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Microwave dielectric properties of low-temperature sintered $Li_3AlB_2O_6$ ceramic

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Abstract

The $Li_3AlB_2O_6$ ceramic were prepared by using the conventional solid-state reaction method; these pellets were sintered at the temperature range of 650–775 °C for 2 h in air. The X-ray powder diffraction pattern of the $Li_3AlB_2O_6$ ceramic sintered at 650 °C showed a single phase which corresponded to the triclinic phase with a space group of $P\bar{1}$; the crystallization of the ceramics was observed with increasing the sintering temperatures from 650 to 775 °C. The dielectric constant of the $Li_3AlB_2O_6$ ceramic increased slightly from 4.2 to 5.4 as the sintering temperatures were increased from 650 to 775 °C, whereas the $Q \times f$ value of the ceramic ranged from 12,460 to 20,448 GHz. The improvement in the $Q \times f$ value is substantially related to the crystallization of the $Li_3AlB_2O_6$ ceramic. The temperature coefficient of resonant frequency of the ceramic showed the large negative values, ranging from −290 to −201 ppm/°C. However, by the addition of 5 wt% TiB compound, the τ_f value of the $Li_3AlB_2O_6$ ceramic was improved ($\tau_f \fallingdotseq 10$ ppm/°C); a dielectric constant of 4.2 and $Q \times f$ value of 13,027 GHz were obtained at the sintering temperature of 675 °C.

Keywords: Powders-solid-state reaction; Dielectric property; X-ray methods; Glass ceramics

1. Introduction

In low temperature sintered microwave dielectric ceramics, much attention has been paid to fabricate the multilayer microwave devices as a low temperature co-fired ceramic (LTCC); in this case, the sintering temperature of the dielectric ceramics should be lower than the melting point of silver. In order to reduce the sintering temperature of the microwave dielectric ceramics, there are many attempts such as the addition of B_2O_3, Bi_2O_3, CuO, V_2O_5 and their composites as the sintering aids [1–5]. With the addition of a sintering aid, however, the microwave dielectric properties of low-temperature sintered ceramics lowered in comparison with those of the ceramics without the addition of the sintering aid because of the chemical reaction between these ceramics and sintering aid. Thus, there is considerable interest in the development of new materials with low sintering temperatures.

Recently, Chen and co-workers[6] reported the crystal structure of the $Li_3AlB_2O_6$ ceramic, which was produced at the sintering temperature of 650 °C. Therefore, the $Li_3AlB_2O_6$ ceramic is considered to be one of the attractive candidates for the LTCC material because of its low sintering temperature; the microwave dielectric properties of the $Li_3AlB_2O_6$ ceramic have not been reported to date. Thus, this paper focuses on the development of a new LTCC material; the microwave dielectric properties, crystal structure and microstructure of the $Li_3AlB_2O_6$ ceramic were investigated in this study.

2. Experimental method

The starting materials used in this study were $LiCO_3$, Al_2O_3 and HBO_3 powders with 99.9% purity; these powders were weighted on the basis of the stoichiometric proportion, and then mixed with acetone. A mixture of these powders was calcined at 600 °C for 20 h in air, ground with a polyvinyl alcohol and uniaxially pressed into the pellets with a pressure of 100 MPa. The differential thermal analysis (DTA) and

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thermogravimetry (TG) of the calcined powder were preformed in order to clarify the thermal stability of the $Li_3AlB_2O_6$ ceramic. Subsequently, the samples were sintered in the temperature range of 650–775 °C for 10 h in air; the apparent density was measured with the Archimedes method. The microwave dielectric properties of the samples were evaluated by the Hakki and Coleman method;[8,9] the temperature coefficient of resonant frequency was calculated from the resonant frequencies obtained at the two temperatures of 20 and 80 °C. The synthesized phases were identified by using the X-ray powder diffraction (XRPD) with the Cu Kα radiation in the 2θ range of 10–60°. The microstructure observation and the qualitative and quantitative analyses of elements in the grains were performed by using the field emission electron microscopy (FE-SEM) and energy dispersive X-ray analysis (EDX).

3. Results and discussion

Fig. 1 shows the DTA and TG curves of the $Li_3AlB_2O_6$ ceramic after calcining at 600 °C. In the temperature range of 25–1000 °C, the weight loss was not observed. An alternative, the DTA curve showed the endothermic peaks at the temperatures of around 800 and 850 °C as shown in Fig. 1. According to the thermodynamic approach reported by Chen and co-workers,[10] it is considered that the endothermic peak at 800 °C implies the decomposition of the $Li_3AlB_2O_6$ ceramic into the Li_2AlBO_4 and α-$LiBO_2$ ceramics. Moreover, it is known that the Li_2AlBO_4 ceramic decomposes into the β-$LiBO_2$ ceramic and a liquid phase at the temperature of around 850 °C; the endothermic reaction is observed at these temperatures. Therefore, from these results, it is considered that the $Li_3AlB_2O_6$ ceramic is stable below the sintering temperature of 800 °C.

The XRPD patterns of the $Li_3AlB_2O_6$ ceramic sintered at the various temperatures for 10 h in air are shown in Fig. 2. At the sintering temperatures below 800 °C, the single phase of the $Li_3AlB_2O_6$ ceramic which has a triclinic structure with the space group of $P\bar{1}$[7] was obtained. Moreover, with

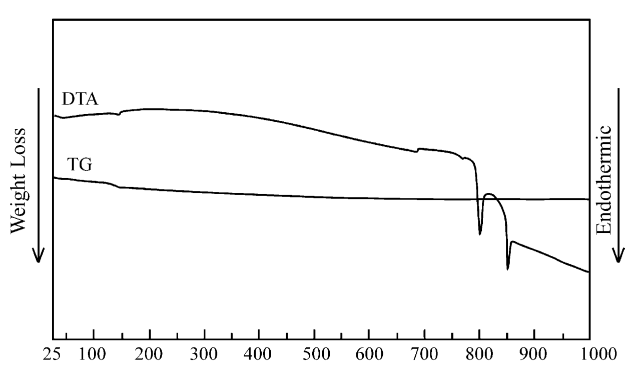

Fig. 1. DTA and TG curves of $Li_3AlB_2O_6$ ceramics after calcining at 600 °C for 20 h in air.

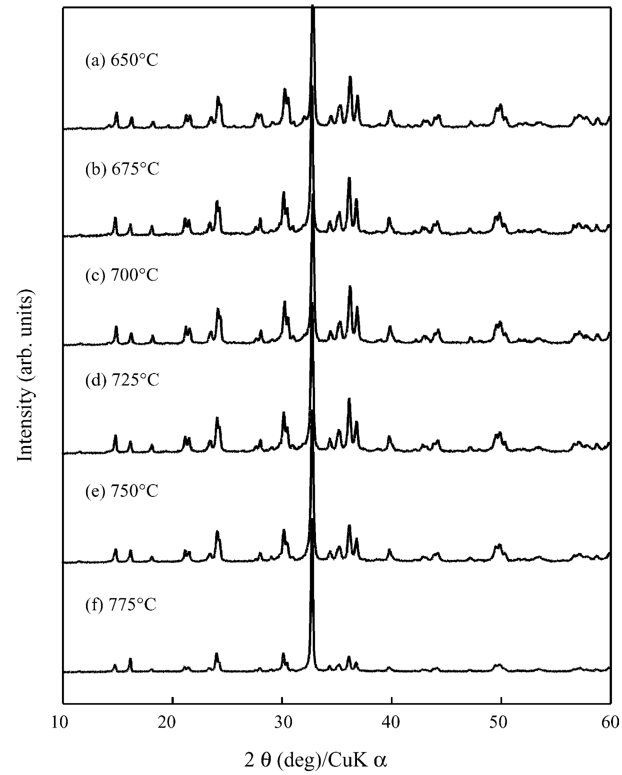

Fig. 2. XRPD patterns of $Li_3AlB_2O_6$ ceramics sintered at the temperature arrange of 650–775 °C for 10 h in air.

increasing the sintering temperatures from 650 to 775 °C, the crystallization of the phase is observed; it is found that the crystallized phase is obtained at the sintering temperature of 775 °C. At the sintering temperatures higher than 775 °C, the presence of the secondary phases, i.e., the Li_2AlBO_4 and α-$LiBO_2$ ceramics, were detected in the XRPD patterns of the samples; therefore, this result is related to the decomposition of the $Li_3AlB_2O_6$ ceramic into the Li_2AlBO_4 and α-$LiBO_2$ ceramics which was observed from the DTA-TG curves of the $Li_3AlB_2O_6$ ceramic as mentioned above.

The relationship between the sintering temperature and apparent density of the $Li_3AlB_2O_6$ ceramic is shown in Fig. 3 as a function of sintering temperature. The remarkable differences in the apparent density of the ceramics were not observed with the increase in the sintering temperature; thus, the effect of variations in the sintering temperature on apparent density of the ceramics may be small. Thus, it was found that the $Li_3AlB_2O_6$ ceramic could be sintered at the low sintering temperatures ranging from 650 to 775 °C, which are lower than the melting point of Ag; therefore, in this ceramic the element of Ag can be used for the multilayer microwave devices as a electrode material.

The sintering temperature dependence of the dielectric constant and the $Q \times f$ values of the $Li_3AlB_2O_6$ ceramic is shown in Fig. 4; the details on the microwave dielectric properties of the ceramics are also listed in Table 1. The dielectric constants of the samples ranged from 4.2 to 5.4 with increasing the sintering temperatures from 650 to

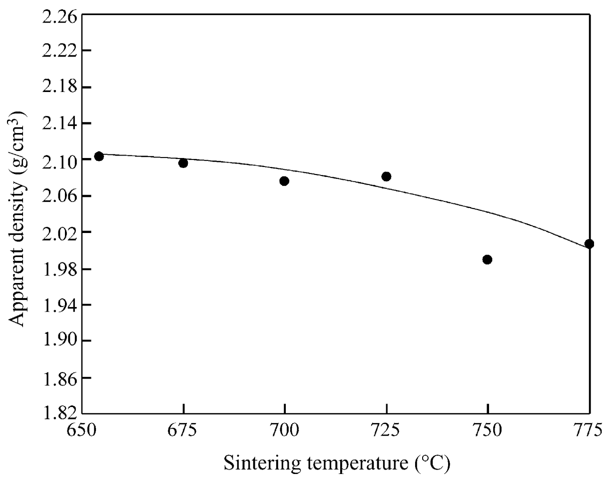

Fig. 3. Effect of sintering temperature on apparent density of $Li_3AlB_2O_6$ ceramics as a function of sintering temperature.

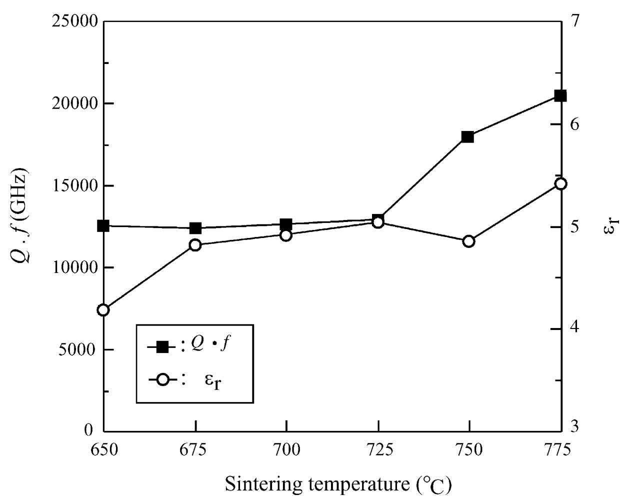

Fig. 4. Sintering temperature dependence of dielectric constant (ε_r) and quality factor ($Q \times f$) of $Li_3AlB_2O_6$ ceramics.

775 °C. Such ceramics with a low dielectric constant are considered to be suitable for application in the multilayered microwave devices as a dielectric substrate. Moreover, comparing the dielectric constant of the $Li_3AlB_2O_6$ ceramic with that of alumina-based LTCC material reported by Dai et al.,[11] a lower dielectric constant was obtained in this study. The influence of sintering temperature on the $Q \times f$ values of the ceramics is also shown in Fig. 4 as a function of sintering temperature. The $Q \times f$ values of the $Li_3AlB_2O_6$ ceramic slightly increased from 12,460 to 20,500 GHz with increasing the sintering temperatures from 650 to 775 °C; thus, the sintering temperature dependence of $Q \times f$ value was recognized. These $Q \times f$ values obtained in this study are higher than those of alumina-based LTCC material ($Q = 600$ at 2 GHz and sintering temperature of 845 °C).[11] The improvement in the $Q \times f$ value which depends on the sintering temperature is related to the crystallization of the $Li_3AlB_2O_6$ ceramic which is observed in the XRPD patterns as shown in Fig. 2; the relationship between the improvement in the $Q \times f$ value and the crystallization which relates to the morphological changes in the ceramic can be investigated in terms of the FE-SEM observation. Fig. 5 shows the surface FE-SEM micrographs of the $Li_3AlB_2O_6$ ceramics sintered at 650 and 775 °C for 10 h in air. When comparing the microstructure of ceramics sintered at 650 °C with that of the sample sintered at 775 °C, the grain growth of the microstructure was observed with an increase in the sintering temperature; the formation of a secondary phase in the ceramics was not observed from the EDX result as well as the XRPD analysis. Thus, it is

Table 1
Microwave dielectric properties of $Li_3AlB_2O_6$ ceramics sintered at various temperatures

T (°C)	f (GHz)	ε_r	$Q \times f$ (GHz)	τ_f (ppm/°C)
650	16.782	4.2	12460	−290
675	17.022	4.8	12360	−206
700	16.908	4.9	12609	−201
725	16.779	5.1	12831	−208
750	18.031	4.8	18299	−247
775	17.369	5.4	20448	−244

T: sintering temperature; f: resonant frequency: ε_r: dielectric constant: $Q \times f$, quality factor; τ_f: temperature coefficient of resonant frequency.

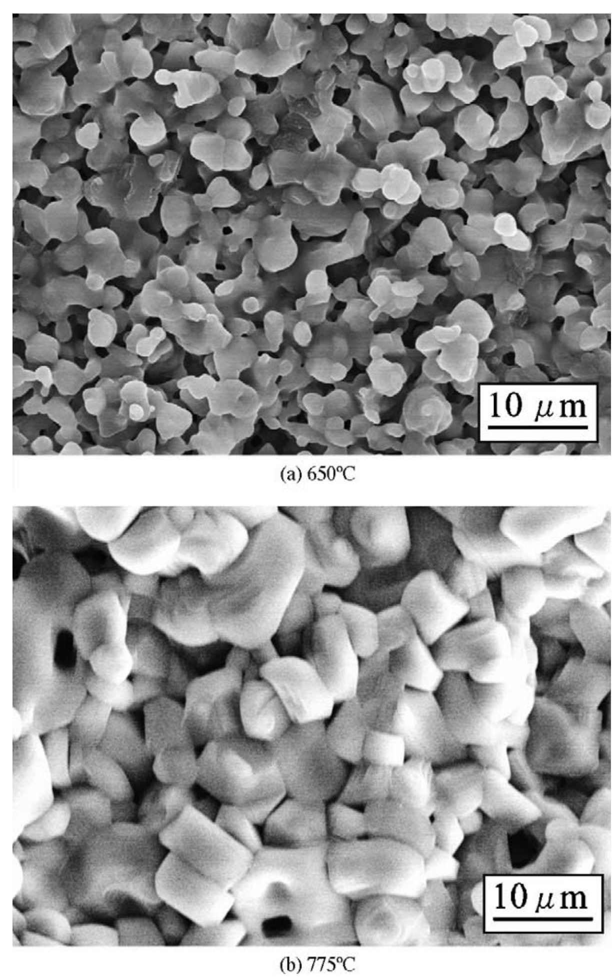

Fig. 5. FE-SEM photographs of $Li_3AlB_2O_6$ ceramics sintered at 650 and 775 °C for 10 h in air.

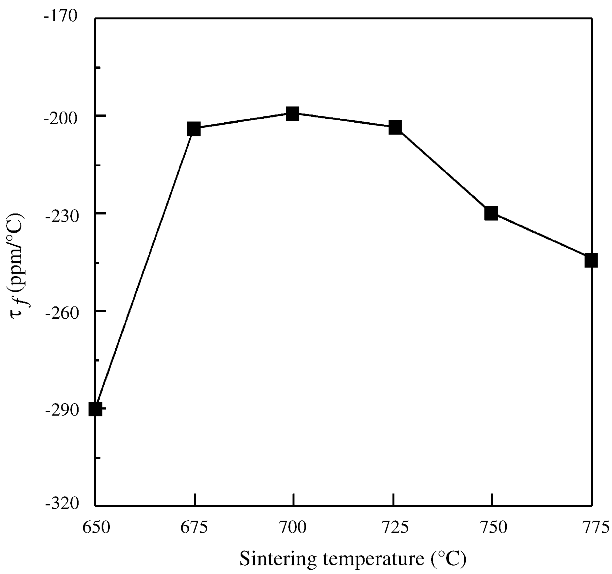

Fig. 6. Variations in temperature coefficient of resonant frequency (τ_f) of $Li_3AlB_2O_6$ ceramics as a function of sintering temperature.

considered that the improvement in the $Q \times f$ value is due to the morphological change in the crystallization of the ceramics.

As for the variations in the temperature coefficient of resonant frequency, the τ_f values of the ceramics exhibited the large negative values, ranging from −290 to −201 ppm/ °C as shown in Fig. 6; a near zero τ_f value is required for the commercial applications. Thus, in order to improve the τ_f value of the ceramic, the addition of TiB compound was performed in this study; the $Li_3AlB_2O_6$ ceramic with 5 wt% TiB addition was sintered at the temperature of 675 °C for 10h in air. The XRPD pattern of the $Li_3AlB_2O_6$ ceramic with 5 wt% TiB addition exhibited the unknown phases which arose from the chemical reaction between the $Li_3AlB_2O_6$ and TiB compounds, Although the τ_f value of the ceramic was improved by the TiB addition. From the results of EDX analyses in the microstructure of the samples as shown in Fig. 7, the presence of Ti in the grain marked as *A* was not observed, whereas the concentration of Ti in the grain marked *B* was analyzed to be approximately 8.7 at%; the presence of Ti rich phase was observed in the microstructure. As a result, the $Li_3AlB_2O_6$ ceramic with 5 wt% TiB addition sintered at 675 °C has a dielectric constant of 4.2 and a $Q \times f$ value of 13,027 GHz with a τ_f value of 10 ppm/ °C; thus, the microwave dielectric properties of the $Li_3AlB_2O_6$ ceramic with 5 wt% TiB addition are considered to be appropriate as a LTCC material.

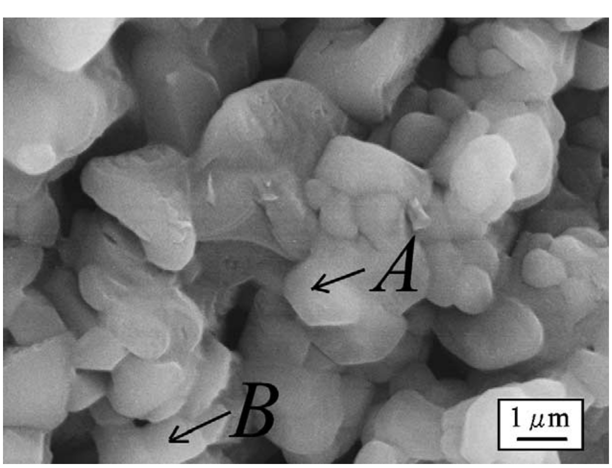

Fig. 7. FE-SEM photograph of $Li_3AlB_2O_6$ ceramic with 5 wt% TiB addition sintered at 675 °C for 10 h in air.

4. Conclusions

The Microwave dielectric properties of the $Li_3AlB_2O_6$ ceramic were investigated to develop a new low temperature co-fired ceramic for use in the multilayer microwave devices. The $Li_3AlB_2O_6$ ceramics were sintered in the temperature range of 650–775 °C; from the XRPD analysis, it was found that the crystallization of the ceramic occurred with increasing the sintering temperatures from 650 to 775 °C. As for the microwave dielectric properties of the ceramics, the dielectric constant of the Li_3AlBO_6 ceramic ranged from 4.2 to 5.4, whereas the $Q \times f$ value of the ceramic increased from 12,460 to 20,500 GHz with an increase in the sintering temperature; it is considered that the increase in the $Q \times f$ value of the ceramic closely relates to the crystallization of the ceramic. Thus, in this system, it was found that a low dielectric constant with a high $Q \times f$ value was obtained at the low sintering temperatures; these dielectric properties of the ceramic were considered to be suitable for use as a LTCC material, though the temperature coefficient of resonant frequency of the ceramics exhibited the large negative values ranging from −290 to −201 ppm/ °C. Moreover, in the case of TiB addition, the τ_f value of 10 ppm/ °C was obtained in the ceramic at the sintering temperature of 675 °C; the $Q \times f$ and dielectric constant values were 13,027 GHz and 4.2, respectively.

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