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Affecting factors on low-temperature sintering of $0.85CaWO_4$-$0.15SmNbO_4$ ceramics

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Abstract This study was focused on the effect of sintering additive and particle size on the low temperature sintering of $0.85CaWO_4$-$0.15SmNbO_4$ ceramics. With an increase of CaV_2O_6 content, the sintering temperature of the specimens was reduced from 1150°C to 800°C. The dielectric constant (K) and Qf value were increased with CaV_2O_6 content. These results are due to the enhancement of the density by the liquid phase sintering. Temperature coefficient of resonant frequency (TCF) was slightly shifted to the positive value with CaV_2O_6 content. Typically, K of 12.64, Qf of 23,106 GHz, TCF of −34 ppm/°C were obtained for the specimens with 7 wt.% CaV_2O_6 sintered at 900°C for 3 h.

Key words $0.85CaWO_4$-$0.15SmNbO_4$, Dielectric properties, Milling, Sintering

1. Introduction

Low temperature co-fired ceramics (LTCC) have been widely investigated due to their applications for the multilayer microwave components which can miniaturize the microwave devices. In the multilayer structures, the sintering temperature of the dielectric materials has to be reduced to or below 900°C so as to co-fired with highly conductive embedded electrode such as Ag (the melting point of Ag is about 961°C). Therefore, it is important to reduce the sintering temperature of microwave dielectric materials with good properties for the practical applications.

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].

A recent investigation [4] has shown the attrition mill to be highly effective device for rapid grinding of solid materials to sizes as small as 20 nm equivalent spherical diameter, having very large surfaces areas. This milling method has promise in producing high-quality ceramic powders for sintering and other uses.

From our preliminary research, $0.85CaWO_4$-$0.15SmNbO_4$ sintered at 1150°C for 3 h showed good microwave dielectric properties, K of 11.6, Qf of 61000, TCF of −25.0 ppm/°C [5], which could be applicable to the substrate materials with high signal propagation velocity. However sintering temperature was too high to co-fire with Ag electrode. Also, CaV_2O_6 is a good candidate to reduce the sintering temperature of $0.85CaWO_4$-$0.15SmNbO_4$ because the melting point of CaV_2O_6 is 778°C [6].

Therefore this study was focused on the effect of sintering additive and particle size on the low temperature sintering of $0.85CaWO_4$-$0.15SmNbO_4$ ceramics. Also, the dielectric properties and physical properties of the ceramics were investigated as a function of the sintering temperature and CaV_2O_6 content from 3 wt.% to 9 wt.%.

2. Experimental

High-purity oxide powders of $CaCO_3$ (99.0 %), WO_3 (99.9 %), Sm_2O_3 (99.9 %), Nb_2O_5 (99.9 %), V_2O_5 (99.9 %) were used as starting materials. $CaWO_4$ and $SmNbO_4$ were calcined at 700°C and 1100°C for 3 h, respectively. These calcined powders were weighed according to the composition of $0.85CaWO_4$-$0.15SmNbO_4$, and then milled with ZrO_2 balls for 24 h in ethanol (99.9 %). Two different sets of powder mixtures were prepared to investigate the effects of particle size. The details are given in Table 1. The slurries of powder mixtures were dried and re-milled for 24 h with addition of CaV_2O_6, which was synthesized by the calcinations of $CaCO_3$ and V_2O_5 at 550°C for 3 h. The powders were isostatically pressed into a 15 mm diameter disks under a pressure of 1450 kg/cm^2, followed by a sintering at 800~900°C for 3 h at a heating rate of 300°C/h in air.

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Table 1
Powder Preparation and milling methods

Name	Starting materials	Calcination	Milling	Average particle size	Additive
Set1 (AM)	$0.85CaWO_4$-$0.15SmNbO_4$	1100°C/3 h	Attrition-milling (700 rpm/2 h)	0.39 μm	CaV_2O_6 (3~9 wt.%)
Set2 (BM)			Ball-milling (10 h)	1.39 μm	

Average particle size and the distribution were measured by the diffraction particle sizer (Mastersizer Micro plus, Malvern Co., England). Powder X-ray diffraction analysis (D/Max-3C, Rigaku Co., Japan) was used to determine the crystalline phases of the calcined and the sintered specimens. The apparent density of the sintered specimens was obtained using ASTM C373-72. The microstructures of the specimens were observed by scanning electron microscopy (SEM, JEOL JSM-6500F, Japan). Dielectric constant (K) and Qf value of the sintered specimens were measured by the post resonant method developed by Hakki and Coleman [7] at 7~9 GHz. The temperature coefficient of resonant frequency (TCF) was measured by cavity method [8] in temperature range from 25°C to 80°C.

3. Results and Discussion

Figure 1 shows the analysis of average size distribution of powders obtained by an attrition-milling (AM) and a ball-milling (BM), respectively. From analysis results, the particle size distribution prepared by an attrition-milling for 2 h (AM) seems to be a uniform, while that of prepared by a conventional ball-milling for 10 h (BM) showed a bimodal.

Figure 2 shows the morphology of powders obtained from different milling conditions. The powders prepared by AM lead to fair grains, whereas the powders obtained by BM showed irregular rectangular grains. Due to the differences of grain shapes with milling method, the average particle size of powders prepared by AM was smaller than that of a BM, and then the particle size was 0.39 μm for AM and 1.39 μm for BM, respectively, as shown in Fig 1.

Figure 3 shows X-ray diffraction patterns of $0.85CaWO_4$-$0.15SmNbO_4$ specimens sintered at 900°C for 3 h, as a function of CaV_2O_6 content and milling conditions. The complete solid solutions with the $CaWO_4$ type of the tetragonal scheelite structure were obtained, and no secondary phase was detected through the entire composition range. It could be predicted that CaV_2O_6 did not chemically reacted with $0.85CaWO_4$-$0.15SmNbO_4$ and only existed as liquid phase at sintering temperature. Similar tendency of XRD patterns was obtained for the specimens sintered from 800°C to 850°C for 3 h.

Figure 4 shows SEM micrographs of $0.85CaWO_4$-$0.15SmNbO_4$ specimens sintered at 900°C for 3 h with various CaV_2O_6 content. With increasing CaV_2O_6 content, the grain size of the specimens prepared by BM was increased. For the specimens prepared by AM, the grain size was increased with CaV_2O_6 content up to 7 wt.% and then slightly decreased.

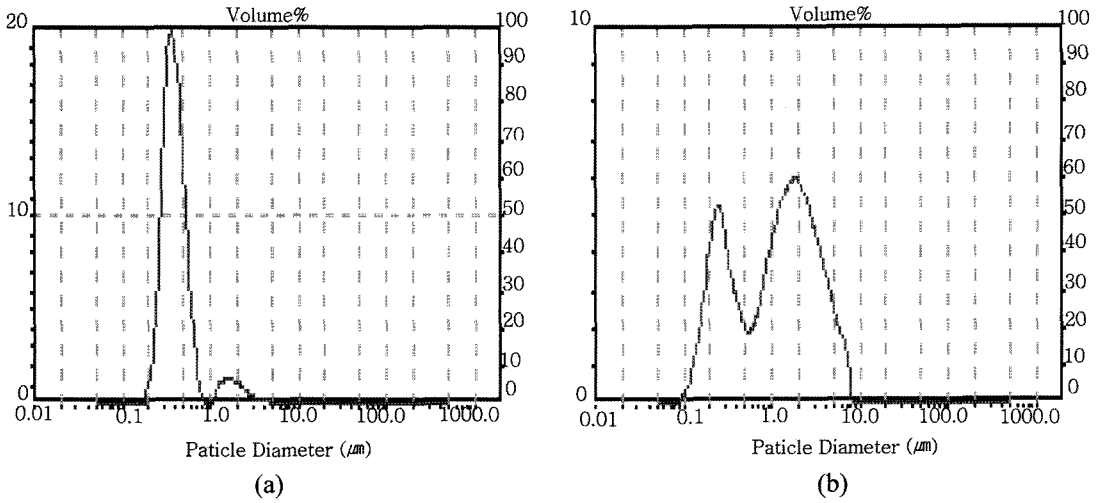

Fig. 1. Analysis of particle size distribution; (a) Attrition-milling, (b) Ball-milling.

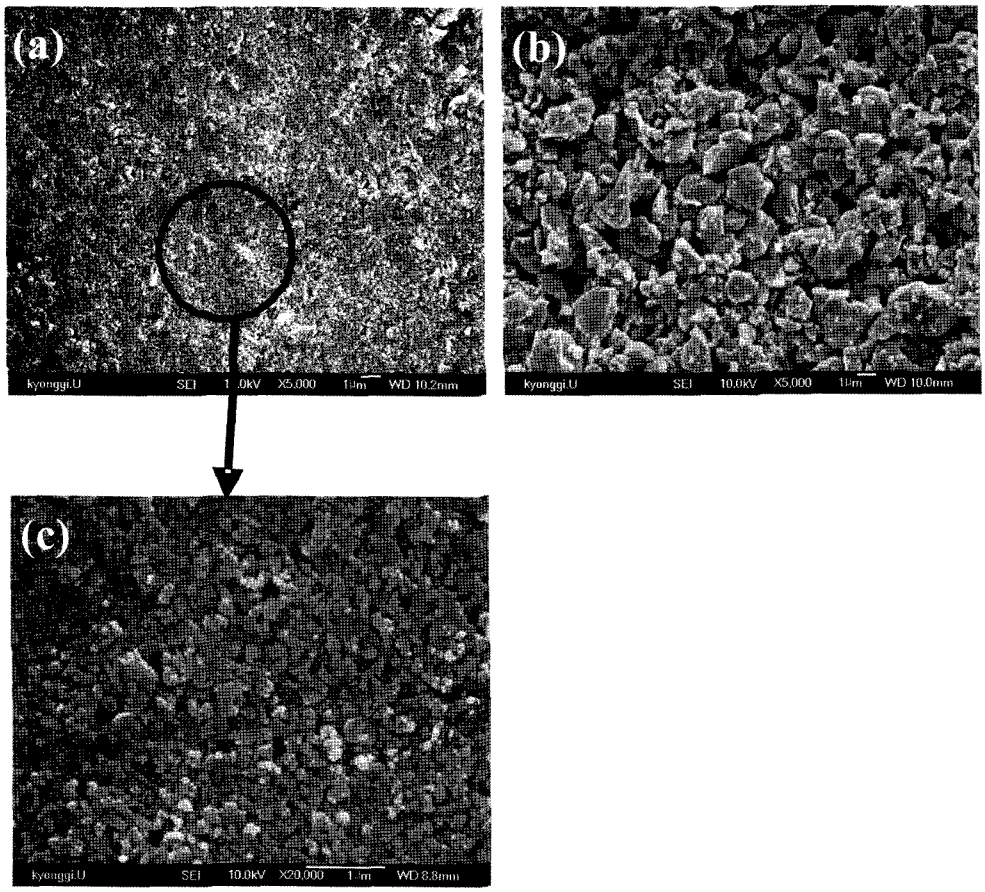

Fig. 2. Morphology of milled powders obtained with different milling conditions; (a) Attrition-milling (× 5000), (b) Ball-milling (× 5000), (c) Attrition-milling (× 20000).

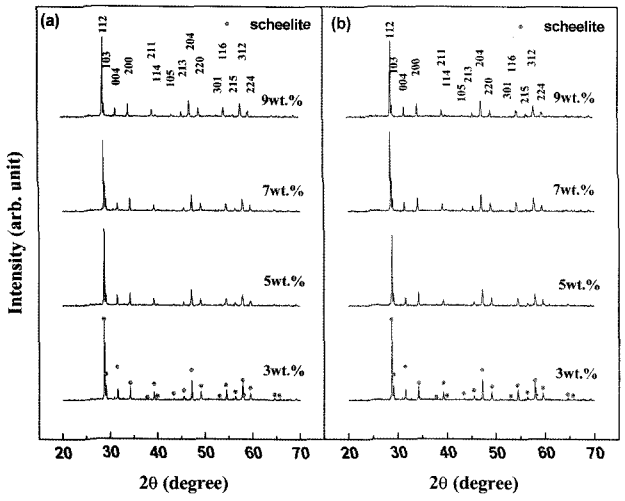

Fig. 3. X-ray diffraction pattern of $0.85CaWO_4$-$0.15SmNbO_4$ specimens with CaV_2O_6 sintered at 900°C for 3 h; (a) Attrition-milling, (b) Ball-milling.

Figure 5 shows apparent densities of $0.85CaWO_4$-$0.15SmNbO_4$ specimens sintered from 800°C to 900°C for 3 h, as a function of CaV_2O_6 content and milling conditions. The sintered density of the specimens prepared by AM as well as BM was dependent on the sintering temperature as well as CaV_2O_6 content. For the specimens prepared by AM, the specimens with 7 wt.% CaV_2O_6 sintered at 900°C for 3h showed the similar density of pure $0.85CaWO_4$-$0.15SmNbO_4$ sintered at 1150°C for 3 h [5]. However, density of the specimens prepared by AM was increased up to 7 wt.% and then slightly decreased. These results are agreed with the result of microstructure in Fig. 4. Comparing to the density of the specimens sintered at 900°C, the sintered density was improved by the addition of CaV_2O_6 for the specimens sintered at 800°C and/or 850°C. For the same sintering conditions, apparent density of the specimens prepared by AM was higher than that of the specimens prepared by BM. These results are due to the increase of sinterability resulted from the smaller particle size.

Figure 6 shows microwave dielectric properties of $0.85CaWO_4$-$0.15SmNbO_4$ specimens sintered at 900°C for 3 h. For the specimens prepared by BM, the microwave dielectric properties of specimens with 3 wt.% CaV_2O_6 sintered from 800°C to 900°C could not be measured due to the lower density, as confirmed in Fig.

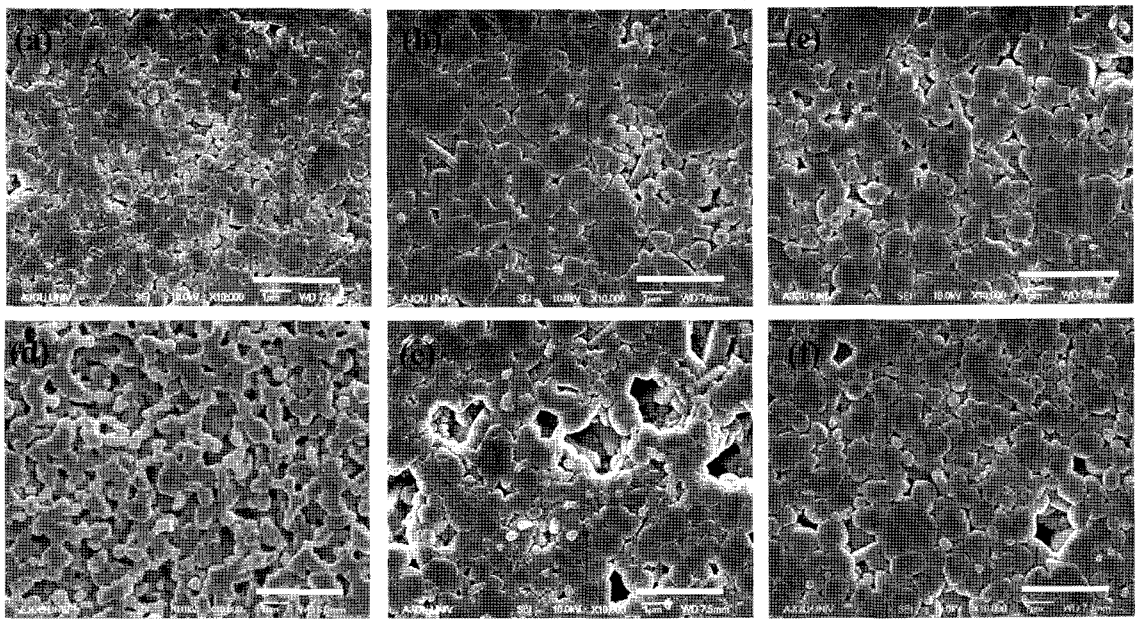

Fig. 4. SEM photographs of the specimens sintered at 900°C for 3 h as a function of milling condition and CaV_2O_6 (x); (a) AM, x = 3 wt.% (b) AM, x = 7 wt.% (c) AM, x = 9 wt.% (d) BM, x = 3 wt.% (e) BM, x = 7 wt.% (f) BM, x = 9 wt.%.

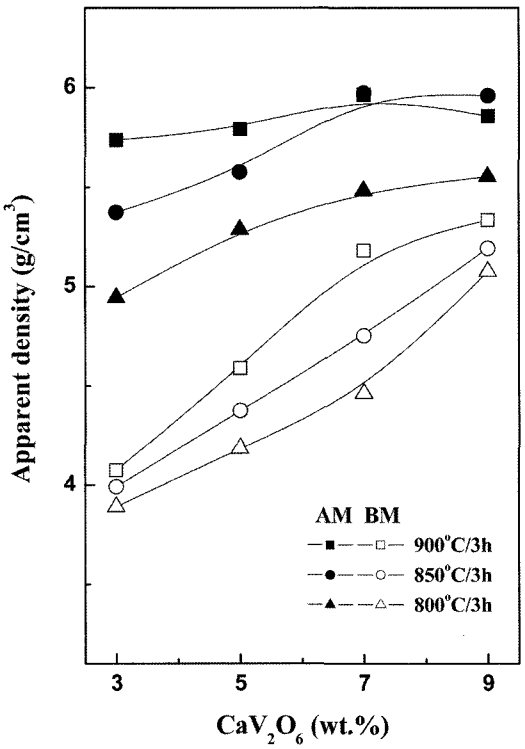

Fig. 5. Apparent density of $0.85CaWO_4$-$0.15SmNbO_4$ specimens with CaV_2O_6 sintered from 800 to 900°C for 3 h.

5. For the specimens prepared by AM as well as BM, the dielectric constant (K) increases with CaV_2O_6 content. K of the specimens prepared by AM sintered at 900°C for 3 h was increased up to 7 wt.% CaV_2O_6 and then slightly decreased, which was consistent with the variation of density in Fig. 5. K of the specimens prepared by AM was higher than that of a BM due to the difference of density. Therefore, K of $0.85CaWO_4$-$0.15SmNbO_4$ with CaV_2O_6 content was depended on the density and microstructure of the specimens.

It has been reported that Qf value was dependent on the secondary phase, density, impurities and grain size [9]. Complete solid solutions of specimens were obtained through the entire composition range and no remarkable changes were found in XRD patterns with CaV_2O_6 content, as shown in Fig. 3. Qf value of the specimens was increased with the increase of sintering temperature and CaV_2O_6 content. These results are due to the enhancement of the density and grain size of the specimens with CaV_2O_6 content, as confirmed in Fig. 4. However, the specimens prepared by AM with CaV_2O_6 sintered at 900°C for 3 h was increased with the increase of CaV_2O_6 content up to x = 7 wt.% and then decreased due to the increase of porosity, as shown in Fig. 4. For the specimens with same CaV_2O_6 content, Qf value was increased with the sintering temperature. Moreover, the Qf value of the prepared by AM was higher than that of a BM due to the increase of sinterability resulted from the smaller particle size.

Temperature coefficient of resonant frequency (TCF) was slightly shifted to the positive value with CaV_2O_6 content. These results are agreed with the report that TCF was increased to the positive value with the amount of additives [10, 11]. For the specimens sin-

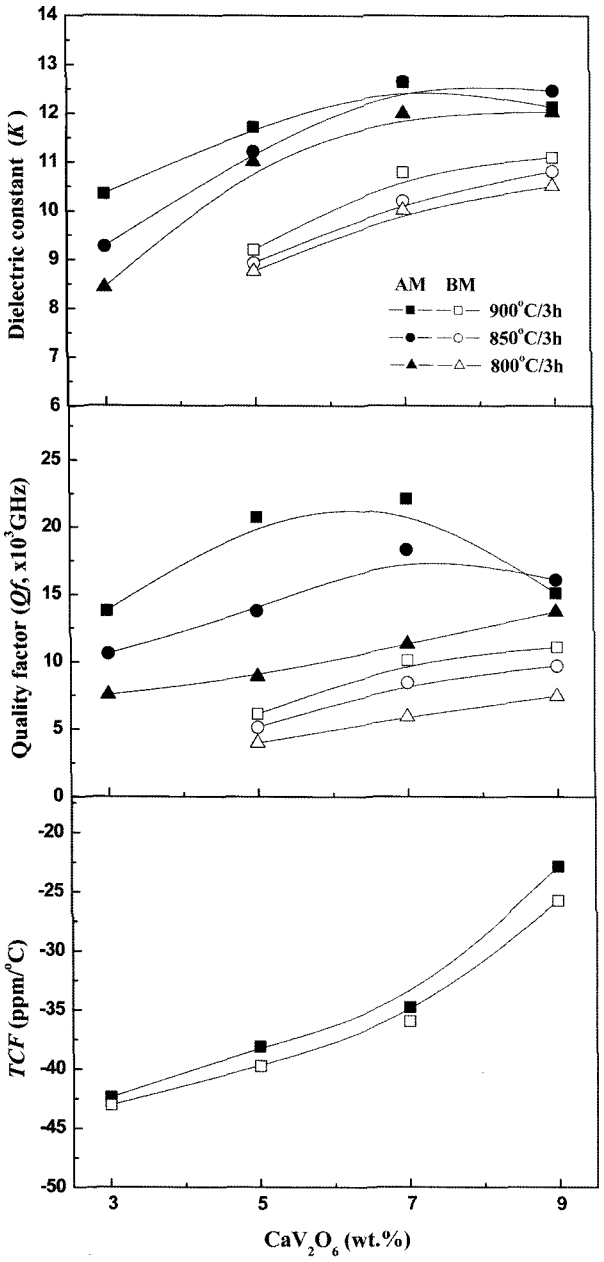

Fig. 6. Microwave dielectric properties of $0.85CaWO_4$-$0.15SmNbO_4$ specimens with CaV_2O_6 sintered from 800 to 900°C for 3 h.

tered at 900°C, *TCF* of the specimens prepared by AM was larger than that of the specimens prepared by BM. These results could be attributed to the increase of sinterability resulted from the smaller particle size.

4. Conclusion

The effects of sintering agent CaV_2O_6 and particle size on the microwave dielectric properties of $0.85CaWO_4$-$0.15SmNbO_4$ ceramics was investigated as a function of sintering temperature. For the specimens of $0.85CaWO_4$-$0.15SmNbO_4$ sintered from 800°C to 900°C for 3 h, a single phase with tetragonal scheelite structure was obtained with CaV_2O_6 content from 3 wt.% to 9 wt.%. With the increase of CaV_2O_6 content, dielectric constant (K) and Qf value of the specimens was increased with the increase of the sintering temperature. These results are due to the enhancement of the density by liquid phase sintering of CaV_2O_6 with low melting point of 778°C. Microwave dielectric properties of the specimens prepared by AM were larger than those of the specimens prepared by BM due to the enhancement of the density by smaller particle size. For the specimens sintered 900°C by AM, however, K and Qf of the specimens with 9 wt.% CaV_2O_6 were decreased due to the increase of porosity. Temperature coefficient of resonant frequency (*TCF*) was shifted to the positive value with the increase of CaV_2O_6 content. The addition of CaV_2O_6 as a sintering agent to $0.85CaWO_4$-$0.15SmNbO_4$ could lower the sintering temperature up to 800°C.

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