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Effect of Li₂CO₃-H₃BO₃ on the microwave dielectric properties of 0.8Ca_{0.85}Nd_{0.1}TiO₃-0.2SmAlO₃ ceramics

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 $0.8Ca_{0.85}Nd_{0.1}TiO_3-0.2SmAlO_3$ (CNT-SA) ceramics with Li₂CO₃-H₃BO₃ were prepared by a conventional solid-state reaction method to develop new microwave dielectric materials with a low sintering temperature. With the addition of 8 wt.% Li₂CO₃-H₃BO₃, the sintering temperature of CNT-SA ceramics was effectively reduced to 950°C without degradation of the microwave dielectric properties. These results are due to the enhancement of the density by liquid phase sintering. The dielectric constant (*K*) and *Qf* value of the specimens depended on the density and grain size. The temperature coefficient of the resonant frequency (*TCF*) of the specimens was largely affected by the relative ratio of H₃BO₃ to Li₂CO₃. Good microwave dielectric properties with values of *K*=50.6, *Qf*=8,100 GHz, and *TCF*=19.7 ppm/°C were obtained in CNT-SA ceramics with 8 wt.% Li₂CO₃-H₃BO₃ sintered at 950°C for 4 h.

Key words: Low temperature Sintering, Microwave dielectric properties, 0.8Ca_{0.85}Nd_{0.1}TiO₃-0.2SmAlO₃, Li₂CO₃-H₃BO₃.

Introduction

Recently, low temperature co-fired ceramics (LTCC) for multilayer devices have been extensively investigated due to the design and functional benefits realized upon the miniaturization of microwave dielectric components [1]. For the application of LTCC multilayer devices [2, 3], it is necessary to reduce the sintering temperature of microwave dielectric ceramics which can be cofired with metallic electrodes such as silver (960°C) and copper (1050°C) [4]. Various attempts have been made to reduce the sintering temperature of microwave dielectrics using sintering aids for practical applications [5-7]. Typically, Li₂O [8] and B₂O₃ [9] have been suggested as promising sintering aids for the densification at relatively low sintering temperatures. Single components with a low-melting point are often used as sintering aids, but they easily form a complex compound with matrix ceramics, which deteriorate the dielectric properties of ceramics [8, 9]. However, complex additives Li₂O-B₂O₃ are much effective in reducing the sintering temperature of ceramics with good microwave dielectric properties [10-12]. Also, it has been reported [13] that the binary Li₂O-B₂O₃ system shows various lithium boron oxides with melting points below 917°C. Therefore, the effectiveness of various lithium boron oxide on the low-temperature sintering of microwave dielectrics should be investigated.

In our preliminary experiment, 0.8Ca_{0.85}Nd_{0.1}TiO₃-

0.2SmAlO₃ (CNT-SA) ceramics sintered at 1300°C for 4 h showed good microwave dielectric properties; K= 57, Qf=8,500 GHz and TCF=23 ppm/°C. Although the microwave dielectric properties of the CNT-SA ceramics are good enough, it is not easy to apply this ceramic in practical LTCC devices since the sintering temperature is relatively high.

In the present study reported here, the effect of H_3BO_3 -Li₂CO₃ content and the relative amount of H_3BO_3 to Li₂CO₃ on the sinterability and the microwave dielectric properties of CNT-SA ceramics were investigated to develop a new LTCC with good dielectric properties.

Experimental Procedure

 $0.8Ca_{0.85}Nd_{0.1}TiO_3$ - $0.2SmAlO_3$ (CNT-SA) ceramics were prepared by a conventional solid-state reaction from the oxide powders with purities above 99.9%. The powders were separately prepared according to the desired compositions of $Ca_{0.85}Nd_{0.10}TiO_3$ and SmAlO₃, and ground with ZrO₂ balls for 24 h in distilled water. The powders prepared of $Ca_{0.85}Nd_{0.10}TiO_3$ and SmAlO₃ were dried and calcined at 1100°C, and 1400°C for 3 h, respectively. The calcined powders were mixed according to the composition of 0.8CNT-0.2SA and calcined at 1250°C for 3 h. The calcined CNT-SA powders were re-milled for 24 h with the addition of Li₂CO₃-H₃BO₃, and pressed into 10 mm diameter disks under a pressure of 1500 kg/cm², isostatically. These disks were sintered from 850°C to 975°C for 4 h in the air.

The crystalline phases in the specimens were identified by powder X-ray diffraction analyses (XRD, D/ Max-3C, Rigaku, Japan). The microstructure of the

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sintered specimens was observed by a scanning electron microscope (SEM, JEOL, JSM 820, Japan). The sintered density of the specimens was measured by the Archimedes method. The dielectric constant (K) and unloaded Q value at 7-9 GHz were measured by the post resonant method [14]. The temperature coefficient of the resonant frequency (*TCF*) was measured by the cavity method [15] in the temperature range from 20°C to 80°C.

Results and Discussion

Phase evaluation and physical properties of sintered ceramics

Figure 1 shows the X-ray diffraction (XRD) patterns of 0.8Ca_{0.85}Nd_{0.1}TiO₃-0.2SmAlO₃ (CNT-SA) with Li₂CO₃-H₃BO₃ and/or 8 wt.% (1-x)Li₂CO₃-xH₃BO₃ specimens sintered at 950°C for 4 h, respectively. With the increase of Li₂CO₃-H₃BO₃ content, the single perovskite phase with the orthorhombic structure was detected up to 4 wt.%, and then Li₆B₄O₉ was detected as the secondary phase on further additions of Li₂CO₃- H_3BO_3 . With the increase of H_3BO_3 content (x), secondary phases were detected such as Li₆B₄O₉, LiBO₂ and LiB_3O_5 . The unknown phases detected at x=0.1 and 0.3 of (1-x)Li₂CO₃-xH₃BO₃ could be attributed to Lirich lithium boron oxides, however, it can not be confirmed so far because the phase diagram and/or JCPDS files of Li-rich lithium boron oxides have not been reported. Based on the XRD patterns of the specimens, reaction compounds between the CNT-SA and Li₂CO₃-H₃BO₃ were not detected, and in turn, the chemical reactions between the CNT-SA and Li₂CO₃-H₃BO₃ were not confirmed. Also, there was no remarkable changes in XRD patterns with H₃BO₃ content (x) of (1-x)-Li₂CO₃-xH₃BO₃. A similar tendency of the XRD patterns was obtained for the specimens sintered from 850°C to



Fig. 1. X-ray diffraction patterns of $0.8Ca_{0.85}Nd_{0.1}TiO_3$ - $0.2SmAlO_3$ specimens with (a) Li_2CO_3 - H_3BO_3 and (b) 8 wt.% (1-x) Li_2CO_3 -x H_3BO_3 sintered at 950°C for 4 h.

 Table 1. The secondary phases detected by XRD patterns and their melting points

Li ₂ CO ₃ -H ₃ BO ₃ content	Secondary phases	Melting point (°C) [11]
6 wt.% Li ₂ CO ₃ -H ₃ BO ₃	Li ₆ B ₄ O ₉	700
8 wt.% Li ₂ CO ₃ -H ₃ BO ₃	Li ₆ B ₄ O ₉	700
10 wt.% Li ₂ CO ₃ -H ₃ BO ₃	Li ₆ B ₄ O ₉	700
8 wt.% 0.9Li ₂ CO ₃ -0.1H ₃ BO ₃	Unknown	-
8 wt.% 0.7Li ₂ CO ₃ -0.3H ₃ BO ₃	Unknown	-
8 wt.% 0.5Li ₂ CO ₃ -0.5H ₃ BO ₃	Li ₆ B ₄ O ₉	700
8 wt.% 0.3Li ₂ CO ₃ -0.7H ₃ BO ₃	LiBO ₂	849
8 wt.% 0.1Li ₂ CO ₃ -0.9H ₃ BO ₃	LiB ₃ O ₅	834



Fig. 2. Apparent density of $0.8Ca_{0.85}Nd_{0.1}TiO_3-0.2SmAlO_3$ specimens with $Li_2CO_3-H_3BO_3$ sintered from 850°C to 975°C for 4 h (a) and 8 wt.% (1-x)Li_2CO_3-xH_3BO_3 sintered at 950°C for 4 h (b).

975°C. Table 1 summarizes the secondary phases detected by XRD patterns and their melting points [13].

Figure 2 shows the apparent densities of CNT-SA with Li₂CO₃-H₃BO₃ and/or 8 wt.% (1-x)Li₂CO₃-xH₃BO₃ specimens as a function of sintering temperature, and H₃BO₃ content (x), respectively. Generally, the effectiveness of sintering aids depended on several factors such as sintering temperature, viscosity, solubility and glass wettability [16]. As shown in Fig. 2(a), the apparent density of the specimens with the designated wt.% Li₂CO₃-H₃BO₃ increased remarkably with an increase of the sintering temperature. These results are due to the increase of Li₆B₄O₉ with a low melting point $(700^{\circ}C)$ [13] by the addition of Li₂CO₃-H₃BO₃. On the other hand, the apparent density of the specimens with the designated sintering temperature was increased with Li₂CO₃-H₃BO₃ content up to 8 wt.%, and then decreased probably due to an excess amount of liquid phase, $Li_6B_4O_9$.

For the specimens with 8 wt.% $(1-x)Li_2CO_3-xH_3BO_3$ sintered at 950°C, the apparent density increased with H_3BO_3 content (x) up to x=0.5, and then decreased, as shown in Fig. 2(b). These results are due to the melting point difference of secondary phases with x of (1-x)-



Fig. 3. SEM photographs of $0.8Ca_{0.85}Nd_{0.1}TiO_3-0.2SmAlO_3$ specimens with $Li_2CO_3-H_3BO_3$ sintered at $875^{\circ}C$ ((a), (b)) and $950^{\circ}C$ ((c), (d)), and with 8.0 wt.% (1-x)Li_2CO_3-xH_3BO_3 sintered at $950^{\circ}C$ ((e), (f), (g)) for 4 h.

 Li_2CO_3 -xH₃BO₃, as confirmed in Table 1. LiBO₂ and/ or LiB₃O₅ were detected for the specimens with H₃BO₃ contents (x) above x=0.5, which have higher melting points than Li₆B₄O₉. Therefore, the apparent density of CNT-SA ceramics with Li₂CO₃-H₃BO₃ was dependent on the amount of liquid phases as well as the melting point of sintering aids.

SEM micrographs of CNT-SA with Li₂CO₃-H₃BO₃ and/or 8 wt.% (1-x)Li₂CO₃-xH₃BO₃ specimens sintered at 875°C and/or 950°C for 4 h are shown in Fig. 3. The grain size of the specimens increased with an increase of the sintering temperature and Li₂CO₃-H₃BO₃ content. However, the grain size of the specimens with 4 wt.% Li₂CO₃-H₃BO₃ did not change markedly with the sintering temperature. For the specimens with 8 wt.% (1-x)Li₂CO₃-xH₃BO₃ sintered at 950°C, the grain size increased with H₃BO₃ content (x) up to x=0.5, and then decreased. These results are in agreement with the results of density measurements in Fig. 2.

Microwave dielectric properties of sintered ceramics

Figure 4 shows the dielectric constant (*K*) of CNT-SA with $Li_2CO_3-H_3BO_3$ and/or 8 wt.% (1-x) $Li_2CO_3-xH_3BO_3$ specimens as a function of sintering temperature, and H_3BO_3 content (x). It has been reported [17, 18] that the dielectric constant (*K*) at microwave frequencies is strongly dependent on the dielectric polarizability, density and the grain size. Compared to the matrix phase of CNT-SA, a small amount of $Li_2CO_3-H_3BO_3$ was added in this study. Therefore, the effect of the dielectric polarizability on the dielectric constant (*K*) could be neglected. Due to the enhancement of the sintered density, the *K* of the specimens was increased



Fig. 4. Dielectric constant (*K*) of $0.8Ca_{0.85}Nd_{0.1}TiO_3$ - $0.2SmAlO_3$ specimens with Li₂CO₃-H₃BO₃ sintered from 850°C to 975°C for 4 h (a) and 8 wt.% (1-x)Li₂CO₃-xH₃BO₃ sintered at 950°C for 4 h (b).

with the Li₂CO₃-H₃BO₃ content up to 8 wt.% as well as the sintering temperature. As shown in Fig. 4(b), with an increase of the H₃BO₃ content (x), the *K* of the specimens sintered at 950°C for 4 h increased up to x=0.5 and then decreased, which was consistent with the density data of Fig. 3(b). Therefore, the *K* of CNT-SA ceramics with Li₂CO₃-H₃BO₃ and/or H₃BO₃ content (x) depended on the sintered density and the grain size of the specimens.

Figure 5 shows the quality factor (Qf) of CNT-SA with Li₂CO₃-H₃BO₃ and/or 8 wt.% (1-x)Li₂CO₃-xH₃BO₃ specimens as a function of sintering temperature, and H₃BO₃ content (x). With the addition of Li₂CO₃-H₃BO₃



Fig. 5. Quality factor (Qf) of $0.8Ca_{0.85}Nd_{0.1}TiO_3-0.2SmAlO_3$ specimens with Li₂CO₃-H₃BO₃ sintered from 850°C to 975°C for 4 h (a) and 8 wt.% (1-x)Li₂CO₃-xH₃BO₃ sintered at 950°C for 4 h (b).



Fig. 6. TCF of $0.8Ca_{0.85}Nd_{0.1}TiO_3-0.2SmAlO_3$ specimens with (a) $Li_2CO_3-H_3BO_3$ and (b) 8 wt.% (1-x)Li_2CO_3-xH_3BO_3 sintered at 950 $^\circ$ C for 4 h.

above 6 wt.%, the *Qf* value of the specimens markedly increased with an increase of the sintering temperature. With the addition of Li₂CO₃-H₃BO₃ below 4 wt.%, however, the *Qf* value of the specimens was not markedly changed with the sintering temperature. These results are due to the enhancement of the density and grain size of the specimens with the Li₂CO₃-H₃BO₃ content, as confirmed in Fig. 3. With an increase of the Li₂CO₃-H₃BO₃ content, the *Qf* value of the specimens with the designated sintering temperature increased up to 8.0 wt.% and then decreased. As shown in Fig. 5(b), the *Qf* value of the specimens sintered at 950°C for 4 h increased with an increase of the H₃BO₃ content (x) up to x=0.5, and then decreased due to the changes of grain size, as confirmed in Fig. 3.

Figure 6 shows the temperature coefficient of the resonant frequency (*TCF*) of CNT-SA with Li_2CO_3 -H₃BO₃ and/or 8 wt.% (1-x) Li_2CO_3 -xH₃BO₃ specimens sintered at 950°C for 4 h. The *TCF* of the specimens

decreased with an increase of the Li₂CO₃-H₃BO₃ content. These results are similar to the results for the $(Ca_{1-x}Nd_{2x/3})TiO_3$ system reported by Wei and Jean [19]. The *TCF* is known to be related to the composition and any second phase in the materials. With an increase of the H₃BO₃ content (x), the *TCF* of the specimens increased up to x=0.5, and then decreased due to the decrease of unknown secondary phases, and a decrease of the density by the change of the H₃BO₃ content. Also, the *TCF* of the specimens was more affected by the relative content of the H₃BO₃ to the Li₂CO₃ than to the Li₂CO₃-H₃BO₃ content.

Conclusions

The effects of the Li₂CO₃-H₃BO₃ content and relative amounts of H₃BO₃ to Li₂CO₃ on the sintering temperature and the microwave dielectric properties of 0.8-Ca_{0.85}Nd_{0.1}TiO₃-0.2SmAlO₃ (CNT-SA) ceramics were investigated. With the addition of 8 wt.% Li₂CO₃-H₃BO₃, the sintering temperature of CNT-SA ceramics was effectively reduced from 1300°C to 950°C without a degradation of the microwave dielectric properties. These results are due to the enhancement of the density by the formation of Li₆B₄O₉ with a low melting point (700°C) as the effective liquid sintering agent. With an addition of Li₂CO₃-H₃BO₃ above 6 wt.%, the Qf value of the specimens increased with the sintering temperature due to the increase of the grain size. The dielectric constant (K) and the TCF of the specimens depended on the density and secondary phases. The TCF of the specimens was more affected by the relative content of the H₃BO₃ to the Li₂CO₃ than to the Li₂CO₃-H₃BO₃ content.

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