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Mixture behavior and microwave dielectric properties of $(1-x)CaWO_4$–$xTiO_2$

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Abstract

The microwave dielectric characteristics and mixture behavior of $(1-x)CaWO_4$–$xTiO_2$ ceramics prepared with conventional solid-state route were studied using a network analyzer and X-ray power diffraction, respectively. The $CaWO_4$ compound had good properties (low permittivity and high quality factor) for microwave applications, but it had a high negative temperature coefficient of resonant frequency ($\tau_f = -53$). Hence, in order to tune the dielectric properties, $(1-x)CaWO_4$–$xTiO_2$ were prepared for different values of x. X-ray powder diffraction and SEM analysis revealed that $CaWO_4$ and TiO_2 coexisted as a mixture. The mixture formation and dielectric properties could be explained by mixture rule. In particular, at $x = 2.6$, good microwave dielectric properties were obtained: $Qf = 27{,}000$, $\varepsilon_r = 17.48$, and $\tau_f = \sim 0$ ppm/°C.

Keywords: Mixing; Composites; Dielectric properties; Tungstate; TiO_2

1. Introduction

According to the development of high-frequency communication technology, microwave dielectric materials with stable temperature coefficient of resonant frequency (near zero) and lower dielectric loss (higher quality factor value) have been required. Searching for microwave dielectric materials with both stable temperature coefficient of resonant frequency and higher quality factor is constantly needed in ceramic material research.[1] In our previous study, compounds with the general formula AWO_4 (A = Mg, Mn, Zn, Ca, Sr, Ba) are found promising materials for microwave substrate application.[2] These materials exhibit good microwave properties, high quality factor and low permittivity but with a high negative temperature coefficient resonant frequency around −50 ppm/°C. The most popular method of achieving stable temperature coefficient of resonant frequency is mixing materials, which have opposite value.[3] In this way mixed materials form solid solution or mixture and show stable temperature coefficient of resonant frequency. The present investigation revealed that the τ_f of $CaWO_4$ can be adjusted to zero with TiO_2 addition.

2. Experimental

The used starting materials were $CaCO_3$ (high purity chemicals, 99.99%), WO_3 (high purity chemicals, 99.9%) and TiO_2 (high purity chemicals, 99.9%). The $CaWO_4$ powders were prepared using conventional mixed oxide method by calcining at 800 °C for 2 h. $CaWO_4$ and TiO_2 powders were mixed for varying composition according to the formula $(1-x)CaWO_4$–$xTiO_2$ ($x = 0.0$, 0.1, 0.15, 0.2, 0.24, 0.25, 0.26, 0.3, 0.4, 0.5, 0.7, 0.9 and 1.0) and were ball-milled with ZrO_2 balls for 24 h using ethanol. After drying milled powders, it was granulated and mixed with 1 wt% of poly vinyl alcohol (PVA), dried and pressed at 1000 kg/cm^2 into the form of a pellet. The pellets were sintered in the temperature range of 1200–1300 °C for 2 h at a heating rate of 5 °C/min. The bulk density of the sintered sample was measured using the Archimedes' method. The phase constitution of the sintered sample was identified by X-ray powder diffraction (XRD: Model M18XHF, Mac Science Instruments, Japan) in the 2θ range of 20°–60°. The microstructure of the sintered samples was examined using a scanning electron microscope (SEM: Model JSM-5600, JEOL, Japan). The microwave dielectric properties were measured using a network analyzer (Model HP8720C, Hewlett Packard, U.S.A) in the frequency range of 8–12 GHz. The quality factor (Qf) was measured by the transmission cavity method using a Cu cavity and a Teflon

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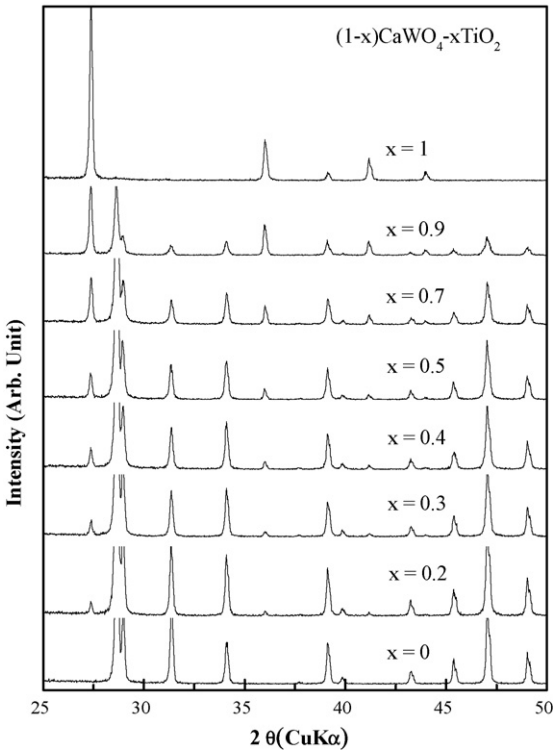

Fig. 1. Powder diffraction patterns of $(1-x)CaWO_4$–$xTiO_2$ mixed phases for $x = 0$, 0.2, 0.3, 0.4, 0.5, 0.7, 0.9 and 1.

supporter. The dielectric constant (ε_r) was measured using the post resonator method and the temperature coefficient of the resonant frequency (τ_f) was measured using an Invar cavity in the temperature range of 20–80 °C.

3. Result and discussion

Fig. 1 represents the X-ray diffraction (XRD) patterns for $x = 0$, 0.2, 0.3, 0.4, 0.5, 0.7, 0.9 and 1 in $(1-x)CaWO_4$–$xTiO_2$. With increasing TiO_2 content, the intensity of the reflections of $CaWO_4$ phase decreased and those of TiO_2 phase increased without peak shift. The XRD pattern data indicates that $CaWO_4$ and TiO_2 behave as mixture and not a solid solution and no second phase was found. Therefore, the dielectric properties of $(1-x)CaWO_4$–$xTiO_2$ are proportional to their variation of the molar concentration. Fig. 2 shows the morphologies of $CaWO_4$, mixture of $CaWO_4$ and TiO_2 and TiO_2. The $(1-x)CaWO_4$–$xTiO_2$ samples sintered at 1300 °C had over 97% relative density indicating that all samples have dense microstructure. Therefore, we could exclude the influence of porosity on the dielectric properties. The pure $CaWO_4$ (Fig. 2a) and TiO_2 (Fig. 2c) have large grains; on the other hand mixture of $CaWO_4$ and TiO_2 (Fig. 2b) has relatively small grain size. The grain size have influence on the dielectric properties especially quality factor. Fig. 2b seems that each grains have different phase, and this confirmed by BSE image in Fig. 3. The brighter grains are $CaWO_4$ and darker grains are TiO_2. The $CaWO_4$ and TiO_2 grains are randomly distributed and the average grain size of $CaWO_4$ is larger than that of TiO_2.

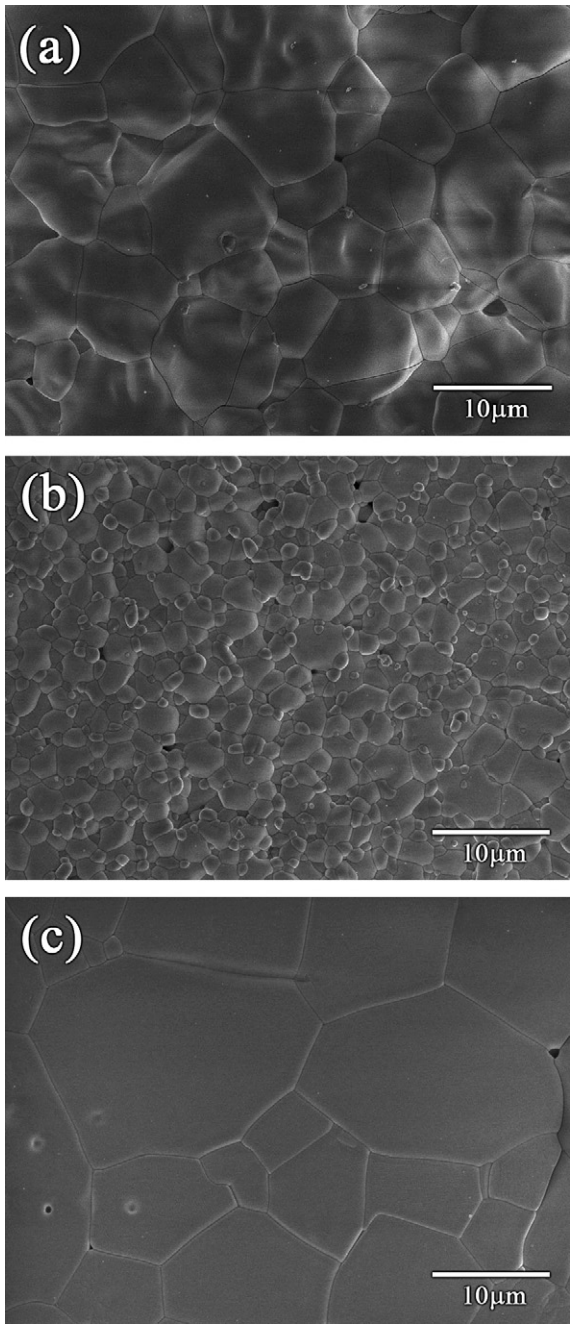

Fig. 2. Scanning electron micrographs of $(1-x)CaWO_4$–$xTiO_2$ samples sintered at 1300 °C for 2 h with (a) $x = 0$, (b) $x = 0.5$ and (c) $x = 1$.

The microwave dielectric properties of $CaWO_4$ are found to be interesting since the dielectric constant and loss of this composition is low enough for microwave substrate applications.[2] The variation of the dielectric constant of $(1-x)CaWO_4$–$xTiO_2$ is plotted in Fig. 4. The dielectric constant of $(1-x)CaWO_4$–$xTiO_2$ should lie between the values of the individual components. The most commonly used equation for predicting the dielectric constant of the mixture composition is the Maxwell–Wagner's equation shown in Eq. (1)[4]

$$\varepsilon_c = \nu_1\varepsilon_1 + \nu_2\varepsilon_2 \quad (1)$$

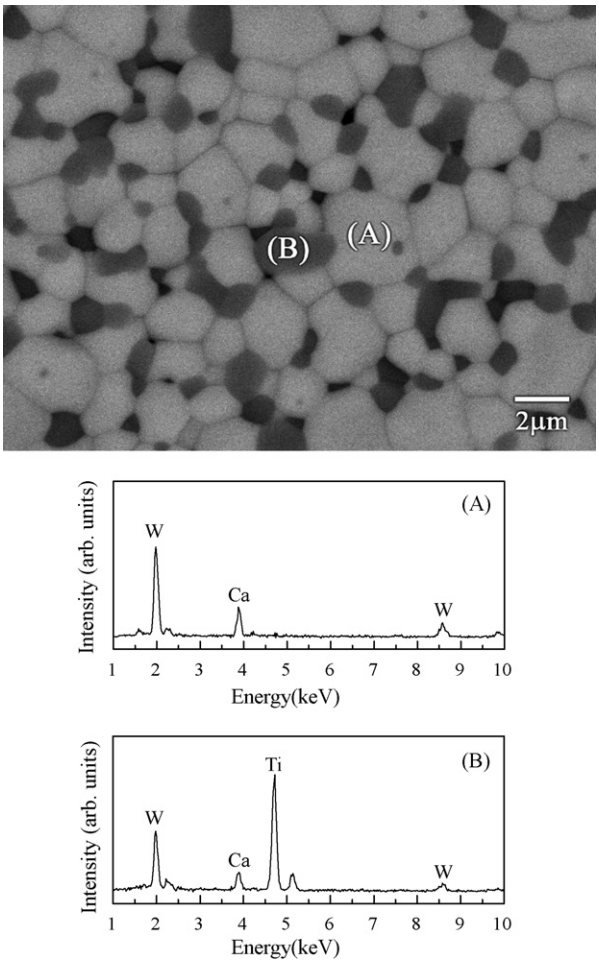

Fig. 3. BSE image and EDS spectra of $0.5CaWO_4$–$0.5TiO_2$ samples sintered at 1300 °C for 2 h. (A) A phase, $CaWO_4$; (B) B phase, TiO_2.

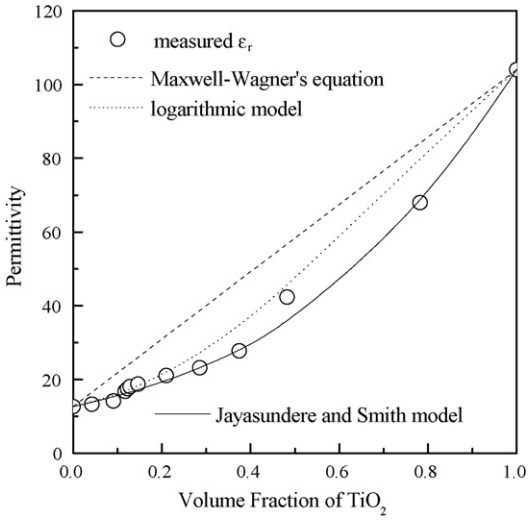

Fig. 4. Variation of the permittivity of $(1-x)CaWO_4$–$xTiO_2$ as a function of volume fraction of TiO_2.

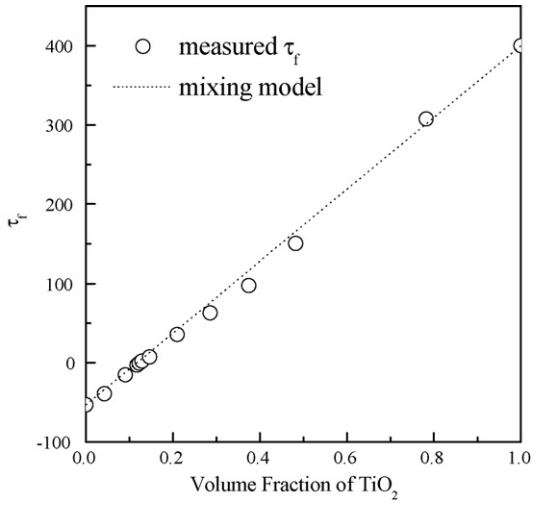

Fig. 5. Variation of the temperature coefficient of resonant frequency of $(1-x)CaWO_4$–$xTiO_2$ as a function of volume fraction of TiO_2.

where ν and ε are the volume fraction and relative dielectric constant of phase.

Lichtenecker suggested more accurate mixture model, which is the logarithmic model. In the logarithmic model, predicted dielectric constant follows equation (Eq. (2)), which better characteristics as observed in composite systems.[5]

$$\ln \varepsilon_c = \nu_1 \ln \varepsilon_1 + \nu_2 \ln \varepsilon_2 \quad (2)$$

More recently, Jayasundere–Smith suggested more accurate formula, which considered interactive effects between the fields of neighboring spheres. According to this model, permittivity of mixed ceramic composition can be predicted as follows[6,7]

$$\varepsilon_c = \frac{\varepsilon_1\nu_2 + \varepsilon_2\nu_2[3\varepsilon_1/(\varepsilon_2+2\varepsilon_1)][1+3\nu_2(\varepsilon_2-\varepsilon_1)/(\varepsilon_2+2\varepsilon_1)]}{\nu_1 + \nu_2(3\varepsilon_1)/(\varepsilon_2+2\varepsilon_1)[1+3\nu_2(\varepsilon_2-\varepsilon_1)/(\varepsilon_2+2\varepsilon_1)]} \quad (3)$$

For small volume fractions, these interactive effects of neighboring spheres can be negligible.

In our case, Jayasundere–Smith formula is more accurate for predicting the permittivity of $(1-x)CaWO_4$–$xTiO_2$ than other models, because addition of TiO_2 is not small volume fraction.

The temperature coefficient of resonant frequency (τ_f) of pure $CaWO_4$ is −53 ppm/°C and that of TiO_2 is 400 ppm/°C. The mixed $CaWO_4$–TiO_2 is shown randomly mixed phases, hence, the τ_f of the mixture phase can be predicted using a general mixture formula (Eq. (4))[5,8]

$$\tau_{f,mixture} = \nu_1\tau_{f1} + \nu_2\tau_{f2} \quad (4)$$

Generally variation of τ_f in a random mixture is proportional to the molar variation of the constituent phases. The τ_f value of mixed $CaWO_4$–TiO_2 also has good agreement with the value predicted by general mixture formula.

Fig. 5 shows the variation of measured and predicted τ_f of the mixed phases of $CaWO_4$–TiO_2. From Fig. 5, it is obvious that the variation of mixed phase of $CaWO_4$–TiO_2 exist around

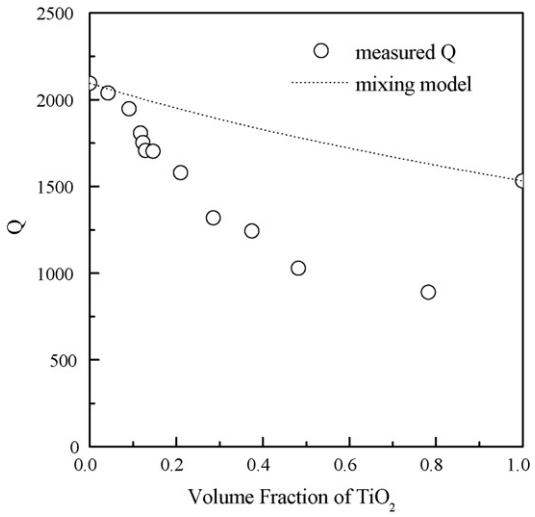

Fig. 6. Variation of the Q of $(1-x)CaWO_4$–$xTiO_2$ as a function of volume fraction of TiO_2.

the straight line, which is predicted by the rule of mixtures. The zero τ_f composition of $(1-x)CaWO_4$–$xTiO_2$ was predicted around $x=0.25$ and the measured τ_f of $0.75CaWO_4$–$0.25TiO_2$ and $0.74CaWO_4$–$0.26TiO_2$ were -2.8 and 0.41, respectively, and can be approximated to zero.

The measured and predicted Q_s in the mixed phase were plotted in Fig. 6. In a ceramic resonator, the energy dissipation is determined mainly by the dielectric loss of the material ($\tan\delta$), and the Q value is given as[8]

$$Q = \frac{1}{\tan\delta} \tag{5}$$

Because the loss is an additive quantity, dielectric loss of the mixed composition can be expressed in the form of

$$\tan\delta = \nu_1 \tan\delta_1 + \nu_2 \tan\delta_2 \tag{6}$$

where $\tan\delta_1$ and $\tan\delta_2$ are the loss of two components.

From Eqs. (5) and (6), Q value has following relation

$$\frac{1}{Q} = \frac{\nu_1}{Q_1} + \frac{\nu_2}{Q_2} \tag{7}$$

where Q_1 and Q_2 are the Q values of the two components and Q is the resultant Q value of the mixture.

While measured value of ε_r and τ_f are well matched with the predicted value, in the case of Q there are large deviations. The quality factor (Qf) is affected by extrinsic factors such as defect concentration, impurities, grain size and porosity. Because of few defects and impurities and little porosity, we considered average grain size is the main factor of this deviation with predicted and measured value. Generally, as the average grain size increased, the number of grain boundaries per unit volume, which are sources of loss decreased, therefore, the $\tan\delta$ would decrease.[9] In Fig. 2, the pure $CaWO_4$ and TiO_2 have much larger grain sizes than those of mixed composition. This relatively small grain size made many grain boundaries and these boundaries would result in large dielectric loss. Therefore, the measured Q has much lower value than that of predicted Q value. The quality factor (Qf) has more radical change than change of Q. The maximum Qf is 52,000 GHz (at $x=0$) and minimum Qf is 8400 GHz (at $x=0.7$). The resonant frequency of samples with the same dimensions should decrease linearly from $CaWO_4$ to TiO_2 rich compositions, because of TiO_2 have larger dielectric constants.[1] Therefore, decreasing Q and f cause quality factor (Qf) to have radical change. At $x=0.26$, where τ_f assumes minimum value, quality factor (Qf) was 27,000 GHz.

4. Conclusion

The mixture behavior and microwave dielectric properties of $CaWO_4$ with TiO_2 system were investigated. The dielectric constant was increased with the molar addition of TiO_2 into $CaWO_4$ to form mixtures based on $(1-x)CaWO_4$–$xTiO_2$. The analysis of the crystal structure by XRD indicated that no additional second phase was formed and $(1-x)CaWO_4$–$xTiO_2$ exist as mixture in the entire range. The densities of mixture were over 97% of theoretical density and effects of porosity on dielectric properties could be excluded. The permittivity of $CaWO_4$ and TiO_2 mixture is well predicted by the Jayasundere–Smith formula. The value of temperature coefficient of resonant frequency well followed general mixture rule. In the case of Q value, effect of grain size is distinguished. The mixed $CaWO_4$ and TiO_2 had relatively smaller grain than pure $CaWO_4$ and TiO_2 and this difference make deviation of measured value from predicted value. The $0.74CaWO_4$–$0.26TiO_2$ dielectric ceramic with $\varepsilon_r = 17.48$, $Qf = 27{,}000$ GHz and temperature stability is proposed as a suitable microwave dielectric material.

Acknowledgements

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