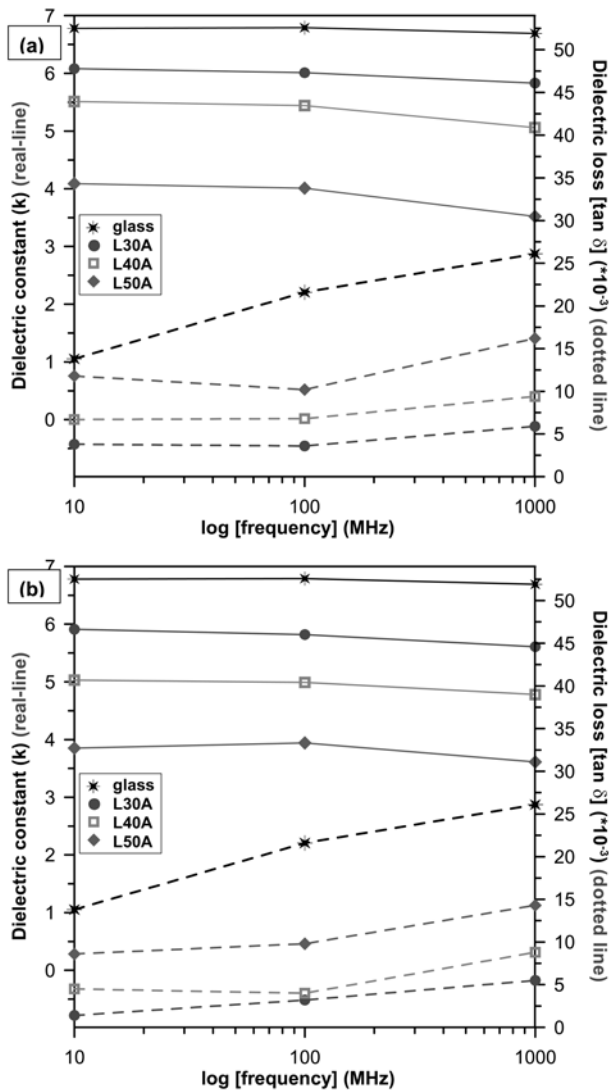
Also, the EDS spectrum [Fig. 5(b)] shows that no Ag peak intensity is detected about 10  $\mu\text{m}$  from the Ag layer. This implies that no Ag diffused into the L30A composite at 850 °C in 30 min.

#### Dielectric Properties of LAB/ $\text{Al}_2\text{O}_3$ Composite

Several die-pressed LAB/ $\text{Al}_2\text{O}_3$  cylinder specimens were sintered at 800 °C for 1 h, or 800 °C/1 h-850 °C/10 min in air. Table 1 and Fig. 6 list the results of the sintered density and dielectric properties of various L2/ $\text{Al}_2\text{O}_3$  (LAB-A) glass-ceramic composites. There was a tendency that the dielectric constant decreased slightly as the content of  $\text{Al}_2\text{O}_3$  filler increased, and the dielectric loss ( $\tan \delta$ ) increased as the content of  $\text{Al}_2\text{O}_3$  filler increased, as sintering at 800 °C for 1 h. Also, pure L2 glass as a reference was also tested, and showed a relatively high dielectric constant and loss.

$\text{LaBO}_3$  is the major phase which crystallizes at 850 °C. In order to compare the influence of  $\text{LaBO}_3$ , the above samples in a dense state were heat-treated at 850 °C for 10 min. The results are shown in Fig. 7. The tendency of  $\text{Al}_2\text{O}_3$  addition is similar to the results in Fig. 6. However, the dielectric loss obviously reduced to lower values after the crystallization of  $\text{LaBO}_3$  as the k value was similar. Considering the LAB-A samples,

<sup>1</sup>The details of crystallization kinetics are reported in our next article which has been submitted to J. Europ. Ceram. Soc.

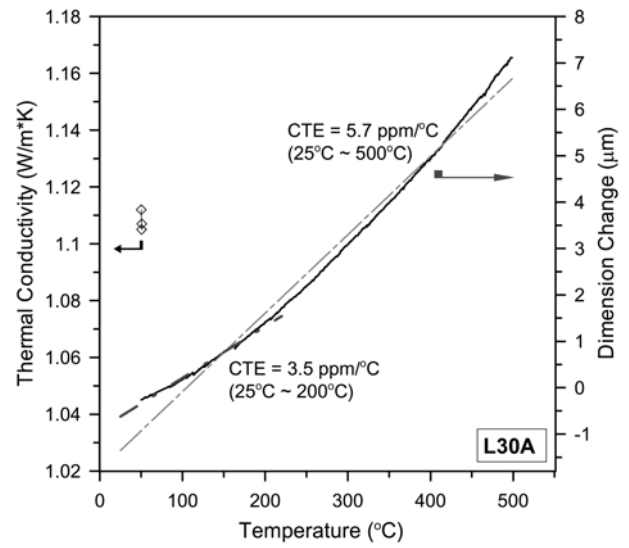


**Fig. 6.** Relationship between dielectric constant (solid line) and dielectric loss (dotted line) as a function of testing frequency of various LAB-A composites and L2 glass. The samples had been sintered at (a) 800 °C for 1 h. (b) 850 °C for 10 min in air.

the  $\tan \delta$  value increased as the content of  $\text{Al}_2\text{O}_3$  increased due to the residual porosity. Herein the disadvantages of  $\text{Al}_2\text{O}_3$  additions are noted, retarding densification and increasing the overall dielectric constant. The L30A glass-ceramic composite appears to have a lower dielectric constant (5.6-5.9) and  $\tan \delta$  value ( $1.4$  to  $5.5 \times 10^{-3}$ ) in the test range of 10-1000 MHz. The composite is applicable as a low  $k$  substrate for microwave applications.

#### CTE, Thermal Conductivity and Dissolving Test

The thermal conductivity and coefficient of thermal expansion (CTE) for the L30A glass-ceramic composite are shown in Fig. 7. The average thermal conductivity of the L30A composite by three testing measurements was 1.11 W/m<sup>2</sup>K. Besides, the L30A composite presented a CTE value of 5.7 ppm/K from 50 °C to 500 °C and 3.5 ppm/K from 25 °C to 200 °C,



**Fig. 7.** Thermal conductivity and dimensional change of the L30A glass-ceramic composite (800 °C for 1 h, 850 °C for 10 min in air) plotted against temperature.

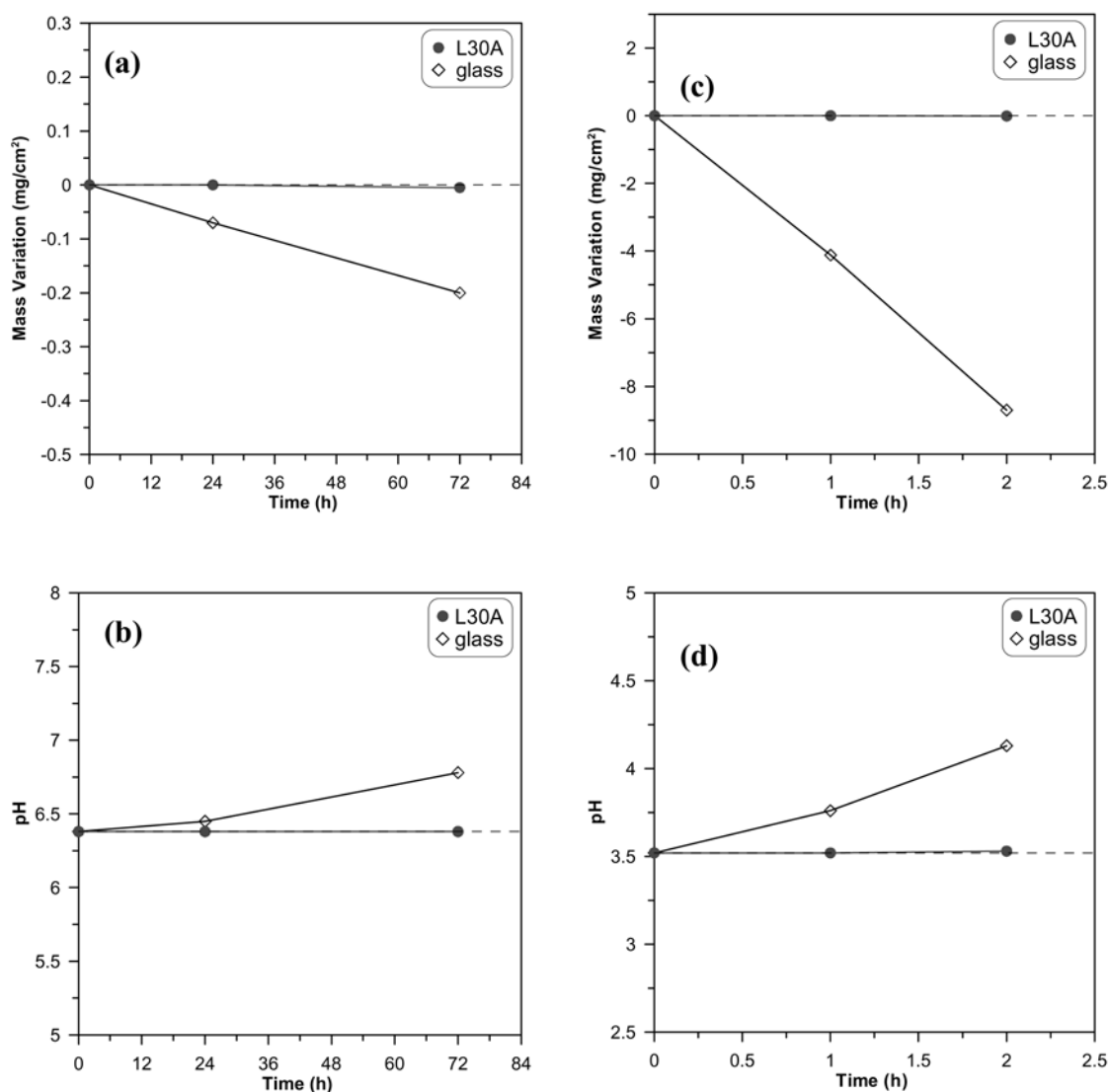
which is close to that of a Si chip (4 ppm/K). The mismatch between the L30A substrate and a Si chip is minimal. The values are acceptable and suitable for a substrate material used for microwave applications [3].

Figure 8 shows the dissolution results for sintered L2 glass and L30A composite. The samples showed distinct dissolution results, of which the L30A had no apparent mass loss and a very small pH variation in D.I. water and acid solution (pH = 3.5). However, the pH value changed from 3.5 to 4.2 [Fig. 8(c)] as the glass was tested in the acid solution. The mass loss of the L2 glass was nearly 9 mg/cm<sup>2</sup> on testing in an acidic condition, which was almost 45 times higher than the testing result in the neutral aqueous solution.

In a recent report by Gaillardet and Allegre [15], boron ions were said to exist in sea-water as a boric  $\text{B}(\text{OH})_3$  and the borate  $\text{B}(\text{OH})_4^-$  species. The relative proportion of two species is dependent on the pH of solution. The pH value in the solution increases because of the  $[\text{B}(\text{OH})_4^-]$ , which means the pH value of the test solution changes with the dissolution of borate glass. Besides, the L30A sample is dense and nearly completely crystallized. Very little glass left in the composite is very important for a resistance to aqueous and acidic solutions used in a dissolution test. For applications of the boron-containing formulation, e.g. L30A, the component has a reasonable resistance to a high humidity environment as well.

#### Conclusions

One LAB (10% $\text{La}_2\text{O}_3$ -10% $\text{Al}_2\text{O}_3$ - $\text{B}_2\text{O}_3$ ) glass (L2) made into a composite with  $\text{Al}_2\text{O}_3$  was densified by optimizing the sintering conditions so to reach densities better than 99% T.D., and gave excellent dielectric



**Fig. 8.** (a) and (c) Mass variation as a function of aging time for the L2 glass and L30A glass-ceramic composites; (b) and (d) pH variation of the solutions containing water or acid plotted against the aging time.

properties for microwave applications. The followings are asummary of the properties of the LAB glass and the composites.

The LAB-A composite was cofired with Ag to temperatures as high as 950 °C. No new compound could be found between the L30A and Ag layer. The interface also showed good bonding and dense features after cofiring.

The dielectric constant of the LAB/ $\text{Al}_2\text{O}_3$  glass-ceramic composite is in the range of 5.6 to 5.9, which decreases as the content of the  $\text{Al}_2\text{O}_3$  filler increases, due to the residual porosity. In addition, the CTE and thermal conductivity of the L30A composite showed 5.7 ppm/K between 25 °C to 500 °C and 1.1 W/m\*K, respectively. The L30A glass-ceramic composite showed acceptable acid resistance. However, the L2 glass showed an apparent dissolution in D.I. water and in the acid solution.

## Acknowledgements

The authors would like to thank Professor A. Roosen for valuable discussions, and the tape casting facility offered by Department of Materials Science, University of Erlangen-Nuremberg, Germany. The financial support by NSC 92-2911-I-002-011 in Taiwan is also appreciated.

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