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Low-temperature sintering of $0.85CaWO_4$–$0.15LaNbO_4$ ceramics

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Abstract

Microwave dielectric properties of $0.85CaWO_4$–$0.15LaNbO_4$ (CWLN) ceramics were investigated as a function of H_3BO_3, Li_2CO_3 content and sintering temperature. With the co-addition of 3.0 wt.% H_3BO_3–1.0 wt.% Li_2CO_3, the sintering temperature could be effectively reduced from 1150 °C for pure CWLN ceramics to 900 °C without any degradation of dielectric properties. These results are due to the enhancement of the sinterability of CWLN by liquid phase sintering. For the specimens with H_3BO_3–Li_2CO_3 sintered at 900 °C for 3 h, the dielectric constant (K) did not changed remarkably. However, the quality factor (Qf) and the temperature coefficient of resonant frequency (TCF) increased up to $y = 1.0$ of 3.0 wt.% H_3BO_3–y wt.% Li_2CO_3, and then decreased due to the formation of the secondary phases. Typically, K of 11.8, Qf of 45,200 GHz and TCF of −23.1 ppm/°C were obtained for the specimens of CWLN with 3.0 wt.% H_3BO_3–1.0 wt.% Li_2CO_3 sintered at 900 °C for 3 h.

Keywords: A. Sintering; B. Grain size; C. Dielectric properties; $0.85CaWO_4$–$0.15LaNbO_4$

1. Introduction

The rapidly growing wireless industry needs a new high-performance material to build low loss and thermally stable integrated packages such as filters, duplexers, voltage-controlled oscillators and antennas [1,2]. Multilayer microwave components have been investigated to miniaturize resonant devices for volume efficiency. In multilayer structures, the ceramics with low sintering temperature are needed to co-fire with low-cost and low-melting point electrodes, such as silver with a melting point of 961 °C. However, most of the ceramic materials with good dielectric properties have a sintering temperature above 1150 °C. Therefore, the addition of sintering aids such as low-melting point glasses and/or oxides are required to reduce the sintering temperature, due to the most effective, simple and inexpensive method.

Several kinds of low-melting point sintering aids and a various synthetic glasses have been investigated to reduce the sintering temperature of microwave dielectric materials effectively [3–7]. Typically, Boron oxide and lithium oxide are the well-known liquid phase sintering promoters, and multi-component glasses are more effective than single component glass to reduce the sintering temperature of ceramics with good microwave dielectric properties [8].

In our preliminary experiment, $0.85CaWO_4$–$0.15LaNbO_4$ (CWLN) ceramics sintered at 1150 °C for 3 h showed a good microwave dielectric properties; $K = 11.7$, $Qf = 61{,}600$ GHz and $TCF = -15.3$ ppm/°C. Although the microwave dielectric properties of the CWLN ceramics are good, it is not easy to apply this ceramics for the practical devices since the sintering temperature is relatively high.

In this work, H_3BO_3 and Li_2CO_3 were selected to search the new sintering additives suitable to CWLN ceramics. Dependence of the sinterability on the relative amount of H_3BO_3 to Li_2CO_3 was discussed. Physical and microwave dielectric properties of CWLN ceramics were investigated as a function of the sintering temperature and H_3BO_3 and/or Li_2CO_3 content.

2. Experimental procedure

High-purity (≥99.9%) oxide powders of $CaCO_3$, La_2O_3, WO_3, and Nb_2O_5 were used as starting powders. The powders were separately prepared according to the desired stoichiometric $CaWO_4$ and $LaNbO_4$ and ground with ZrO_2 balls for 24 h in ethanol. Prepared powders of $CaWO_4$ and $LaNbO_4$ were dried and calcined at 700 °C, and 1100 °C for 3 h, respectively. The calcined powders were mixed according to the composition of $0.85CaWO_4$–$0.15LaNbO_4$ (CWLN) and calcined at 1100 °C

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for 3 h. The calcined CWLN powders were re-milled for 24 h with the addition of H_3BO_3–Li_2CO_3, and pressed into 15 mm diameter disks under the pressure of 1500 kg/cm^2, isostatically. These disks were sintered from 850 °C to 950 °C for 3 h in the air.

Crystalline phases of the specimens were identified by the powder X-ray diffraction analyses (D/Max-3C, Rigaku, Japan). Microstructure of the sintered specimens was observed by a scanning electron microscope (JEOL, JSM 820, Japan). The sintered density of the specimens was measured by the Archimedes method. Dielectric constant (K) and unloaded Q value at 9–11 GHz were measured by the post-resonant method [9]. The temperature coefficient of the resonant frequency (TCF) was measured by the cavity method [10] in the temperature range from 20 °C to 80 °C.

3. Results and discussion

Powder X-ray diffraction patterns of 0.85$CaWO_4$–0.15$LaNbO_4$ (CWLN) with H_3BO_3–Li_2CO_3 specimens sintered at 900 °C for 3 h are shown in Fig. 1. For the co-addition of H_3BO_3 and Li_2CO_3, a single phase with scheelite structure was obtained at a given composition ranges, however, the secondary phases such as $LaNbO_4$, $LaNb_5O_{14}$ and $La_{14}W_8O_{45}$ were detected for the specimens with 3.0 wt.% H_3BO_3–1.5 and/or 2.0 wt.% Li_2CO_3. Also, there were no remarkable changes in XRD patterns with H_3BO_3–Li_2CO_3 content.

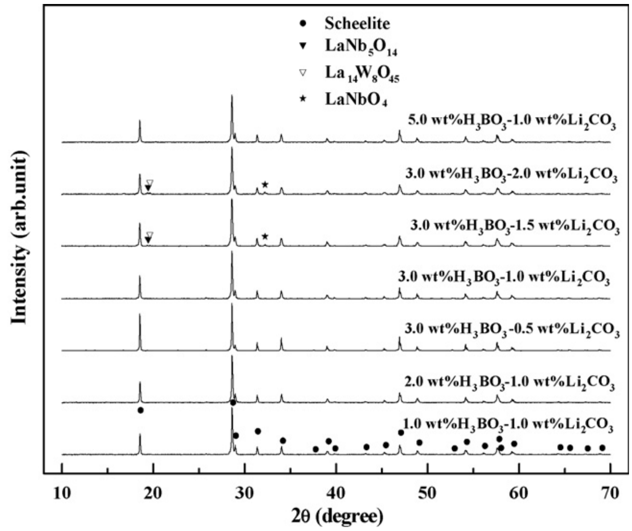

Fig. 1. X-ray diffraction patterns of 0.85$CaWO_4$–0.15$LaNbO_4$ with H_3BO_3–Li_2CO_3 content sintered at 900 °C for 3 h.

Fig. 2 shows the apparent densities of CWLN with H_3BO_3–Li_2CO_3 as a function of sintering temperature, and H_3BO_3 content, respectively. The apparent density of the pure CWLN specimens was remarkably increased with the sintering temperature, and shows a maximum value at 1150 °C. As shown in Fig. 2(a), the apparent density of the specimens with 3.0 wt.% H_3BO_3–y wt.% Li_2CO_3 was increased with increasing sintering temperature. These results are due to the increase of liquid phase (849 °C: B_2O_3–Li_2O) by the co-addition of H_3BO_3–Li_2CO_3. On the other hand, the apparent density of the specimens was decreased with Li_2CO_3 content due to the increase of excess liquid phase. For CWLN with 3.0 wt.% H_3BO_3–0.5 wt.% Li_2CO_3, the apparent density of the specimens shows a maximum value at 900 °C, and the same value of density was obtained for the pure CWLN specimens sintered at 1150 °C. Hence, the sintering temperature of CWLN could be reduced from 1150 °C to 900 °C by the co-addition of H_3BO_3–Li_2CO_3. Generally, the effectiveness of sintering aids depends on the several factors, such as sintering temperature, viscosity, solubility and glass wettability [11]. Viscosity, solubility and glass wettability of H_3BO_3–Li_2CO_3 in this work might be probably changed with sintering temperature and H_3BO_3–Li_2CO_3 content. For the specimens with x wt.% H_3BO_3–1.0 wt.% Li_2CO_3 sintered at 900 °C (Fig. 2(b)), the density was

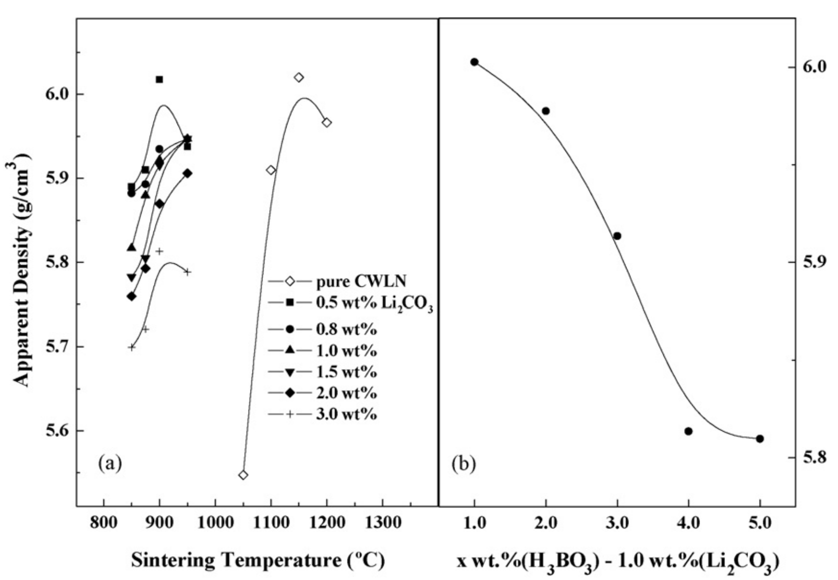

Fig. 2. Apparent density of 0.85$CaWO_4$–0.15$LaNbO_4$ specimens with (a) 3.0 wt.% H_3BO_3–y wt.% Li_2CO_3 sintered at various temperature for 3 h (b) x wt.% H_3BO_3–1.0 wt.% Li_2CO_3 sintered at 900 °C for 3 h.

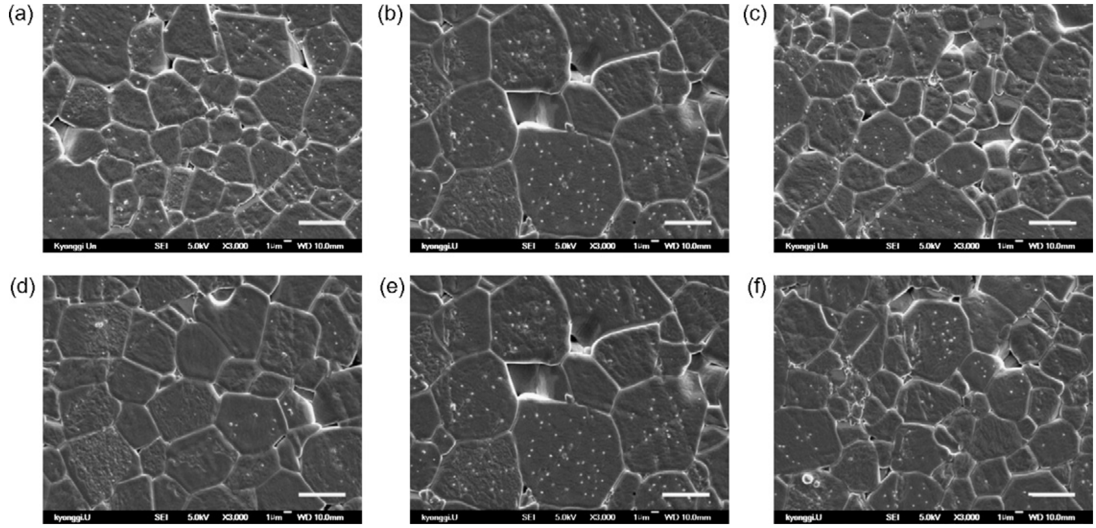

Fig. 3. SEM photographs of $0.85CaWO_4$–$0.15LaNbO_4$ with *x* wt.% H_3BO_3–*y* wt.% Li_2CO_3 specimens at 900 °C for 3 h; (a) $x = 1.0$ wt.%, $y = 1.0$ wt.%; (b) $x = 3.0$ wt.%, $y = 1.0$ wt.%; (c) $x = 5.0$ wt.%, $y = 1.0$ wt.%; (d) $x = 3.0$ wt.%, $y = 0.5$ wt.%; (e) $x = 3.0$ wt.%, $y = 1.0$ wt.%; (f) $x = 3.0$ wt.%, $y = 1.5$ wt.% (bar = 5 μm).

decreased with H_3BO_3 content, which was similar tendency to the behavior of density of the specimens with Li_2CO_3 content. Therefore, the apparent density of CWLN specimens sintered at low temperature was depended on the amount of liquid phase.

SEM photographs of CWLN with H_3BO_3–Li_2CO_3 ceramics sintered at 900 °C for 3 h are shown in Fig. 3. For the specimens with *x* wt.% H_3BO_3–1.0 wt.% Li_2CO_3, the grain size of the specimens was increased up to $x = 3.0$, and then decreased for the further addition of H_3BO_3. For the specimens with 3.0 wt.% H_3BO_3–*y* wt.% Li_2CO_3, the grain size of the specimens was increased up to $y = 1.0$, and then decreased for the further addition of Li_2CO_3. For the specimens with 3.0 wt.% H_3BO_3–1.5 and 2.0 wt.% Li_2CO_3, the secondary phases could not be observed in the SEM micrograph, even though the secondary phases were detected in the XRD patterns of Fig. 1.

Figs. 4 and 5 show the microwave dielectric properties of CWLN with *x* wt.% H_3BO_3–1.0 wt.% Li_2CO_3 and 3.0 wt.% H_3BO_3–*y* wt.% Li_2CO_3ceramics sintered at 900 °C for 3 h, respectively. The dielectric constant (*K*) of the specimens was not changed remarkably with H_3BO_3, Li_2CO_3 content. It has been reported [12] that *Qf* value is affected by secondary phase, density, impurities and grain size. For the specimens with H_3BO_3–Li_2CO_3 sintered at 900 °C, the effect of density on *Qf* value could be neglected because the relative density was higher than 96%. With an increase of H_3BO_3, Li_2CO_3 content, *Qf* value of the specimens was increased up to 3.0 wt.% H_3BO_3–1.0 wt.% Li_2CO_3, and then decreased due to the decrease of grain size, as shown in Fig. 3.

Fig. 6 shows the temperature coefficient of resonant frequency (*TCF*) of CWLN with 3.0 wt.% H_3BO_3–*y* wt.% Li_2CO_3 ceramics sintered at 900 °C for 3 h. *TCF* was largely depended on the temperature coefficient of dielectric constant (*TCK*), which in turn depended on the dielectric constant if there were no secondary phases without the change of crystal structure. For the specimens with 3.0 wt.% H_3BO_3–*y* wt.% Li_2CO_3, *TCF* of the specimens was increased up to $y = 1.0$, and then decreased due to the formation of the secondary phases such as $LaNb_5O_{14}$, $La_{14}W_8O_{45}$ and $LaNbO_4$, as confirmed in

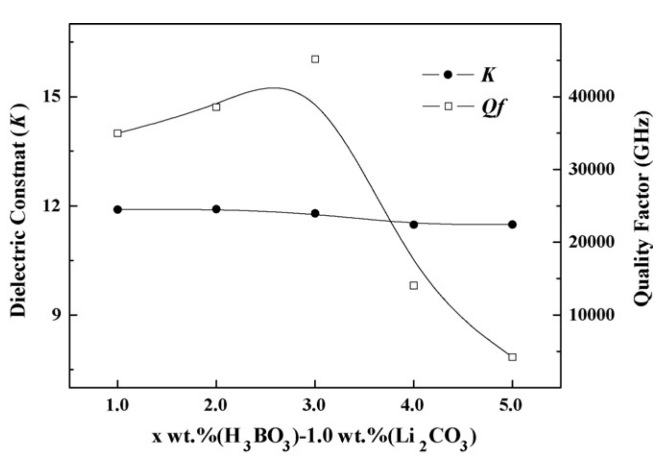

Fig. 4. Microwave dielectric properties of $0.85CaWO_4$–$0.15LaNbO_4$ with *x* wt.% H_3BO_3–1.0 wt.% Li_2CO_3 specimens sintered at 900 °C for 3 h.

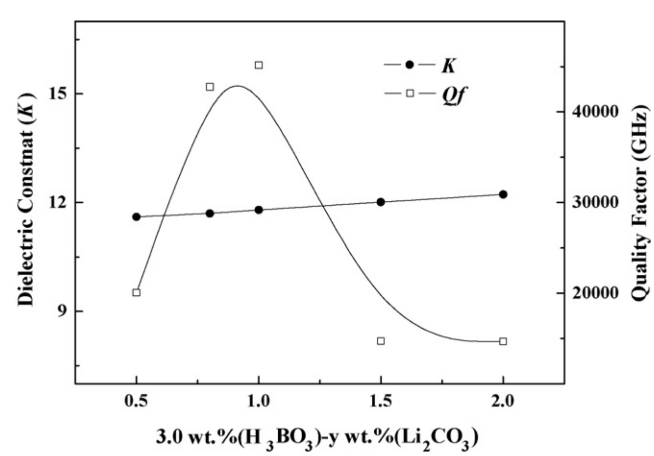

Fig. 5. Microwave dielectric properties of $0.85CaWO_4$–$0.15LaNbO_4$ with 3.0 wt.% H_3BO_3–*y* wt.% Li_2CO_3 specimens sintered at 900 °C for 3 h.

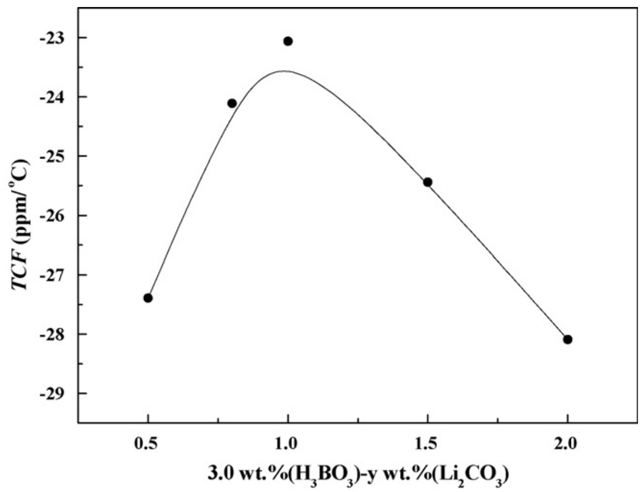

Fig. 6. *TCF* of 0.85$CaWO_4$–0.15$LaNbO_4$ with 3.0 wt.% H_3BO_3–*y* wt.% Li_2CO_3 specimens sintered at 900 °C for 3 h.

Fig. 1. Good microwave dielectric properties of $K = 11.8$, Qf = 45,200 GHz and $TCF = -23.1$ ppm/°C were obtained for the specimens with 3.0 wt.% H_3BO_3–1.0 wt.% Li_2CO_3 sintered at 900 °C, which is 250 °C lower than that of pure CWLN. These results are caused by the effect of H_3BO_3–Li_2CO_3 on the sinterability.

4. Conclusions

Effects of H_3BO_3–Li_2CO_3 on the sinterability and microwave dielectric properties of 0.85$CaWO_4$–0.15$LaNbO_4$ (CWLN) ceramics were investigated. For the specimens sintered at 900 °C for 3 h, the dielectric constant (*K*) did not changed remarkably by the co-addition of H_3BO_3–Li_2CO_3. For the specimens with 3.0 wt.% H_3BO_3–1.0 wt.% Li_2CO_3, the quality factor (*Qf*) showed the maximum value due to the largest grain size, and the sintering temperature of CWLN ceramics was effectively reduced from 1150 °C to 900 °C without degradation of dielectric properties. These results are due to the enhancement of the sinterability of CWLN by liquid phase sintering. The temperature coefficient of resonant frequency (*TCF*) of the specimens increased up to $y = 1.0$ of 3.0 wt.% H_3BO_3–*y* wt.% Li_2CO_3, and then decreased due to the secondary phases such as $LaNbO_4$, $LaNb_5O_{14}$ and $La_{14}W_8O_{45}$.

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