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Low Temperature Sintering and Microwave Dielectric Properties of $0.85CaWO_4$-$0.15LnNbO_4$ (Ln = La, Sm) Ceramics

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Abstract Microwave dielectric properties of $0.85CaWO_4$-$0.15LnNbO_4$ (Ln = La, Sm) ceramics were investigated as a function of the sintering temperature and Li_2WO_4 content from 0.8 wt.% to 1.5 wt.%. A single phase with tetragonal scheelite structure was obtained at a given composition ranges. For the specimens with Li_2WO_4, the sintering temperature could be effectively reduced from 1150°C to 900°C due to the enhancement of sinterability. Dielectric constant (K) of the specimens with $LaNbO_4$ and $SmNbO_4$ was increased with the increase of sintering temperature and/or Li_2WO_4 content. However, K of the specimens with $LaNbO_4$ was higher than that of $SmNbO_4$ due to the larger dielectric polarizability (α) of $LaNbO_4$ (18.08Å) than that of $SmNbO_4$ (16.75Å). With an increase of Li_2WO_4 content, Qf value of the specimens with $SmNbO_4$ was decreased, while that of the specimens with $LaNbO_4$ was increased. Temperature coefficient of resonant frequency (TCF) was increased with the increase of Li_2WO_4 content.

Key words Microwave dielectric properties, Low temperature sintering, $0.85CaWO_4$-$0.15LnNbO_4$, Li_2WO_4.

1. Introduction

In the development of wireless telecommunications such as portable and mobile phones, and satellite communications, various microwave dielectric materials have been used on microwave components. With the demand for the miniaturization of microwave components, the dielectric materials which can be co-fired with internal electrode are required to develop the multi-chip module. Even though several types of dielectric materials with good microwave dielectric properties have been reported, most of them should be well sintered above 1150°C. Therefore it is essential to reduce the sintering temperature of dielectric materials to develop the low-temperature co-firing ceramics (LTCC) in order to co-fire with internal conductor, Ag and/or Cu which can ideally be fired below 950°C. Typically, three kinds of methods have been reported to reduce the sintering temperature of dielectric materials such as an addition of low-melting point oxide,[1] chemical processing of powder,[2] and an employment of starting materials with small particle sizes.[3] The addition of low-melting point oxide is more effective than other methods to reduce the sintering temperature of ceramics[1].

From our preliminary research, $0.85CaWO_4$-$0.15LnNbO_4$ (Ln = La, Sm) sintered at 1150°C for 3h showed good microwave dielectric properties, K of 11.6~11.8, Qf of 57000~61000 GHz, TCF of −15.3 ~ −25.0 ppm/°C[4], which could be applicable to the substrate materials with high signal propagation velocity. However the sintering temperature was too high to co-fire with Ag electrode. Li_2WO_4 is a good candidate to reduce the sintering temperature of $0.85CaWO_4$-$0.15LnNbO_4$ because the melting point of Li_2WO_4 is 745°C. Therefore this study was focused on affecting factors on the sinterability and on the microwave dielectric properties of $0.85CaWO_4$-$0.15LnNbO_4$ (Ln = La, Sm) ceramics with Li_2WO_4. Also, the physical properties of the ceramics were investigated as a function of the sintering temperature and Li_2WO_4 content from 0.8 wt.% to 1.5 wt.%.

2. Experimental Procedure

High-purity oxide powders of $CaCO_3$(99.0%), WO_3 (99.9%), La_2O_3(99.9%), Sm_2O_3(99.9%), Nb_2O_5(99.9%), Li_2CO_3 (99.9%) were used as starting materials. $CaWO_4$ and $SmNbO_4$ were calcined at 700°C and 1100°C for 3h, respectively. The powders were weighed according to the composition of $0.85CaWO_4$-$0.15LnNbO_4$ (Ln = La, Sm), and then milled with ZrO_2 balls for 24h in ethanol

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(99.9%). The mixture were dried and calcined at 1100°C for 3h, and then the calcined powders were milled for 2h by attrition method at 700 rpm. The slurry were dried and re-milled for 24h with addition of Li_2WO_4, which was synthesized by the calcinations of Li_2CO_3 and WO_3 at 500°C for 3h. The powders were pressed into a 15 mm diameter disks at 1450 kg/cm^2, isostatically. The pressed specimens were then sintered at 800 to 900°C for 1h at a heating rate of 300°C/h in the air.

Powder X-ray diffraction analysis (D/Max-3C, Rigaku Co., Japan) was used to determine the crystalline phases in the calcined and the sintered specimens. The apparent density was obtained by ASTM C373-72. The sintered specimens were polished by 0.05 μm γ-Al_2O_3, and then themal-etched at 750°C for 30 min. Microstructures of the specimens were observed by scanning electron microscopy (SEM, JEOL JSM-6500F, Japan). Average grain size of the sintered specimens was evaluated by the linear interception method.[5] Dielectric constant (K) and Qf value of the sintered specimens were measured by the post resonant method developed by Hakki and Coleman[6] at 7~9 GHz. The temperature coefficient of resonant frequency (TCF) was measured by cavity method[7] in temperature range from 25 to 80°C.

3. Results and discussion

Fig. 1 shows X-ray diffraction patterns of $0.85CaWO_4$-$0.15LnNbO_4$ (Ln = La, Sm) with Li_2WO_4 ceramics sintered at 900°C for 1h. A single phase with tetragonal scheelite structure was detected for pure $0.85CaWO_4$-$0.15LnNbO_4$. For the specimens with Li_2WO_4, the complete solid solutions were obtained through the entire composition range and remarkable changes were not found in XRD patterns. Similar tendency of XRD patterns was obtained for the specimens sintered from 800 to 850°C for 1h.

Fig. 2 shows the apparent densities of the specimens with Li_2WO_4 as a function of sintering temperature from 800 to 900°C. For the specimens with $SmNbO_4$ (CW-SN), there was no remarkable change of density with sintering temperature and Li_2WO_4 content. The specimens of CW-SN with Li_2WO_4 showed the similar density of pure CW-SN sintered at 1150°C for 3h. However, the sintered density of $0.85CaWO_4$-

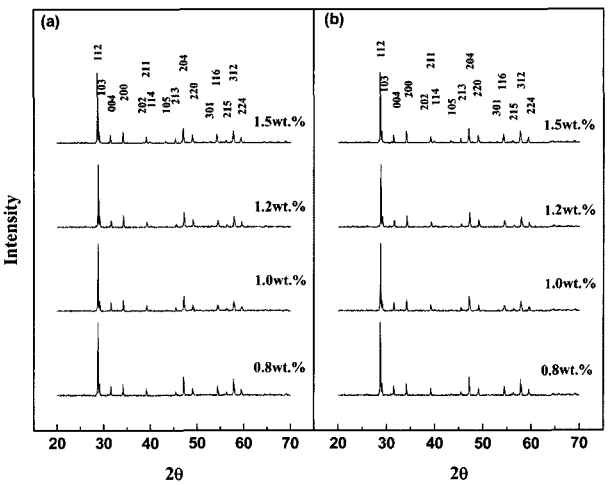

Fig. 1. X-ray diffraction pattern of (a) $0.85CaWO_4$-$0.15LaNbO_4$ (b) $0.85CaWO_4$-$0.15SmNbO_4$ with Li_2WO_4. Specimens were sintered at 900°C for 1h.

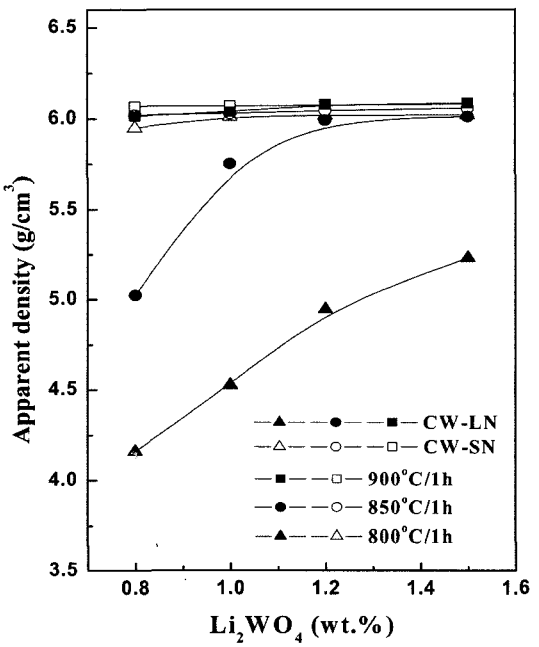

Fig. 2. Apparent density of $0.85CaWO_4$-$0.15LnNbO_4$ (Ln = La, Sm) with Li_2WO_4. Specimens were sintered from 800 to 900°C for 1h.

$0.15LaNbO_4$ (CW-LN) was strongly dependent on the sintering temperature as well as Li_2WO_4 content. The relative densities of the solid solutions showed higher than 95% of theoretical value (CW-LN : 6.17 g/cm^3, CW-SN: 6.20 g/cm^3).[4] Comparing to the density of the specimens sintered at 900°C, the sintered density was improved by the addition of Li_2WO_4 for the specimens sintered at 800 and/or 850°C. Generally, the effecti-

veness of sintering aids depended on several factors such as sintering temperature, viscosity, solubility and wettability[8]. Although the melting point of Li_2WO_4 is 745°C, the difference of sintering behavior between CW-SN and CW-LN would be attributed to the solubility and wettability of Li_2WO_4 on the matrix phase, CW-SN and/or CW-LN.

SEM photographs of $0.85CaWO_4$-$0.15LnNbO_4$ (Ln = La, Sm) with Li_2WO_4 ceramics sintered at 900°C for 1h are shown in Fig. 3. With an increase in the Li_2WO_4 content, the average grain size of the CW-LN slightly increased from 1.30 μm to 2.25 μm, while that of CW-SN decreased from 2.23 μm to 1.14 μm.

Fig. 4 shows the dielectric constant (K) of $0.85CaWO_4$-$0.15LnNbO_4$ (Ln = La, Sm) specimens sintered from 800 .to 900°C for 1h as a function of Li_2WO_4 content. Generally, the dielectric constant (K) at microwave frequency is strongly depended on the dielectric polarizability, density and the grain size.[4,9] The microwave dielectric properties of CW-LN sintered at 800°C could not be measured due to the lower density, as confirmed in fig. 2. For the specimens with the $LaNbO_4$ and/or $SmNbO_4$, K was increased with the increase in the sintering temperature and Li_2WO_4 content. However, K of the specimens with the $SmNbO_4$ sintered above 850°C was increased with the Li_2WO_4 content up to 1.2 wt.% and then decreased slightly due to the decrease of the grain size. Since the relative density of the CW-SN with Li_2WO_4 was higher than 95%, the effect of density on K could be neglected.[10] For the specimens with similar apparent density, K of the specimens with $LaNbO_4$ was higher than that of $SmNbO_4$. These results are due to the larger dielectric polarizability (α) of

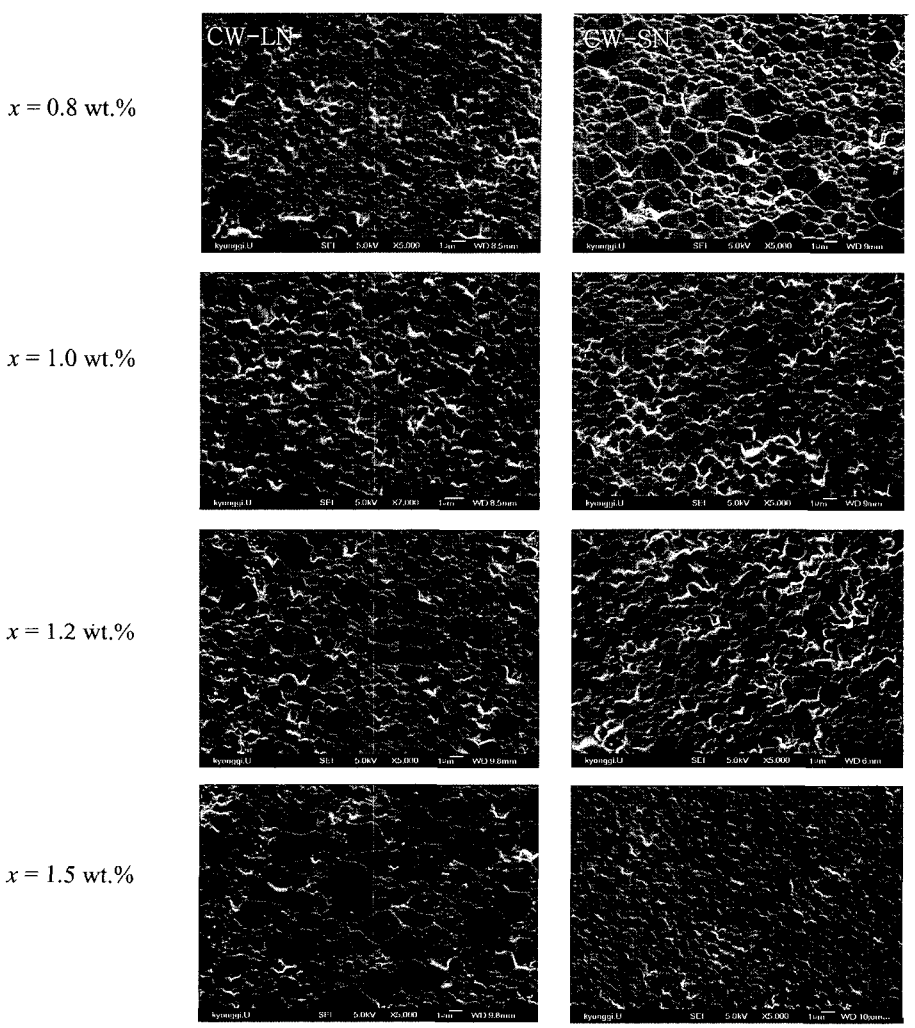

Fig. 3. SEM photographs of $0.85CaWO_4$-$0.15LnNbO_4$ (Ln = La, Sm) with x wt.% Li_2WO_4. Specimens were sintered at 900°C for 1h.

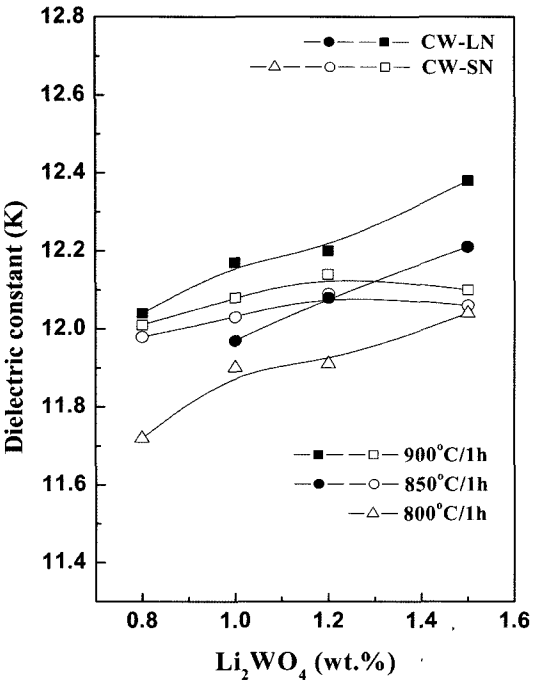

Fig. 4. Dielectric constant (K) of $0.85CaWO_4$-$0.15LnNbO_4$ (Ln = La, Sm) with Li_2WO_4. Specimens were sintered from 800 to 900°C for 1h.

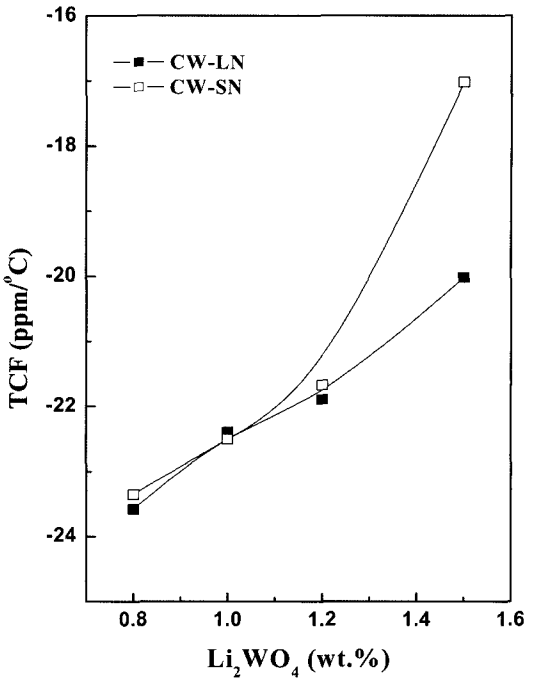

Fig. 6. Temperature coefficient of resonant frequency (TCF) of $0.85CaWO_4$-0. $15LnNbO_4$ (Ln = La, Sm) with Li_2WO_4. Specimens were sintered at 900°C for 1h.

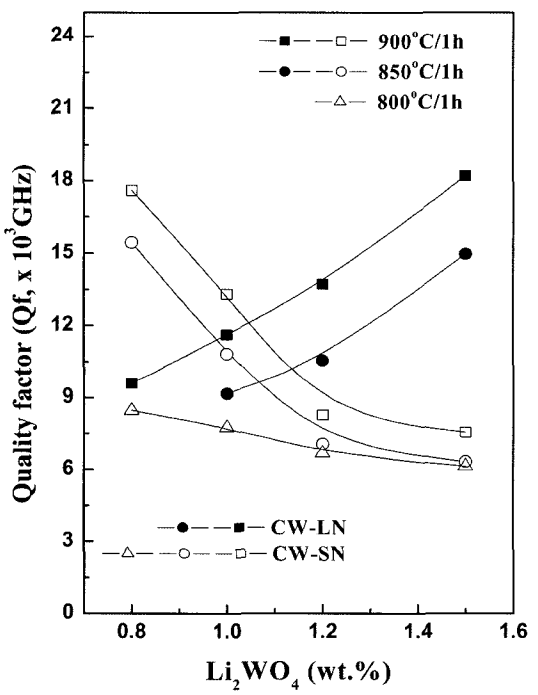

Fig. 5. Quality factor (Qf) of $0.85CaWO_4$-$0.15LnNbO_4$ (Ln = La, Sm) with Li_2WO_4. Specimens were sintered from 800 to 900°C for 1h.

$LaNbO_4$ (18.08Å) than that of $SmNbO_4$ (16.75Å).[4]

Fig. 5 shows the quality factor (Qf) of $0.85CaWO_4$-$0.15LnNbO_4$ (Ln = La, Sm) specimens sintered from 800 to 900°C for 1h as a function of Li_2WO_4 content. It has been reported that the Qf value depends on the intrinsic loss is mainly caused by a lattice vibration mode as well as the extrinsic factors such as microstructure, secondary phases and density, and grain size.[10] However, effect of density on the Qf values of the $0.85CaWO_4$-$0.15LnNbO_4$ (Ln = La, Sm) specimens sintered at 900°C could be neglected because the relative density was higher than 95%.[10] And then, the complete solid solutions of specimens were obtained through the entire composition range and no remarkable changes were found in XRD patterns with Li_2WO_4 content, as shown in Fig. 1. With the increase of Li_2WO_4 content, Qf value of the specimens with $SmNbO_4$ was decreased, while that of the specimens with $LaNbO_4$ was increased. These results are due to the changes in the grain size, as confirmed in Fig. 3. For the specimens with same composition, Qf value was increased with the sintering temperature.

Fig. 6 shows the temperature coefficient of resonant frequency (TCF) of $0.85CaWO_4$-$0.15LnNbO_4$ (Ln = La, Sm) specimens sintered at 900°C for 1h as a function of Li_2WO_4 content. TCF was slightly shifted to the positive value with Li_2WO_4 content. These results are

agreed with the report[12),13)] that *TC*F was increased to the positive value with the amount of additives.

4. Conclusion

Effects of Li_2WO_4 on the sinterbility and microwave dielectric properties of $0.85CaWO_4$-$0.15LnNbO_4$ (Ln = La, Sm) ceramics were investigated. $0.85CaWO_4$-$0.15LnNbO_4$ (Ln = La, Sm) with scheelite structure was obtained through the entire composition range and no remarkable changes in XRD patterns with Li_2WO_4 content. Dielectric constant (K) with Li_2WO_4 content depended on the changes of density and polarizability. With the increase of Li_2WO_4 content, Qf value of the specimens with $SmNbO_4$ was decreased, while that of the specimens with $LaNbO_4$ was increased. These results were due to the effects of microstructure. *TCF* was slightly shifted to the positive value with Li_2WO_4 content. With the addition of Li_2WO_4 content, the sintering temperature of the specimens was reduced from 1150 to 900°C.

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