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Microwave dielectric properties and sintering behaviors of scheelite compound $CaMoO_4$

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Abstract

The microwave dielectric properties, sintering behaviors of scheelite compound $CaMoO_4$ were investigated using dilatometry, X-ray diffraction, scanning electron microscopy and network analyzer. To improve the sintering property of $CaMoO_4$, samples with different Ca/Mo ratio were prepared. The bulk densities of $CaMo_{(x)}O_4$ (for $x = 1.02$, 1.05, 1.08) samples were higher than those of pure $CaMoO_4$ over all temperature range. The well-sintered $CaMo_{(x)}O_4$ (for $x = 1.02$) sample with ~95.7% of the theoretical density shows $Q \times f$ value of 71,000 GHz and dielectric constant (ε_r) = 10.3. The effects of liquid phase formation on sintering process and dielectric properties were discussed. Sample with hot-press sintering was also prepared in order to investigate dielectric properties of fully dense $CaMoO_4$, which exhibited quality factor ($Q \times f$), ~55,000 GHz and dielectric constant (ε_r) = 11.7.

Keywords: Hot pressing; Sintering; Porosity; Substrates

1. Introduction

Recently, Molybdenum (Mo) containing mixed oxides have been of practical interest because of their attractive luminescence property[1] and possibility of negative electrode (anode) materials.[2,3] The scheelite compound has been investigated as a host crystal for laser applications. Also, the dielectric constant and the anisotropy of the dielectric constant (ε') of single crystals (grown by the Czochralski method) were firstly reported by Brower and Fang.[4] The dielectric constant (ε') parallel to *a*-axis of $CaMoO_4$ single crystal was 24.0 ± 0.2; parallel to *c*-axis, 20.0 ± 0.2 at 1.59 kHz. The dielectric loss ($\tan \delta$) for both orientations of $CaMoO_4$ specimen was 10^{-3} or less. Unfortunately, not many works have been done on the dielectric properties for microwave application.

Dielectric ceramic substrate with low permittivity and high-*Q* is required to minimize cross-coupling with conductors and to maintain overall high-*Q* circuits by lowering power dissipation. Alumina ($\varepsilon_r = 10$, $Q \times f = 100{,}000$, $\tau_f = -50$ ppm/°C) is the standard material for the manufacturing of hybrid circuits via thick or thin film technology and for high integrated multilayer circuits produced via co-firing of metallized green tapes. We thought that $CaMoO_4$ ceramic could be selected as a possible candidate for microwave dielectric material because of its low permittivity and high-*Q* ($\varepsilon_r = 11.7$, $Q \times f = 55{,}000$, $\tau_f = -60$ ppm/°C), such alumina.

To investigate possibility of microwave application of $CaMoO_4$ ceramic, the sintering behavior and microwave dielectric properties of dense $CaMoO_4$ ceramic were examined. In our study, as a way of obtaining fully dense ceramic, the specimens were uniaxially pressed during sintering at 1100 °C for 1 h under pressure of 16 MPa (hot-press method). But hot-press method has many problems on the commercial uses, so the samples with different Ca/Mo ratio were prepared to control sintering behavior of $CaMoO_4$.

2. Experimental procedure

The powders were prepared by conventional mixed oxide method. $CaCO_3$, MoO_3 (High Purity Chemical Lab., Japan) powders with 99.99 and 99.9% purity were weighed and mixed for 24 h with stabilized zirconia media and ethanol. The mixed slurry was dried and then powders were calcined at 800–1100 °C for 2 h in air and then the calcined powder was granulated with an organic binder after ball milling for 24 h. The milled powders

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were uniaxially pressed into disks 8 mm in diameter and 2–4 mm thick under a pressure of 1000 kg/cm^2. Pellets were sintered at 900–1350 °C for 2 h in air with a heating rate of 5 °C/min. The bulk density of the sintered specimens was determined by the Archimedes' method.

To obtain dense samples, the specimens were uniaxially pressed during sintering at 1100 °C for 1 h under pressure of 16 MPa. Shrinkage of the specimens during heating was measured using a horizontal-loading dilatometer with Al_2O_3 rams and boats (Model DII, 420C, Netzsch Instruments, Germany). The X-ray powder diffraction (XRD) studies were performed with X-ray diffractometer (XRD: Model M18XHF, Mac Science Instruments, Japan). Polished and thermally etched surfaces of sintered specimens were examined using scanning electron microscopy (SEM: Model XL20, Philips, The Netherlands). The microwave dielectric properties of sintered samples were measured at x-band frequencies (14–17 GHz) using a network analyzer (model HP8720C, Hewlett Packard, Palo Alto, CA). The quality factor ($Q \times f$) was measured by the transmission cavity method using a Cu cavity and Teflon supporter.[5] Relative dielectric constant (ε_r) was measured using the post-resonator method[6] and temperature coefficient of resonant frequency (τ_f) was measured using an Invar cavity in the temperature at range 20–85 °C.[7]

3. Results and discussion

3.1. Sintering behavior of $CaMo_{(x)}O_4$

Fig. 1 shows bulk densities of pure $CaMoO_4$ and the samples with different Ca/Mo ratio, which are $CaMo_{(x)}O_4$ (Ca/Mo = 1/x for x = 1.0, 1.02, 1.05, 1.08) as a function of sintering temperature. The densities of pure $CaMoO_4$ sample significantly decreased at temperature range from 1200 to 1300 °C and has the maximum value of ∼3.85 g/cm^3 (∼90.6% of the theoretical density) at 1000 °C. This result suggests that pure $CaMoO_4$ sample has poor densification characteristic. On the other hand, the densities of $CaMo_{(x)}O_4$ (for x = 1.02, 1.05, 1.08) samples slightly increased with increasing the sintering temperature and decreased with increasing x. The bulk density of $CaMo_{(x)}O_4$ (for x = 1.02) has the maximum value of ∼4.07 g/cm^3 (∼95.7% of the theoretical density) at 1300 °C. The bulk density of hot pressed sample sintered at 1100 °C under pressure of 16 MPa was ∼4.25 g/cm^3 (∼99.9% of the theoretical density). The bulk density of pure $CaMoO_4$ was lower than those of $CaMo_{(x)}O_4$ (for x = 1.02, 1.05, 1.08) over all temperature range. It was considered that densification characteristic of $CaMo_{(x)}O_4$ samples (for x = 1.02, 1.05, 1.08) was better than that of pure $CaMoO_4$ sample. The decrease in density of pure $CaMoO_4$ with increasing sintering temperature was revealed with microstructural investigation.

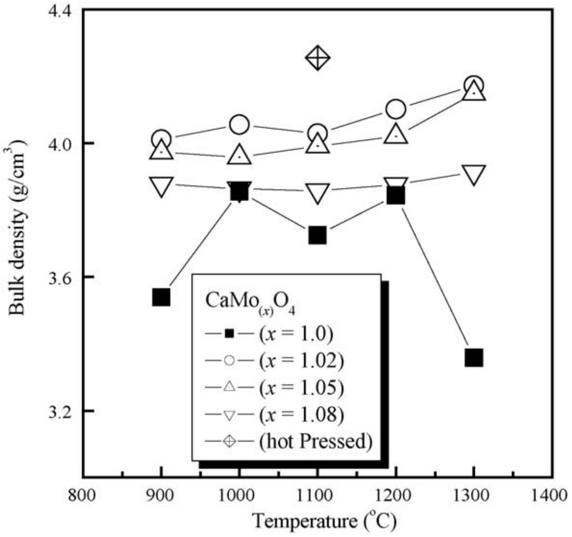

Fig. 1. Bulk densities of $CaMo_{(x)}O_4$ samples as a function of sintering temperature.

Fig. 2 shows SEM micrograph of the $CaMo_{(x)}O_4$ specimens (for x = 1.0, 1.02, 1.08) sintered at 1200–1300 °C for 2 h and hot-pressed at 1100 °C for 1 h under pressure of 16 MPa. The average grain size of pure $CaMoO_4$ samples increased abruptly from 4.5 (Fig. 2(a)) to 18 μm (Fig. 2(b)) with increasing sintering temperature from 1200 to 1300 °C. Dense microstructure was not achieved with increasing sintering temperature. Besides, the grains of $CaMoO_4$ sample sintered at 1300 °C for 2 h (Fig. 2(b)) have micro-crack. This result corresponds well the decrease in the density of pure $CaMoO_4$ with increasing sintering temperature from 1200 to 1300 °C. As shown in Fig. 2(c) and (d), the microscope images of hot pressed $CaMoO_4$ at 1100 °C for 1 h under 16 MPa and $CaMo_{(x)}O_4$ (for x = 1.02) show dense and fine microstructure. The average grain size of the $CaMo_{(x)}O_4$ sintered at 1200 °C increased from 3.5 (Fig. 2(d)) to 12 μm (Fig. 2(e)) with increasing x from 1.02 to 1.08. In addition of more excess Mo ions, grain growth was not accompanied with reduction of porosity, as shown in Fig. 2(e). The densification process is usually inhibited by rapid grain growth. This microstructure variation was consistent with the decrease in density of $CaMo_{(x)}O_4$ (for x = 1.02, 1.05, 1.08) with increasing x.

Fig. 3 shows shrinkage curves of the green compact of $CaMo_{(x)}O_4$ samples (for x = 1.0, 1.02, 1.05, 1.08). The shrinkage of pure $CaMoO_4$ occurred at broad temperature range (700–1200 °C) and final shrinkage (%) was less than 12%. The onset of $CaMo_{(x)}O_4$ (for x = 1.02, 1.05, 1.08) shrinkage occurred at lower temperature and the rapid shrinkage occurred at narrow temperature region (600–800 °C). As x increased, final shrinkage (%) was also increased. For $CaMo_{(x)}O_4$ (x = 1.08) sample, final shrinkage (%) was about ≈15%. In CaO–MoO_3 phase diagram, MoO_3–$CaMoO_4$ system has a binary eutectic temperature at 726 ± 3 °C and MoO_3 = 25 wt.%.[8] So sintered samples of $CaMo_{(x)}O_4$ (x = 1.02, 1.05, 1.08) could have solid $CaMoO_4$ phase and liquid MoO_3 phase over the eutectic temperature. Given that different Ca/Mo ratio system has more liquid MoO_3 phase with increasing x, which might suggest changes in final shrinkage (%). In Fig. 2(d) and (e), it is postulated that the abrupt grain growth of the $CaMo_{(x)}O_4$ sample sintered at 1200 °C with increasing x from 1.02 to 1.08 was caused by MoO_3 rich liquid phase. This results indicate that MoO_3 rich liquid phase could act as a sintering aid for $CaMo_{(x)}O_4$ (for x = 1.02, 1.05, 1.08).

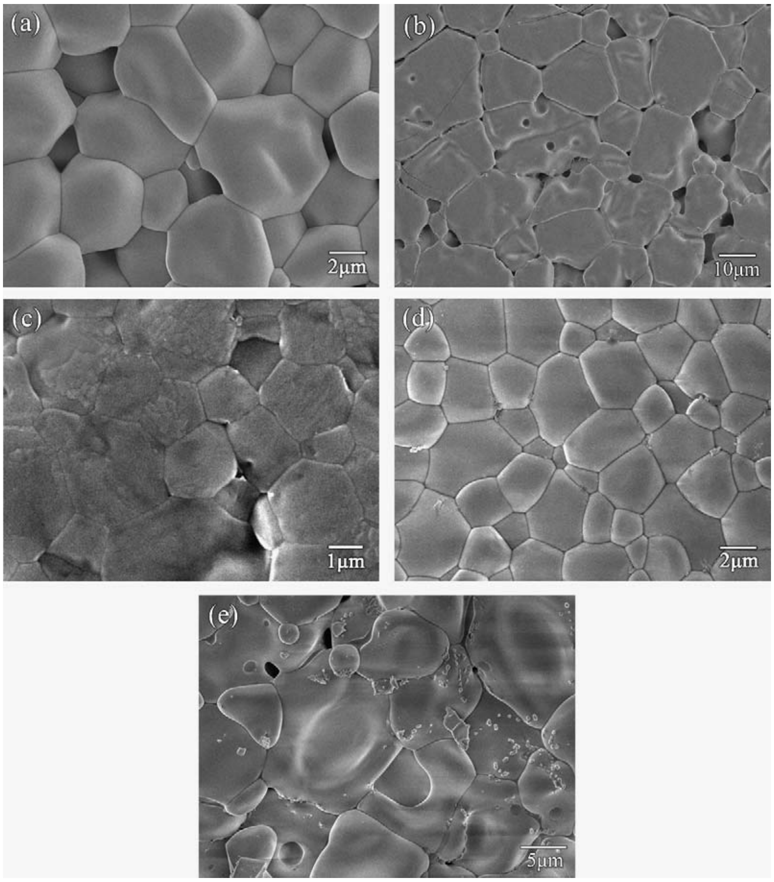

Fig. 2. SEM micrograph of the $CaMoO_4$ specimen: (a) sintered at 1200 °C for 2 h, (b) sintered at 1300 °C for 2 h, (c) hot-pressed at 1100 °C for 1 h under pressure of 16 MPa, (d) $CaMo_{(x)}O_4$ ($x = 1.02$) sintered at 1200 °C for 2 h, and (e) $CaMo_{(x)}O_4$ ($x = 1.08$) sintered at 1200 °C for 2 h.

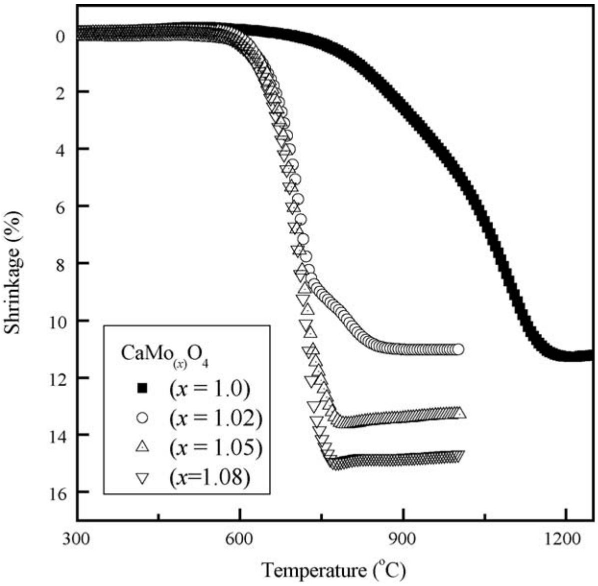

Fig. 3. Shrinkage curves of $CaMo_{(x)}O_4$ samples as a function of sintering temperature.

As shown in Fig. 4(a)–(d), with increasing x, remained MoO_3 phase was increased. It seemed that MoO_3 liquid phase would act as a sintering aid over the eutectic temperature and solely crystallized without formation of another phase under cooling.

It is considered that pure $CaMoO_4$ sample shows lower sinterability that is lower density and dielectric constant, as might be expected, is to be low with comparing that of $CaMoO_4$ (for $x = 1.02$). It is found that different Ca/Mo ratio could control the sintering behavior and improve the sintering properties of $CaMoO_4$.

3.2. Microwave properties of $CaMo_{(x)}O_4$

Fig. 5 shows the microwave dielectric properties of $CaMo_{(x)}O_4$ samples sintered at temperatures range from 1000 to 1300 °C for 2 h and $CaMoO_4$ sample sintered at 1100 °C for 1 h under pressure of 16 MPa. In general, a higher density results in a higher dielectric constant owing to lower porosity ($\varepsilon_r = 1$). Because the sinterability of pure $CaMoO_4$ was poor, pure $CaMoO_4$ sintered at 1100 °C had lower dielectric constant (ε_r) of 9.2 than that of $CaMoO_4$ sample sintered at 1100 °C under 16 MPa ($\varepsilon_r = 11.7$), which well corresponds to density and SEM investigation.

In the case of different Ca/Mo ratio system, as x increased, dielectric constant of $CaMo_{(x)}O_4$ (for $x = 1.02$, 1.05, 1.08)

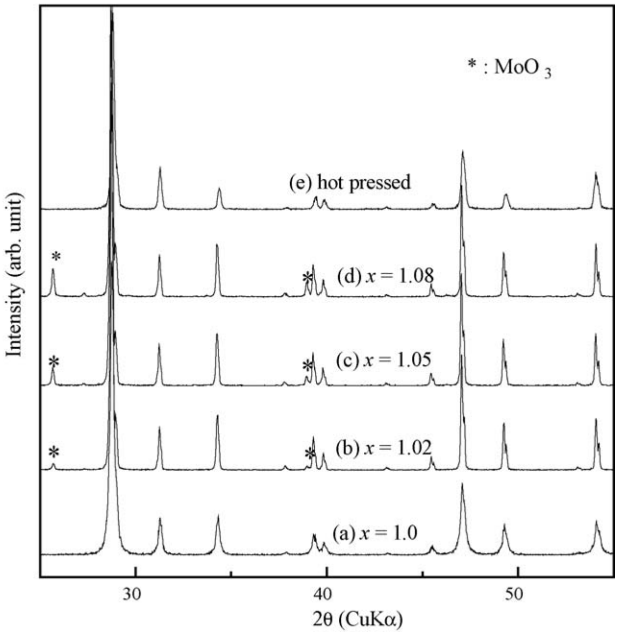

Fig. 4. XRD patterns of $CaMo_{(x)}O_4$ sintered at 1200 °C for 2 h: (a) $x = 1.0$, (b) $x = 1.02$, (c) $x = 1.05$, (d) $x = 1.08$, and (e) hot pressed at 1100 °C for 1 h under pressure of 16 MPa.

samples were decreased. In Section 3.1, we showed that grain growth with increasing x, which could be caused by MoO_3 rich liquid phase, could not reduce porosity in our system. It was found that the dielectric constant showed a close correlation with bulk density, as shown in Figs. 1 and 2. The presence of remaining MoO_3 ($\varepsilon_r = 6.3 \pm 0.02$)[9] phase could affect the decrease in the dielectric properties of $CaMo_{(x)}O_4$ samples, as shown in Fig. 4. For $CaMo_{(x)}O_4$ ($x = 1.02$) sample sintered at 1300 °C for 2 h, maximized dielectric constant (ε_r) and $Q \times f$ value was 10.3 and 71,000 GHz, respectively. It is well known that the Q value was influenced by many factors including bulk density, grain boundary, secondary phase, and other defects (extrinsic) as well as anharmonic lattice vibration (intrinsic). It was believed that the variation in $Q \times f$ factor was primarily correlated with the bulk density in this system, except that $CaMoO_4$ (for $x = 0.08$) and hot pressed sample, which would influenced by another factor. For example, the $Q \times f$ value of hot pressed sample (55,300 GHz) was lower than that of pure $CaMoO_4$ sample (61,600 GHz), regardless of higher density.

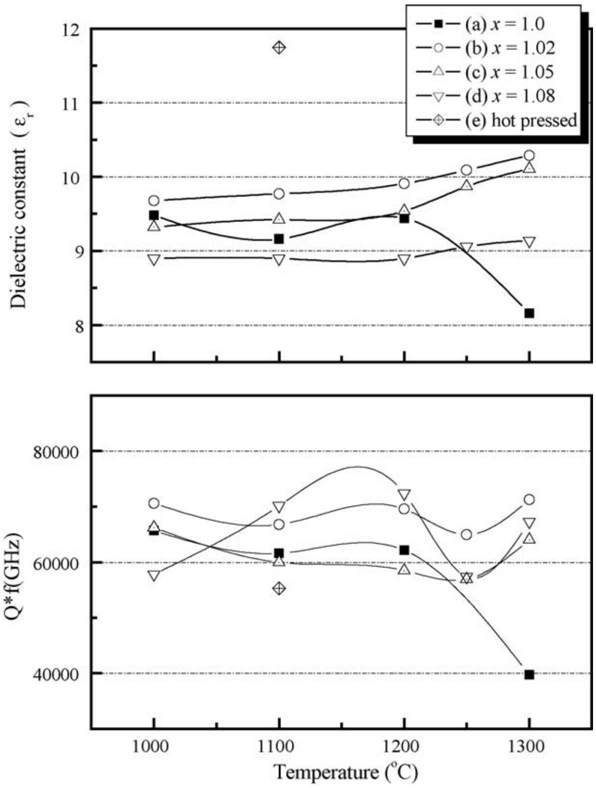

Fig. 5. Microwave properties of $CaMo_{(x)}O_4$ for: (a) $x = 1.0$, (b) $x = 1.02$, (c) $x = 1.05$, (d) $x = 1.08$, and (e) $x = 1.0$ (hot pressed at 1100 °C for 1 h under pressure of 16 MPa).

4. Conclusion

In our study, pure $CaMoO_4$ sample shows lower sinterability. So as a way to obtain fully dense ceramics, the sample prepared by hot pressing (uniaxially pressed at 1100 °C for 1 h under pressure of 16 MPa). Hot-pressed sample with ∼99% of the theoretical density exhibited $Q \times f$ value of ∼55,000 GHz and dielectric constant (ε_r) = 11.7. Because hot-press method was not suitable for commercializing, the samples with different Ca/Mo ratio were prepared to control sintering behavior of $CaMoO_4$. Different Ca/Mo ratio system successfully improved the sintering and dielectric properties of $CaMoO_4$, since MoO_3 rich liquid phase over the eutectic temperature act as sintering aid. $CaMo_{(x)}O_4$ (for $x = 1.02$) sample sintered at 1300 °C for 2 h with ∼95.7% of the theoretical density shows $Q \times f$ value of 71,000 GHz and dielectric constant (ε_r) = 10.3.

Consequently, $CaMo_{(x)}O_4$ ceramic can be selected as a suitable candidate for microwave dielectric material because of its low dielectric constant and high-Q.

Acknowledgments

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