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Low-temperature sintering and microwave dielectric properties of $CaWO_4$ ceramics for LTCC applications

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Abstract

Microwave dielectric properties of $CaWO_4$ ceramics were investigated as a function of H_3BO_3 and/or Bi_2O_3 content and sintering temperature. For a single addition of H_3BO_3 ($1 \leq x$ (wt.%) ≤ 5), the density of specimen increased up to 3 wt.% H_3BO_3, and then decreased. The dielectric constant (*K*) and the quality factor ($Q \times f$) of the specimens sintered at 850 °C showed lower value than those of specimens sintered above 900 °C due to the poor sinterability. With the increase of H_3BO_3 content of 0.5 wt.% Bi_2O_3–$y$$H_3BO_3$ ($5 \leq y$ (wt.%) ≤ 20), the sintering temperature of $CaWO_4$ ceramics could be effectively reduced from 1100 to 850 °C without degradation of dielectric properties. For the specimens sintered at 850 °C for 30 min, *K* was not changed remarkably with Bi_2O_3–H_3BO_3 content; however, $Q \times f$ value increased up to 9 wt.% H_3BO_3 of 0.5 wt.% Bi_2O_3–$y$$H_3BO_3$, and then decreased. The temperature coefficient of resonant frequency (*TCF*) shifted to the positive value with increasing Bi_2O_3–H_3BO_3 content. Typically, *K* of 8.7, $Q \times f$ of 70,220 GHz and *TCF* of −15 ppm/°C were obtained for the specimens with 0.5 wt.% Bi_2O_3–9 wt.% H_3BO_3 sintered at 850 °C for 30 min.

Keywords: Powders-solid state reaction; X-ray methods; Dielectric properties; $CaWO_4$; Functional applications

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] The operating high frequencies of these systems require substrate materials with low dielectric constant (*K*), high quality factor ($Q \times f$) and stable temperature coefficient of the resonant frequency ($TCF \leq 10$ ppm/°C) which are important to those applications.[3] Low *K* is also important because the signal propagation velocity is a function of permittivity.[4] The materials of low *K* (≤10) have been reported such as glass composition of SiO_2–B_2O_3–Al_2O_3,[5] and there was no report for the crystalline ceramics. In our preliminary experiment, $CaWO_4$ ceramics sintered at 1100 °C for 3 h showed a good microwave dielectric properties; $K = 10$, $Q \times f = 75{,}000$ GHz and $TCF = -25$ ppm/°C. In order to develop $CaWO_4$ ceramics as a kind of new LTCCs, it is essential to reduce the sintering temperature of ceramics available to the cofiring with internal conductor, Ag and/or Cu below the melting point of metal.[6]

Therefore, this study was focused on the affecting factors on the sinterability and on the microwave dielectric properties of $CaWO_4$ ceramics with H_3BO_3 and/or Bi_2O_3. Also, the physical properties of the ceramics were investigated as a function of the sintering temperature and H_3BO_3 and/or Bi_2O_3 content.

2. Experimental procedure

$CaCO_3$ (99.9%) and WO_3 (99.9%) were used as starting materials. The powders were weighed according to the formula of $CaWO_4$, and milled with ZrO_2 balls for 24 h in distilled water. The mixtures were dried and calcined at 700 °C for 3 h. The calcined powders were re-milled for 24 h with the addition of Bi_2O_3–H_3BO_3, and pressed into pellets isostatically under the pressure of 142 MPa. These pellets were sintered from 850 to 950 °C for 10 min for 3 h.

Powder X-ray diffraction analysis (D/Max-3C, Rigaku, Japan) was used to determine the crystalline phases in the calcined and the sintered specimens. Polished surface of the sintered specimens was observed using scanning electron microscope (JEOL, JSM 820, Japan). The dielectric constant, and

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unloaded Q-value of the specimens were measured by the post-resonant method[7] at 7–9 GHz. The temperature coefficient of resonant frequency (*TCF*) was measured by the cavity method[8] in the temperature range from 25 to 80 °C.

3. Results and discussion

Powder X-ray diffraction patterns of $CaWO_4$ with xH_3BO_3 ($1 \leq x$ (wt.%) ≤ 5) specimens sintered at 900 °C for 3 h are shown in Fig. 1a, and those with 0.5 wt.% Bi_2O_3–yH_3BO_3 ($5 \leq y$ (wt.%) ≤ 20) specimens sintered at 850 °C for 10 min are shown in Fig. 1b. $CaWO_4$ with scheelite structure was obtained through the entire composition range and no remarkable changes in XRD patterns with Bi_2O_3–H_3BO_3 content. It could be predicted that Bi_2O_3–H_3BO_3 did not chemically reacted with $CaWO_4$ and only existed as liquid phase at sintering temperature.

Fig. 2a shows the apparent densities of $CaWO_4$ ceramics with H_3BO_3 as a function of sintering temperature. The density of the pure $CaWO_4$ ceramics was remarkably decreased with the sintering temperature from 1100 to 850 °C. On the other hand, the density of the specimens with H_3BO_3 was increased with H_3BO_3 content up to 3 wt.%, and then decreased for the further addition of H_3BO_3. In view point of LTCC applications, it is desirable that sintering temperature should be low and sintering time should be short to be compatible with electrode materials such as Ag or Cu. To reduce the sintering temperature and time, the effects of Bi_2O_3 and H_3BO_3 co-addition were investigated for the specimens sintered at 850 °C. For the specimens

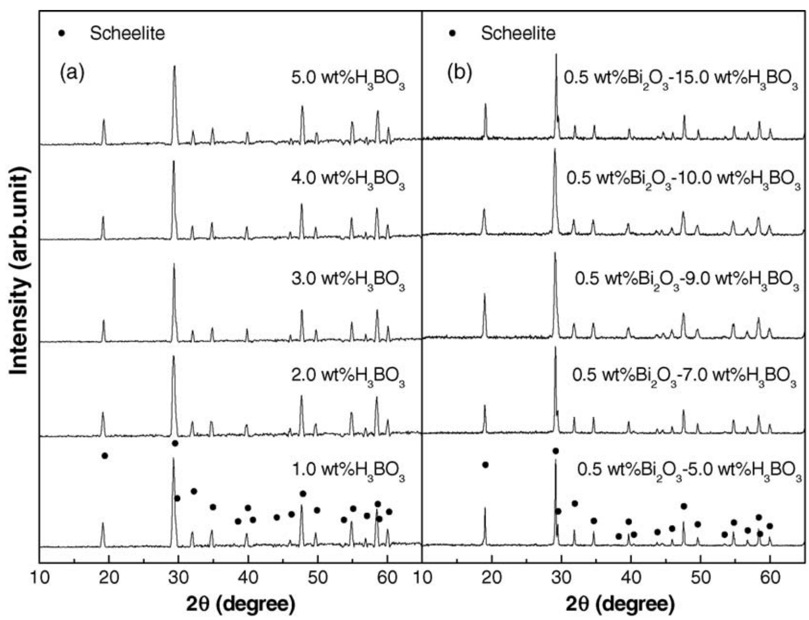

Fig. 1. X-ray diffraction patterns of $CaWO_4$ with H_3BO_3 and Bi_2O_3–H_3BO_3 content sintered at (a) 900 °C for 3 h and (b) 850 °C for 10 min.

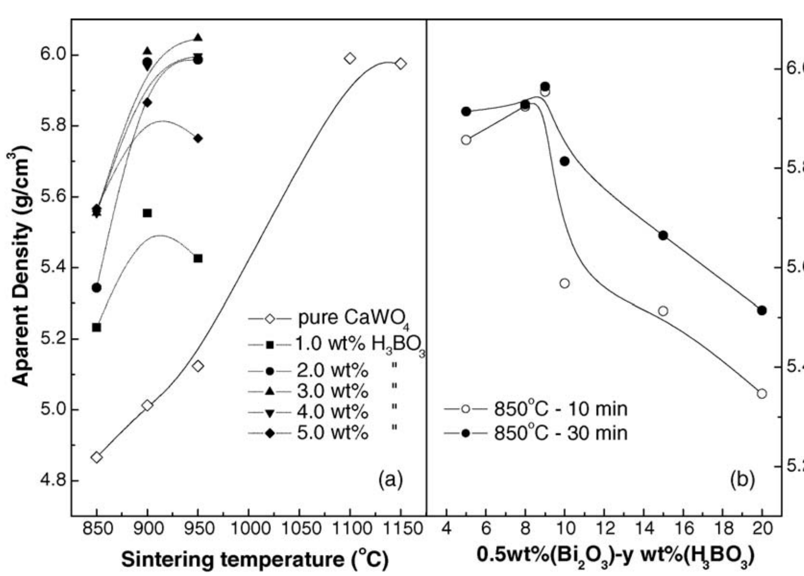

Fig. 2. Apparent density of $CaWO_4$ specimens with (a) x wt.% H_3BO_3 sintered at various temperatures for 3 h and (b) 0.5 wt.% Bi_2O_3–y wt.% H_3BO_3 sintered at 850 °C for 10 and 30 min.

with 0.5 wt.% Bi_2O_3–yH_3BO_3 ($5 \leq y$ (wt.%) ≤ 20), the density was increased up to $y = 9.0$, then decreased probably due to the increase of excess liquid phase, Bi_2O_3–H_3BO_3 in $CaWO_4$ specimens, as shown in Fig. 2b. Therefore, the sintering temperature and time to densify $CaWO_4$ could be effectively controlled by the co-addition of Bi_2O_3 and H_3BO_3.

Fig. 3 shows the microwave dielectric properties of $CaWO_4$ ceramics sintered from 850 to 950 °C for 3 h as a function of H_3BO_3 content. For the specimens sintered at 850 °C, K and $Q \times f$ value showed lower value than those of specimens sintered above 900 °C. These results are due to the poor sinterability as confirmed in Fig. 2. For the specimens sintered above 900 °C, K was remarkably improved with the addition of H_3BO_3. It has been reported[9] that $Q \times f$ value is affected by the secondary phase, density, impurities and grain size. For the specimens with 3 wt.% H_3BO_3 sintered above 900 °C, the effect of density on $Q \times f$ value could be neglected because the relative density was higher than 96%. Also, the grain size of the specimens was not significantly changed with H_3BO_3 content.

Generally, the effectiveness of sintering aids depends on the several factors, such as sintering temperature, viscosity, solubility and glass wettability.[10] Viscosity, solubility and glass wettability of H_3BO_3 in this work might be probably changed with sintering temperature and H_3BO_3 content. $Q \times f$ value of the specimens sintered at 950 °C showed lower value than that of the specimens sintered at 900 °C, which might be due to the excess of liquid phase. Temperature coefficient of resonant frequency (*TCF*) of the specimens sintered at 900 °C was slightly shifted to the positive value with H_3BO_3 content.

SEM photographs of $CaWO_4$ with 0.5 wt.% Bi_2O_3–y wt.% H_3BO_3 ceramics sintered at 850 °C for 10 min are shown in Fig. 4. With the increase of H_3BO_3 content, the grain size was increased up to $y = 9.0$ and liquid phase could be confirmed at the grain boundary of $y = 15.0$ specimen. Consequently, the apparent density of the specimens above $y = 9.0$ was decreased due to an increasing amount of the liquid phase.

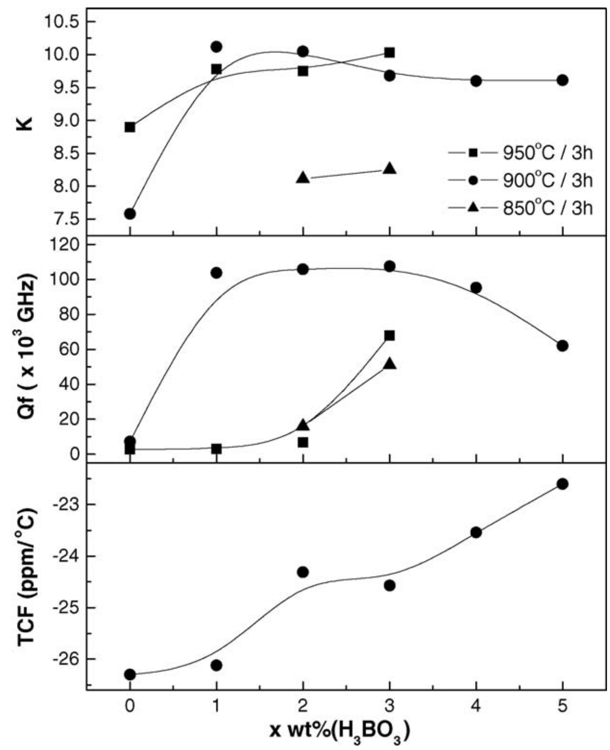

Fig. 3. Microwave dielectric properties of $CaWO_4$ with x wt.% H_3BO_3 specimens sintered from 850 to 950 °C for 3 h.

Fig. 5 shows the microwave dielectric properties of $CaWO_4$ with 0.5 wt.% Bi_2O_3–y wt.% H_3BO_3 ceramics sintered at 850 °C for 10 and 30 min, respectively. K and $Q \times f$ of the specimens

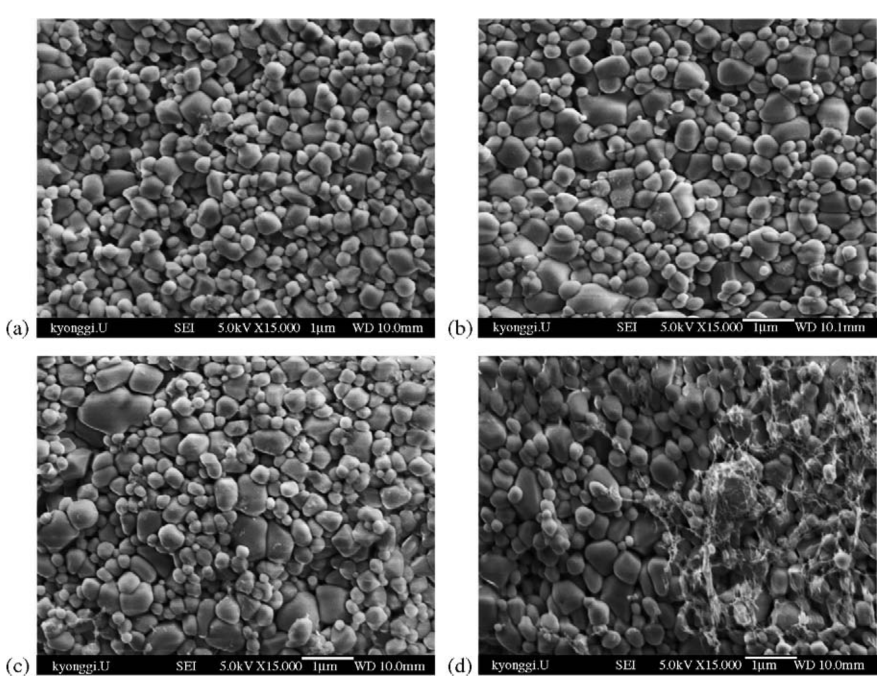

Fig. 4. SEM photographs of $CaWO_4$ with 0.5 wt.% Bi_2O_3–y wt.% H_3BO_3 specimens sintered at 850 °C for 10 min; (a) $y = 5.0$, (b) $y = 7.0$, (c) $y = 9.0$, (d) $y = 15.0$ (bar = 1 μm).

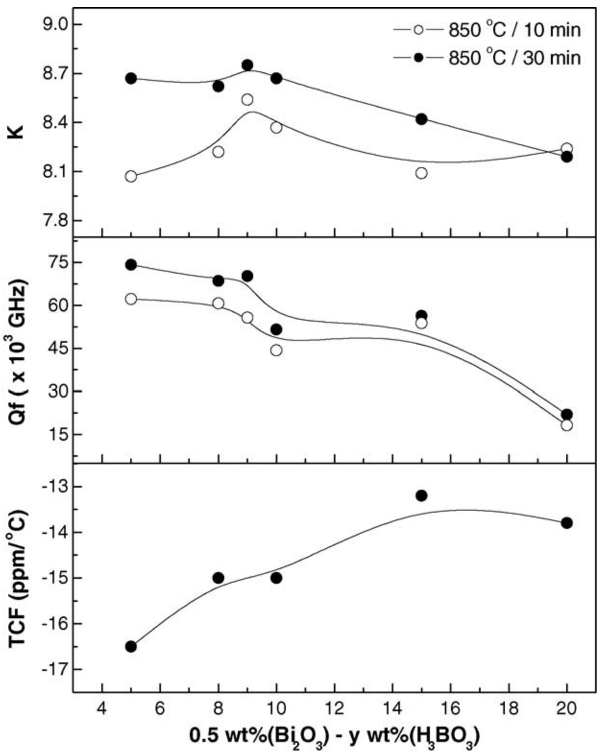

Fig. 5. Microwave dielectric properties of $CaWO_4$ with 0.5 wt.% Bi_2O_3–y wt.% H_3BO_3 specimens sintered at 850 °C for 10 and 30 min.

depended on the content of H_3BO_3 as well as sintering time. For the specimens with H_3BO_3 content lower than 9.0 wt.%, K increased with the sintering time, whereas $Q \times f$ value decreased slightly with the increase of sintering time and H_3BO_3 content. Above 9.0 wt.% H_3BO_3, K decreased slightly, but $Q \times f$ value decreased remarkably with H_3BO_3. These results indicated that the Bi_2O_3–H_3BO_3 additive worked as a sintering agent, but detrimental to $Q \times f$ value because of the excess amount of liquid phase. *TCF* was shifted to the positive value with increasing Bi_2O_3–H_3BO_3 content.

4. Conclusion

Effects of H_3BO_3 and/or Bi_2O_3 content and sintering temperature on the microwave dielectric properties of $CaWO_4$ ceramics were investigated. $CaWO_4$ with scheelite structure was obtained through the entire composition range and no remarkable changes in XRD patterns with H_3BO_3 and/or Bi_2O_3 content. For the specimens with xH_3BO_3 ($1 \leq x$ (wt.%) ≤ 5), K of the specimens sintered above 900 °C was remarkably improved with the addition of H_3BO_3. However, $Q \times f$ value of the specimens sintered at 950 °C showed lower value than that of the specimens sintered at 900 °C. For the specimens with 0.5 wt.% Bi_2O_3–yH_3BO_3 ($5 \leq y$ (wt.%) ≤ 20), the sintering temperature of $CaWO_4$ could be reduced from 1100 to 850 °C, and K and $Q \times f$ of the specimens depended on the content of H_3BO_3 as well as sintering time. Above 9.0 wt.% H_3BO_3 in the additive of 0.5 wt.% Bi_2O_3–yH_3BO_3 ($5 \leq y$ (wt.%) ≤ 20), the additive was found to work as an excellent sintering agent.

Acknowledgement

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