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Microwave dielectric properties of $0.85CaWO_4$–$0.15SmNbO_4$ ceramics with sintering additives

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Abstract

Low-temperature sintering and microwave dielectric properties of $0.85CaWO_4$–$0.15SmNbO_4$ (CWSN) ceramics were investigated as a function of Li_2MoO_4 and/or Li_2WO_4 content. With an addition of Li_2MoO_4 and/or Li_2WO_4, the sintering temperature could be reduced from 1150 °C for pure CWSN ceramics to 800 °C. The dielectric constant (K) was not changed remarkably with Li_2MoO_4 and/or Li_2WO_4 content. Quality factor (Qf) of the specimens was decreased with Li_2WO_4 content, while that of the specimens was increased with Li_2MoO_4 content. Qf values of the specimens with 1.0 wt.% Li_2WO_4 showed larger value than that of the specimens with 2.5 wt.% Li_2MoO_4. The temperature coefficient of resonant frequency (TCF) was shifted to the positive value with increasing Li_2WO_4 and/or Li_2MoO_4 content. Typically, K of 12.03, Qf of 13,300 GHz and TCF of −28.6 ppm/°C were obtained for the specimens with 1.0 wt.% Li_2WO_4 sintered at 800 °C for 1 h.

Keywords: A. Sintering; B. Grain size; C. Dielectric properties; $0.85CaWO_4$–$0.15SmNbO_4$

1. Introduction

With the rapid progress of electronic industry, most of the electronic system could be compact with high performance and numerous functions. Much attention has been paid to low-temperature co-fired ceramics (LTCC) technology to reduce the size of component with various functions.

LTCC technology was enabled to miniaturize the dimensions of the multilayer devices [1–3]. LTCC technology can be defined as a way to produce multilayer circuit with the help of single tape, which are to be used to apply conductive, dielectric and resistive pastes on. These multilayer devices are composed of alternating dielectric ceramics and internal metallic electrode layers. Ag is generally used for the metallic electrode layer because of its high conductivity and low cost. The melting temperature of Ag is 961 °C, whereas the sintering temperature of the microwave dielectric ceramics with high quality is generally high temperature above 1150 °C. Therefore, the sintering temperature of the microwave dielectric ceramics should be reduced to apply Ag as a conductive electrode.

From our preliminary result, $0.85CaWO_4$–O.$15SmNbO_4$ (CWSN) ceramics sintered at 1150 °C for 3 h showed a good microwave dielectric properties; $K = 11.6$, $Qf = 61{,}000$ GHz and $TCF = -25$ ppm/°C. In this study, Li_2MoO_4 and/or Li_2WO_4 were chosen as a sintering additive to reduce the sintering temperature of CWSN ceramics. The physical properties and the microwave dielectric properties of CWSN ceramics with Li_2MoO_4 and/or Li_2WO_4 were investigated.

2. Experimental procedure

High-purity (>99.5%) oxide powders of $CaCO_3$, Sm_2O_3, WO_3, MoO_3, Li_2CO_3 and Nb_2O_5 were used as starting materials. The powders were separately prepared according to the desired stoichiometric $CaWO_4$ and $SmNbO_4$ and ground in ethanol for 24 h in a ball mill with ZrO_2 balls. Prepared powders of $CaWO_4$ and $SmNbO_4$ were dried and calcined at 700 °C for 3 h, and 1100 °C for 3 h, respectively. After calcination, the calcined powders were mixed according to the mole fraction $0.85CaWO_4$–$0.15SmNbO_4$ and re-milled using ZrO_2 ball 24 h in ethanol and then dried. CWSN were calcined at 1100 °C for 3 h, and ground in ethanol for 2 h by an attrition mill with ZrO_2 balls and then dried. The dried powders were re-milled for 24 h with the addition of

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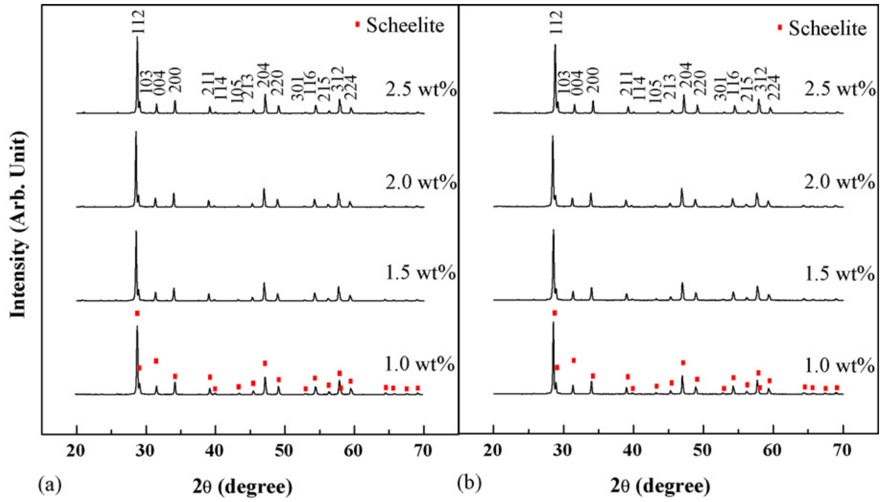

Fig. 1. X-ray diffraction pattern of $0.85CaWO_4$–$0.15SmNbO_4$ with (a) Li_2MoO_4 and/or (b) Li_2WO_4 sintered at 800 °C for 1 h.

Li_2WO_4 and/or Li_2MoO_4, and then dried. The dried powders were pressed into pellets isostatically under the pressure of 142 MPa. These pellets were sintered from 750 to 900 °C for 1 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-6500F, Japan). Microwave dielectric properties of the specimens were measured by the post resonant method [4] at 7–9 GHz for the dielectric constant (*K*) and quality factor (*Qf*), and measured by the cavity method [5] for the thermal stability (*TCF*) in the temperature range from 25 to 80 °C.

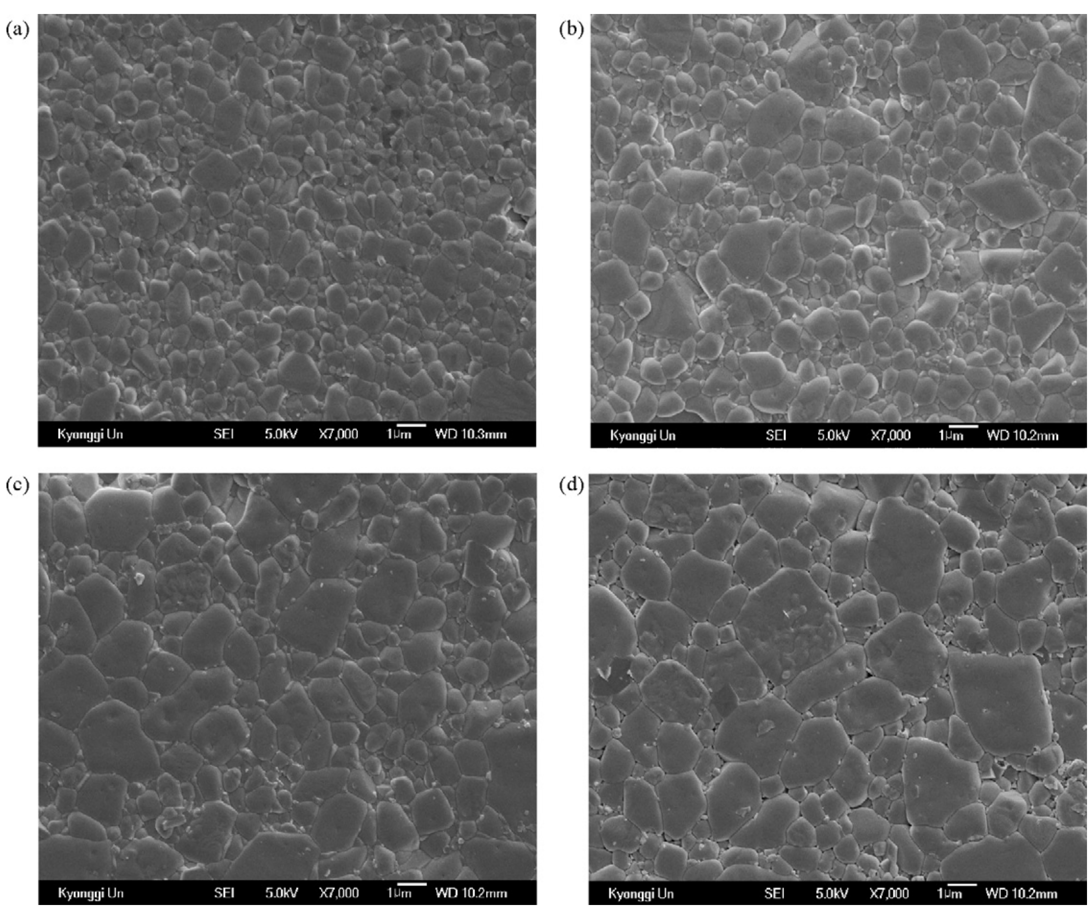

Fig. 2. SEM micrographs of $0.85CaWO_4$–$0.15SmNbO_4$ specimens with Li_2MoO_4 sintered at 800 °C for 1 h; (a) 1.0 wt.%, (b) 1.5 wt.%, (c) 2.0 wt.%, (d) 2.5 wt.%.

3. Results and discussion

3.1. Physical properties

Powder X-ray diffraction patterns of 0.85$CaWO_4$–0.15$SmNbO_4$ with Li_2MoO_4 and/or Li_2WO_4 sintered at 800 °C for 1 h are shown in Fig. 1. A single phase of CWSN with tetragonal scheelite structure was obtained through the entire composition range and no remarkable changes were observed in XRD patterns with Li_2MoO_4 and/or Li_2WO_4 content. Similar XRD patterns were obtained for the specimens sintered from 750 to 900 °C for 1 h. It could be expected that Li_2MoO_4 and/or Li_2WO_4 were not chemically reacted with CWSN and only existed as liquid phase at sintering temperature.

For the specimens with 1 wt.% of Li_2MoO_4 and/or Li_2WO_4, the apparent density was increased with the sintering temperature. Specimens sintered at 750 °C for 1 h showed only 85% of X-ray density due to the poor sinterability; however, the specimens sintered from 800 to 900 °C showed the relative density above 93% of X-ray density, corresponding to density of pure CWSN sintered at 1150 °C for 3 h. Therefore, the sintering temperature of pure CWSN could be reduced from 1150 to 800 °C by an addition of the Li_2MoO_4 and/or Li_2WO_4. Considering the applications for LTCC module, the details of study was carried out for the specimens sintered at 800 °C for 1 h as a function of the amount and the kinds of sintering additives.

Figs. 2 and 3 show SEM micrographs of CWSN ceramics with Li_2MoO_4 and/or Li_2WO_4 sintered at 800 °C for 1 h, respectively. For the specimens with Li_2MoO_4, the grain size was increased with an increase of Li_2MoO_4 content due to an increasing of the liquid phase [6,7], while that of the specimens with Li_2WO_4 was decreased with an increase of Li_2WO_4 content. There results are possibly due to the different amount of liquid phases and the different reaction behaviors of Li_2MoO_4 (m.p. = 703 °C) [8] and/or Li_2WO_4 (m.p. = 745 °C) [8] to the matrix CWSN, which resulted from the difference of melting point of the additives. However, the reaction behaviors between these additives and CWSN are not clear at present and the details are under taking the investigation.

3.2. Microwave dielectric properties

For the substrate applications of microwave dielectric materials, high quality factor is very important factor due to the requirements of high signal propagation velocity.

Fig. 4 shows *Qf* value of CWSN ceramics with Li_2MoO_4 and/or Li_2WO_4 sintered at 800 °C for 1 h. It has been reported

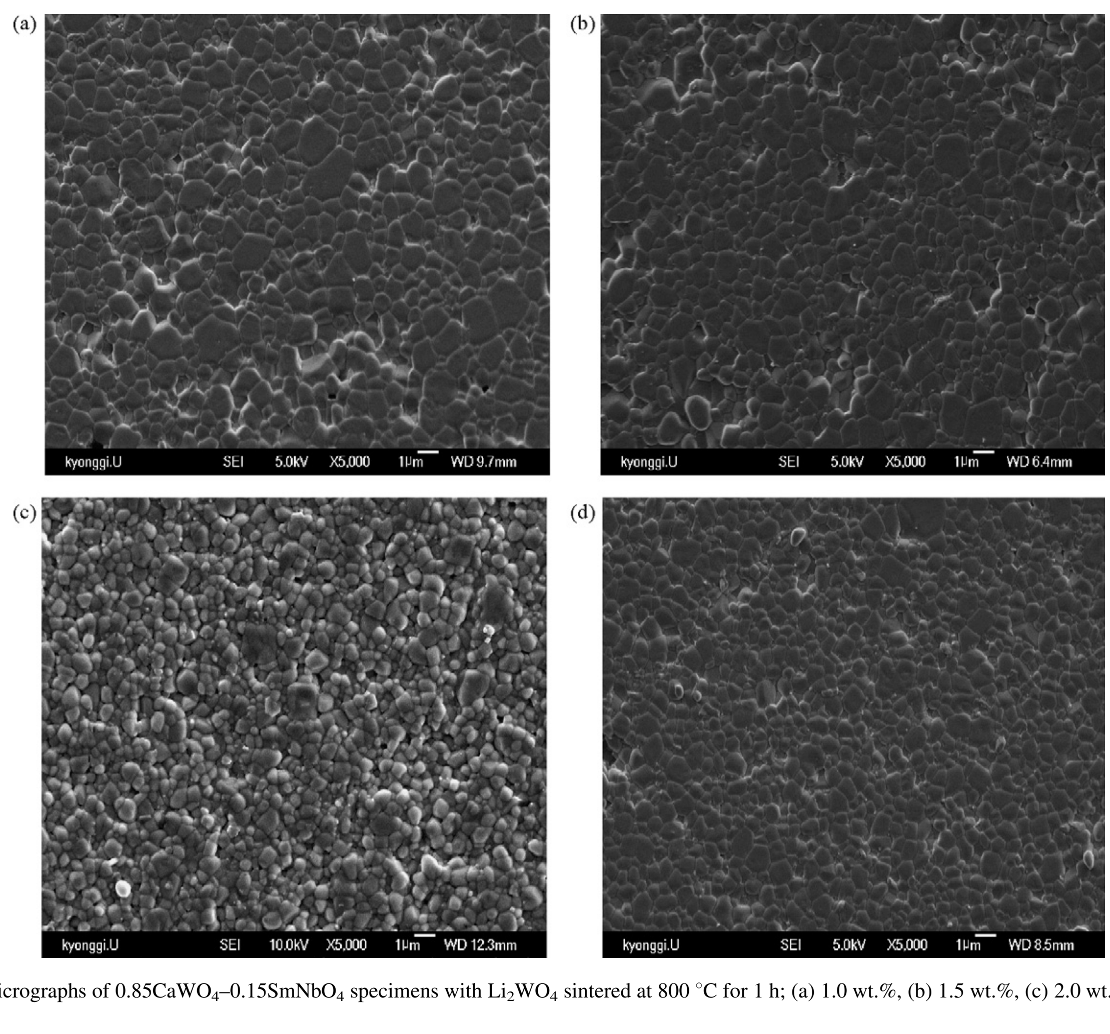

Fig. 3. SEM micrographs of 0.85$CaWO_4$–0.15$SmNbO_4$ specimens with Li_2WO_4 sintered at 800 °C for 1 h; (a) 1.0 wt.%, (b) 1.5 wt.%, (c) 2.0 wt.%, (d) 2.5 wt.%.

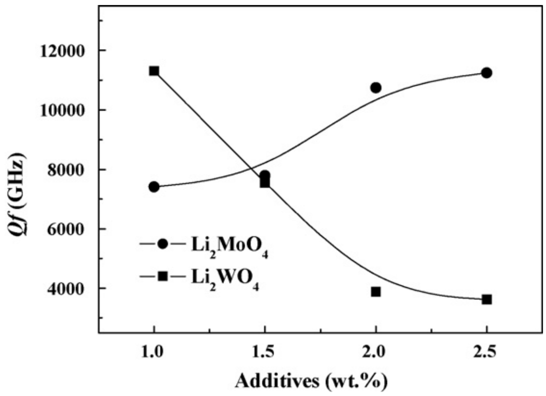

Fig. 4. Quality factor (*Qf*) of $0.85CaWO_4$–$0.15SmNbO_4$ specimens with Li_2MoO_4 and/or Li_2WO_4 sintered at 800 °C for 1 h.

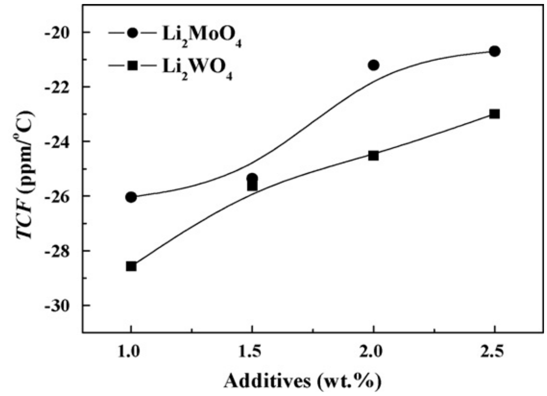

Fig. 6. *TCF* of $0.85CaWO_4$–$0.15SmNbO_4$ specimens with Li_2MoO_4 and/or Li_2WO_4 sintered at 800 °C for 1 h.

that *Qf* value is affected by the secondary phase, density, impurities and grain size [9]. For the specimens with Li_2MoO_4 and/or Li_2WO_4 sintered above 800 °C, the effects of density on the *Qf* value of CWSN were not affected significantly by the density because it showed larger value than 93% of X-ray density. Also, the secondary phase of the specimens could be neglected because the secondary phase was not observed through the entire composition range, as shown in Fig. 1.

With an increase of Li_2MoO_4 and/or Li_2WO_4 content and sintering temperature, *Qf* of the specimens was increased for the addition of Li_2MoO_4, while those of specimens was decreased for the addition of Li_2WO_4 due to the different tendency of grain size with the kind of additives, as confirmed in Figs. 2 and 3. Therefore, *Qf* value of CWSN ceramics sintered at 800 °C for 1 h was depended on the microstructures.

Fig. 5 shows the dielectric constant (*K*) of CWSN ceramics with Li_2MoO_4 and/or Li_2WO_4 sintered at 800 °C for 1 h. *K* of the specimens was not changed remarkably with Li_2MoO_4 and/or Li_2WO_4 content. These results could be attributed to the dependence of *K* on the density.

Fig. 6 shows the temperature coefficient of resonant frequency (*TCF*) of CWSN ceramics with Li_2MoO_4 and/or Li_2WO_4 sintered at 800 °C for 1 h. *TCF* of the specimens was increased from −29 to −21 ppm/°C with increasing Li_2MoO_4 and/or Li_2WO_4 content. These results are agreed with the reports [10,11] that *TCF* was increased to the positive value with the amount of additives.

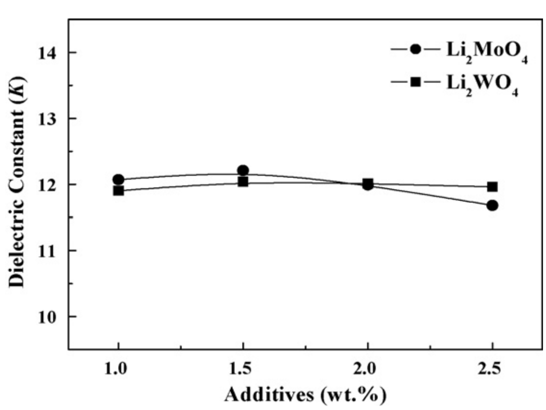

Fig. 5. Dielectric constant (*K*) of $0.85CaWO_4$–$0.15SmNbO_4$ specimens with Li_2MoO_4 and/or Li_2WO_4 sintered at 800 °C for 1 h.

4. Conclusions

With an addition of Li_2MoO_4 and/or Li_2WO_4 from 1.0 to 2.5 wt.%, the sintering temperatures were reduced from 1150 to 800 °C, and a single phase with scheelite structure was obtained through the entire composition range. Dielectric constant (*K*) was not changed remarkably with Li_2MoO_4 and/or Li_2WO_4 content. Qulaity factor (*Qf*) values were increased with Li_2MoO_4 content, while those were decreased with Li_2WO_4 content. These results could be attributed to the changes of grain size with the kind of additives. For the same amount of additives, the microwave dielectric properties were improved with sintering temperature due to the increase of sinterabilities. Temperature coefficient of the resonant frequency (*TCF*) of the specimens sintered at 800 °C for 1 h was increased with Li_2MoO_4 and/or Li_2WO_4 content.

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