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Mixture behavior and microwave dielectric properties of $(1-x)Ca_2P_2O_7$–$xTiO_2$

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Abstract

$(1-x)\beta$-$Ca_2P_2O_7$–$xTiO_2$ were prepared by solid-state reaction. The mixture behavior and microwave dielectric properties were investigated using X-ray powder diffraction and a network analyzer, respectively. X-ray powder diffraction patterns showed that β-$Ca_2P_2O_7$ and TiO_2 existed in a mixture form, which was also confirmed by SEM analysis. It was shown that TiO_2, which has positive temperature coefficient of the resonant frequency (τ_f), compensated the negative τ_f of β-$Ca_2P_2O_7$ (−53 ppm/°C) through mixture formation. The variation of dielectric properties with a function of TiO_2 contents could be explained using mixture rule. In the $0.3 < x < 0.4$ regions, τ_f value could be successfully reduced almost zero. In particular, at $x = 0.3$, good microwave dielectric properties was obtained: $Q \times f = 44{,}000$, $\varepsilon_r = 10.9$, and $\tau_f = -11$ ppm/°C.

Keywords: Inclusions; Dielectric properties; TiO_2

1. Introduction

With the rapid development of modern microwave communication system, such as mobile telephone, high quality microwave dielectric ceramics have been attracted by much scientific and commercial attention. For microwave substrate application, materials should have a low dielectric constant (ε_r) less than 10 and low temperature coefficient of resonant frequency (τ_f). Such as Al_2O_3 and rare-earth aluminates[1,2] have been investigated for substrate application. Recently, pyrophosphate $Ca_2P_2O_7$ compound with dichromate structure was reported for microwave substrate application by Bian et al.[3] Although this materials exhibit good microwave dielectric properties, $Q \times f = 53{,}500$ GHz, $\varepsilon_r = 8.3$, it is need to tune the temperature coefficient of resonant frequency to near-zero because of some large negative temperature coefficient of resonant frequency ($\tau_f = -53$ ppm/°C). The most popular method of tuning the τ_f value involves mixing two or more compositions with different τ_f value. A typical example is found in the (Mg, Ca)TiO_3 system.[4] $CaTiO_3$ has a large positive τ_f, while the τ_f of $MgTiO_3$ is negative. By combining the two components, a near-zero τ_f value can be obtained.

In the present study, β-$Ca_2P_2O_7$ ceramics was mixed with TiO_2 ($\tau_f = +400$ ppm/°C) in order to control the τ_f value. The effects of TiO_2 addition on the mixture formation and microwave dielectric properties of β-$Ca_2P_2O_7$ ceramics were reported. The variation of dielectric properties with a function of TiO_2 volume fraction could be explained by mixture rule.

2. Experimental

High purity $CaCO_3$ (99.9%), $(NH_4)_2HPO_4$ (99%) and TiO_2 (99.9%) were used as raw materials. $Ca_2P_2O_7$ powders were prepared using conventional mixed oxide method. $CaCO_3$ and $(NH_4)_2HPO_4$ were mixed using ball-mill and the mixture was calcined at 1000 °C for 2 h. Mixtures of $Ca_2P_2O_7$ and TiO_2 powders of varying composition were ball-milled in a polyethylene bottle with ZrO_2 balls for 24 h using ethanol as a medium. The milled powders were dried, granulated and pressed at 1000 kg/cm^2 to form pellets 10 mm in diameter and 4 mm thick. The pellets were sintered at 1100–1200 °C for 2 h with a heating rate of 5 °C/min. The phase constitution of the sintered sample was identified by X-ray powder diffraction (XRD: Model M18XHF, MacScience Instruments, Japan) in the 2θ range of 20–60°. The bulk density of the sintered specimens was evaluated by Archimedes' method. The microstructure analysis of the sintered samples was examined using scanning electron microscopy (SEM: Model JSM-5600, JEOL, Japan).

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The microwave dielectric properties of the sintered samples were measured using a network analyzer (Model HP8720C, Hewlett Packard, USA) in the frequency range of 8–12 GHz. The quality factor ($Q \times f$) was measured by the transmission cavity method using a Cu cavity and a Teflon supporter.[5] 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. Results and discussion

3.1. Mixture formation of $Ca_2P_2O_7$–TiO_2

Fig. 1 shows the X-ray diffraction (XRD) profiles of the $(1-x)Ca_2P_2O_7$–$xTiO_2$ samples for various values of x. With increasing TiO_2 content, the intensity of the reflections of $Ca_2P_2O_7$ phase decreased and those of TiO_2 phase increased. At the region of $x \leq 0.4$, all samples were mixture of β-$Ca_2P_2O_7$ and TiO_2 without any observable formation of a second phase. But at $x \geq 0.5$, secondary phase reflection around 31.1° was appeared. We could not identify the secondary phase because of peak overlapping with $Ca_2P_2O_7$ reflection.

Fig. 2 shows SEM photographs of $0.7Ca_2P_2O_7$–$0.3TiO_2$ sample sintered at 1120 °C for 2 h. There were two different shapes of grains, rounded and elongated shape. From EDS spectra in Fig. 2(a) and (b), it was found that $Ca_2P_2O_7$ ($x = 0$) had rounded grains while TiO_2 exhibited elongated grains. In the $0.7Ca_2P_2O_7$–$0.3TiO_2$ sample, a heterogeneous microstructure with both rounded and elongated grains formed, which was in agreement with the XRD results. These results indicate that the formation of a mixture in $(1-x)Ca_2P_2O_7$–$xTiO_2$ samples, because the end members, $Ca_2P_2O_7$ and TiO_2, have distinct microstructural shapes.

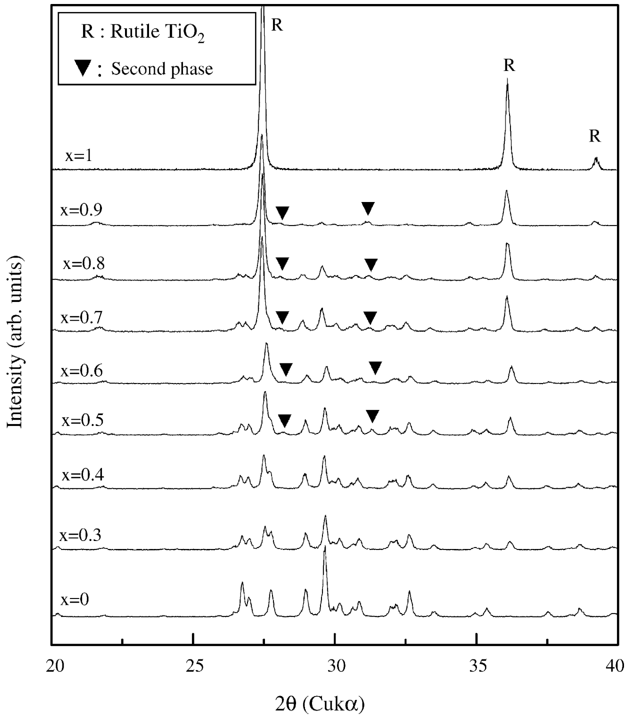

Fig. 1. XRD patterns of $(1-x)Ca_2P_2O_7$–$xTiO_2$ samples sintered at 1120 °C for 2 h showing the mixture phase (rutile-TiO_2 and β-$Ca_2P_2O_7$).

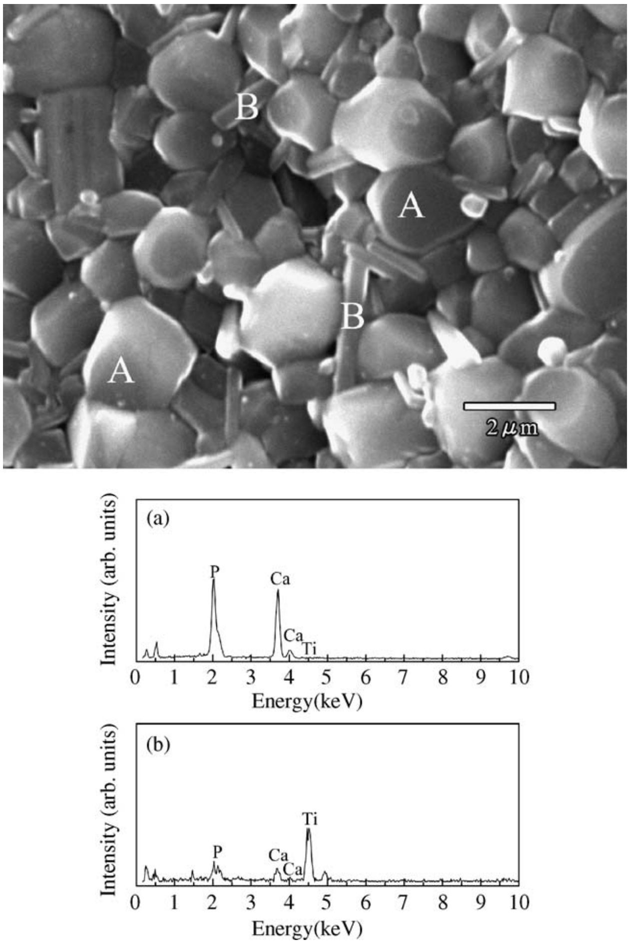

Fig. 2. SEM photograph and EDS spectra of $0.7Ca_2P_2O_7$–$0.3TiO_2$ sintered at 1120 °C for 2 h. (a) A phase: $Ca_2p_2O_7$, (b) B phase: TiO_2.

3.2. Microwave dielectric properties of $Ca_2P_2O_7$–TiO_2

3.2.1. Relative dielectric constant

The relative density (ρ) of $(1-x)Ca_2P_2O_7$–$xTiO_2$ ceramics was shown in Fig. 3, as a function of TiO_2 volume fraction. The theoretical densities (ρ_{th}) of the $(1-x)Ca_2P_2O_7$–$xTiO_2$ ceramics were obtained from

$$\rho_{th} = \frac{(W_1 + W_2)}{(W_1/r_1 + W_2/r_2)},$$

where W_1 and W_2 are the weight fractions of $Ca_2P_2O_7$ and TiO_2 in the mixture, respectively. ρ_1 and ρ_2 represent the densities of $Ca_2P_2O_7$ and TiO_2, respectively. In Fig. 3, all samples had relative theoretical density (ρ) of more than 95%. Because the sintering temperature of TiO_2 is higher than $Ca_2P_2O_7$ about 200 °C, the relative density (ρ) of $(1-x)Ca_2P_2O_7$–$xTiO_2$ samples sintered at 1120 °C have tendency to decrease as increasing TiO_2 content.

The effect of porosity on the dielectric constant was eliminated by applying the Bosman and Havinga's correction,[6] shown

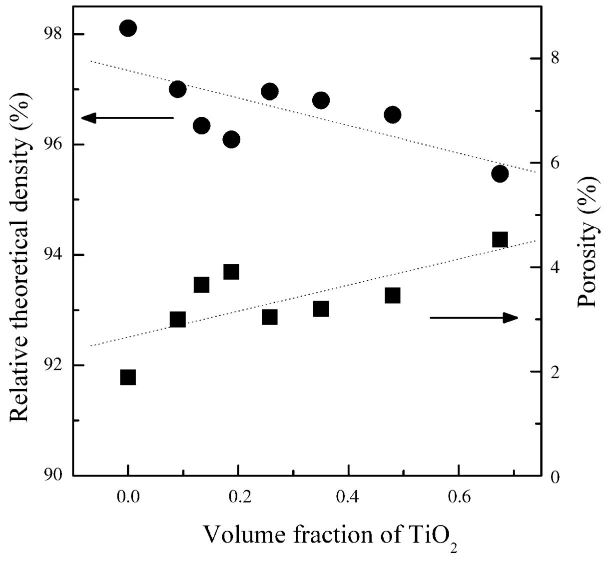

Fig. 3. Relative theoretical density of $(1-x)Ca_2P_2O_7$–$xTiO_2$ samples sintered at 1120 °C for 2 h, as a function of volume fraction of TiO_2.

in Eq. (1), which can be used for dense ceramics having porosity lower than 5%:

$$\varepsilon_{\mathrm{r,\,corrected}} = \varepsilon_{\mathrm{r,\,measured}}(1 + 1.5P), \tag{1}$$

where $\varepsilon_{\mathrm{r,\,corrected}}$ and $\varepsilon_{\mathrm{r,\,measured}}$ are the corrected and measured dielectric constant, respectively, and P is fractional porosity. Fig. 4 shows the measured and corrected dielectric constant of $(1-x)Ca_2P_2O_7$–$xTiO_2$ samples sintered at 1120 °C for 2 h, as a function of TiO_2 volume fraction. The measured dielectric constant ($\varepsilon_{\mathrm{r,\,measured}}$) increased with increasing TiO_2 content, which has large dielectric constant content ($\varepsilon_r = 105$). At a composition of $x = 0.3$, the $\varepsilon_{\mathrm{r,\,measured}} = 10.9$ and $\varepsilon_{\mathrm{r,\,corrected}} = 11.3$.

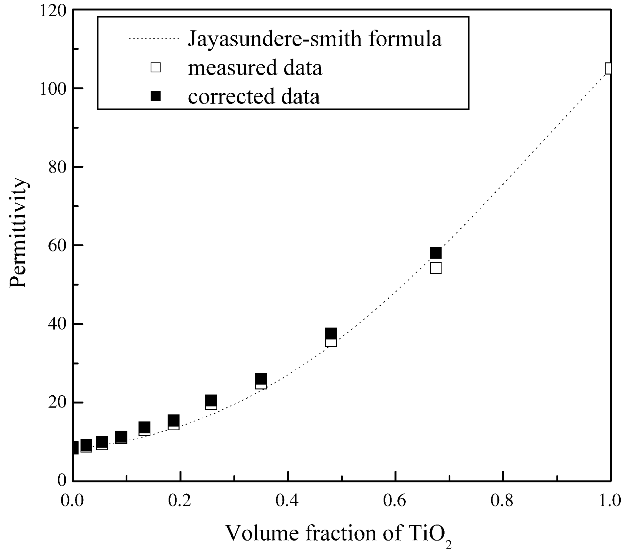

Fig. 4. Comparison between dielectric constant measured by the post-resonator method and calculated by Jayasundere–Smith's formula from the samples sintered at 1120 °C for 2 h.

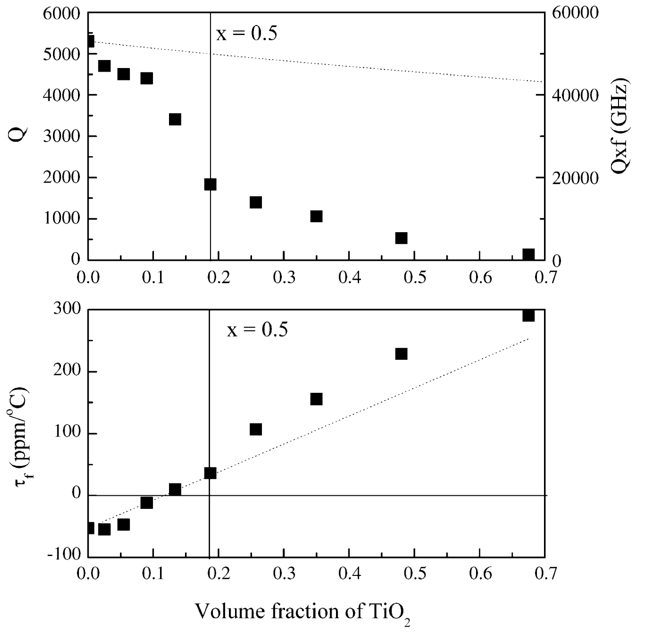

Fig. 5. Quality factor ($Q \times f$) and temperature coefficient of resonant frequency (τ_f) of $(1-x)Ca_2P_2O_7$–$xTiO_2$ sintered 1120 °C for 2 h as a function of TiO_2 volume fraction (vertical line represents: $x = 0.5$, dotted line: calculated values).

The effective dielectric constant of a mixture has been studied by many researchers.[7–9] Among those, Jayasundere and Smith formula[7] is selected, because the dielectric constant of inclusions (TiO_2) is larger than those of the matrix ($Ca_2P_2O_7$). It is an analytic formula for the effective dielectric constant of a binary mixture, derived by modifying the well-known Kerner's expression[8] to include interactions between neighboring spheres. The developed expression, a binary system which is composed of spheres with high dielectric constant (ε_2) dispersed in a matrix with low dielectric constant (ε_1) where $\varepsilon_2 \gg \varepsilon_1$, is a function of the volume fraction of the spheres (v_2) and the matrix (v_1):

$$\varepsilon_{\mathrm{eff}} = \frac{\begin{array}{l}\varepsilon_1 v_2 + \varepsilon_2 v_2[3\varepsilon_1/(\varepsilon_2 + 2\varepsilon_1)] \\ \quad \times [1 + 3v_2(\varepsilon_2 - \varepsilon_1)/(\varepsilon_2 + 2\varepsilon_1)]\end{array}}{\begin{array}{l}v_1 + v_2(3\varepsilon_1)/(\varepsilon_2 + 2\varepsilon_1) \\ \quad \times [1 + 3v_2(\varepsilon_2 - \varepsilon_1)/(\varepsilon_2 + 2\varepsilon_1)]\end{array}}. \tag{2}$$

The measured and calculated dielectric constant (by the Jayasundere–Smith's formula) was plotted in Fig. 4. The ε_r of $(1-x)Ca_2P_2O_7$–$xTiO_2$ is well predicted by the Jayasundere–Smith formula. The Jayasundere–Smith formula was derived from a mixture of spherical inclusions, while the mixture of $Ca_2P_2O_7$–TiO_2 has elongated grain inclusions. However, the measured data were well agreed with the calculated data by formula (2). It attribute to a large dielectric constant difference of two phases. At a composition of $x = 0.3$, the measured and calculated dielectric constant was 10.9 and 10.1, respectively.

3.2.2. Quality factor($Q \times f$) and temperature coefficient of resonant frequency(τ_f)

Fig. 5 shows the quality factor ($Q \times f$) and the temperature coefficient of resonant frequency (τ_f) of the $(1-x)Ca_2P_2O_7$–$xTiO_2$ samples sintered at 1120 °C for 2 h. The Q (=1/tan δ) and τ_f values were calculated in the following relations as a semi-empirical model:

$$\tau_{\text{f, mixture}} = v_1\tau_{\text{f1}} + v_2\tau_{\text{f2}}$$

$$\frac{1}{Q_{\text{mixture}}} = \frac{v_1}{Q_1} + \frac{v_2}{Q_2}$$

The above calculated $\tau_{\text{f, mixture}}$[10] and Q_{mixture}[11] results are also shown in Fig. 5. The Q value decreased with increasing TiO_2 content. The measured Q values agree well with the calculated values for $x < 0.5$. However, at $x \geq 0.5$, the Q value have a large decrease than the calculated value. According to XRD data shown in Fig. 1, unidentified secondary phase was appeared at $x \geq 0.5$. And in Fig. 3, the porosity increased as increasing TiO_2 content. The $Q \times f$ is affected by extrinsic factors such as defect concentration, impurities, grain size, and porosity. Therefore, this large deviation in $Q \times f$ value at $x \geq 0.5$ was related to an appearance of secondary phase and increase of the porosity. In the case of the τ_f, β-$Ca_2P_2O_7$ and rutile-TiO_2 have τ_f values of −53 and +400 ppm/°C, respectively. The measured τ_f values increased with increasing TiO_2 content and agreed well with the calculated values at $x < 0.5$. At the region of $x \geq 0.5$, the small deviation of the τ_f was appeared, which was also influenced by secondary phase. In the $0.3 < x < 0.4$ regions, τ_f value could be successfully reduced almost zero.

4. Conclusion

The mixture behavior and microwave dielectric properties of $(1-x)Ca_2P_2O_7$–$xTiO_2$ system were investigated. It was found that $(1-x)Ca_2P_2O_7$–$xTiO_2$ samples sintered at 1120 °C for 2 h were mixture of $Ca_2P_2O_7$ and TiO_2, without any observable secondary phases at $x < 0.5$. At the region of $x \geq 0.5$, secondary phase was appeared. The ε_r of $(1-x)Ca_2P_2O_7$–$xTiO_2$ is well predicted by the Jayasundere–Smith formula. Although unidentified secondary phase exist at $x \geq 0.5$, the ε_r value was not affected by secondary phase. In the case of Q and τ_f values, however, the $Q \times f$ and τ_f values showed deviation from the corresponding mixing relations due to unidentified secondary phase and porosity at the region of $x \geq 0.5$. At a composition of $x = 0.3$ (volume fraction of $TiO_2 = 0.09$): $Q \times f = 44{,}000$ GHz, $\varepsilon_r = 10.9$, and $\tau_f = -11$ ppm/°C.

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