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Microwave dielectric properties of $(Pb_{0.4}Ca_{0.6})(Fe_{0.5}Ta_{0.5})O_3$ ceramics prepared by mechanochemical processing

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Abstract

The complex perovskite $(Pb_{0.4}Ca_{0.6})(Fe_{0.5}Ta_{0.5})O_3$ ceramics (PCFT) were prepared by mechanochemical process and the microwave dielectric properties were investigated. A single phase PCFT of the perovskite structure was obtained with PbO, $CaCO_3$ and pre-reacted $FeTaO_4$ by high-energy mechanochemical milling and subsequent heat treatment. Without calcination, a single phase of the perovskite structure could be obtained by 60 h milling and sintering at 1000 °C for 3 h, which was lower by 100 °C than that prepared by conventional mixed oxide method. The PCFT specimen sintered at 1050 °C for 3 h showed dielectric constant of 62, $Q{\cdot}f$ of 9000, and the temperature coefficient of resonant frequency (TCF) of −15 ppm/°C.

Keywords: Mechanochemical processing; Microwave ceramics; Dielectric properties; Nanometer-size particles; (Pb,Ca)(Fe,Ta)O_3; Sintering

1. Introduction

With the development of microwave communication systems, several types of dielectric resonator materials have been studied and put into practical use for microwave filters and oscillators. The microwave dielectric materials require a high dielectric constant, low dielectric loss, and a small temperature coefficient of resonant frequency (TCF). Various complex perovskite compounds have been widely investigated for applications in the advanced communication systems.[1,2] For the practical applications of the low temperature cofiring ceramics (LTCC), the sintering aids have been widely used in most complex perovskite compounds with high sintering temperature above 1400 °C. However, a new method using ultra fine ceramic powders as starting materials has been lately paid considerable attention for the low temperature sintering.

Among several techniques, the mechanochemical technique serves effectively the formation of nanocrystalline powders of complex oxides for advanced ceramics.[3] For ceramic materials, the reactivity of starting materials can be improved significantly by mechanochemical processing, and therefore the necessary calcination temperature for the design of the ceramic phase could be reduced effectively.[4] It has been reported that the sintering temperatures of many systems were effectively lowered about 150–200 °C by this mechanochemical processing without any deterioration of their properties.[4–6]

In this study, the complex perovskite $(Pb_{0.4}Ca_{0.6})(Fe_{0.5}Ta_{0.5})O_3$ ceramics (PCFT) were prepared by the mechanochemical process (MP) to reduce the sintering temperature, and the dependence of the microwave dielectric properties on the process condition was investigated.

2. Experimental procedure

$FeTaO_4$ was prepared by heating at 1100 °C for 4 h via the columbite route from Fe_2O_3 and Ta_2O_5. Reagent graded PbO, $CaCO_3$ and pre-reacted $FeTaO_4$ were mixed for 6 h in ethanol with ZrO_2 balls and then dried. To prevent the contamination from the vessel and media used in mechanochemical process, small amounts of powders with the desired composition were premixed for 6 h in a stainless steel vessel with stainless steel balls. After this premixing process, the mixed powder was mechanochemically milled in a shaker milling machine (Model 8000, Spex Industries, Edison, NJ, USA) for 18–60 h at 500 rpm and then reground for 24 h in ethanol

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with ZrO_2 balls. Prepared powders were pressed uniaxially at 700 kg/cm^2 and cold isostatic pressed at 1450 kg/cm^2. These pellets were buried in powders of the same composition to avoid PbO volitilization, and sintered at 900–1150 °C for 3 h.

Powder X-ray diffraction analysis was used to determine the crystalline phases. The density of the specimens was measured by ASTM C373-72.[7] The polished surfaces of the specimens were observed with a scanning electron microscope (SEM, Jeol, JSM 820, Japan). Microwave dielectric properties were measured by the post resonant method with the TE_{011} mode.[8]

3. Results and discussion

Figs. 1 and 2 show the X-ray diffraction (XRD) patterns of the powders prepared by the MP and conventional mixed-oxide method (CMO), respectively. As shown in Fig. 1, the matrix phase of complex perovskite PCFT and small amount of pyrochlore phase were detected in the powders milled mechanochemically for 60 h. With an increase of sintering temperature, the peak intensity of the pyrochlore phase was weakened, and single phase PCFT was obtained for the specimen sintered at 1000 °C for 3 h. For the powders prepared by CMO (Fig. 2), however, the pyrochlore phase was detected for the specimens sintered up to 1000 °C for 3h

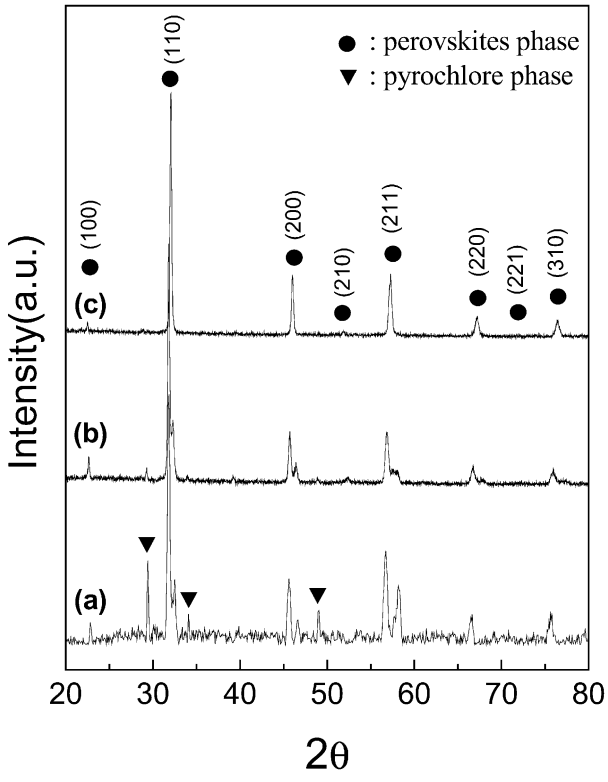

Fig. 2. X-ray diffraction patterns of $(Pb_{0.4}Ca_{0.6})(Fe_{0.5}Ta_{0.5})O_3$ specimens prepared by conventional mixed-oxide method calcined at (a) 900 °C for 3 h and sintered at (b) 1000 °C and (c) 1100 °C for 3 h.

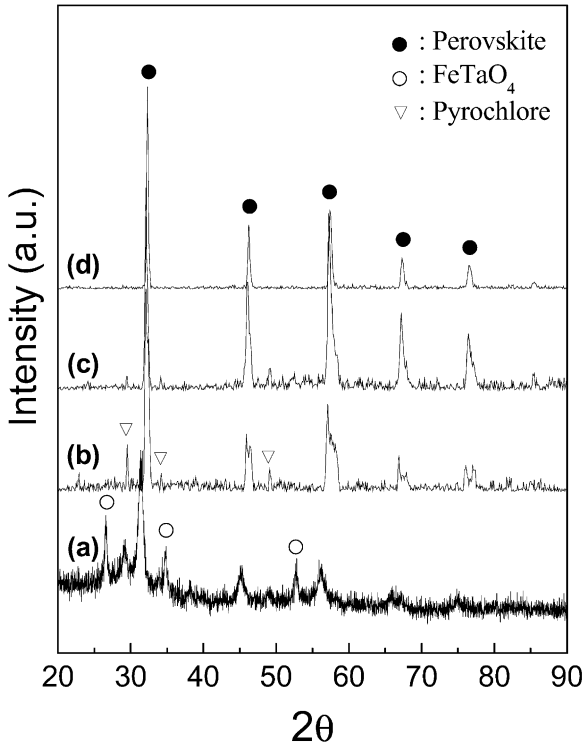

Fig. 1. X-ray diffraction patterns of $(Pb_{0.4}Ca_{0.6})(Fe_{0.5}Ta_{0.5})O_3$ specimens prepared by mechanochemical processing for (a) 60 h and sintered at (b) 900 °C, (c) 950 °C, and (d) 1000 °C for 3h.

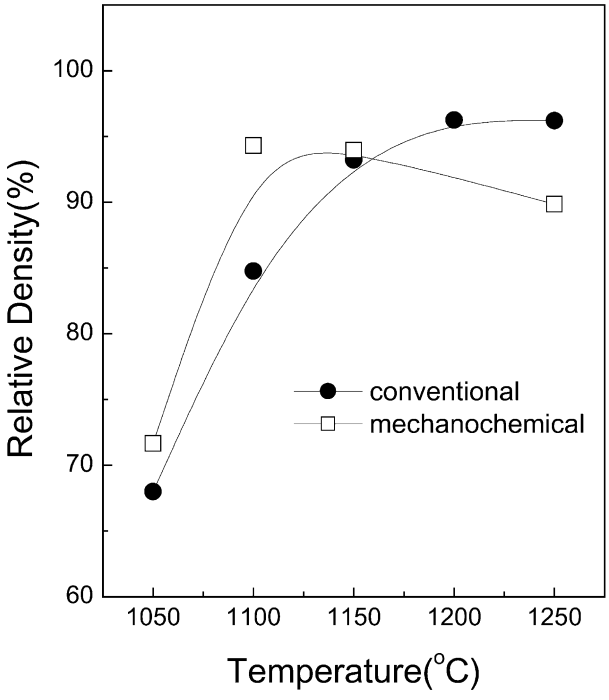

Fig. 3. Relative density of $(Pb_{0.4}Ca_{0.6})(Fe_{0.5}Ta_{0.5})O_3$ specimens sintered at different temperatures.

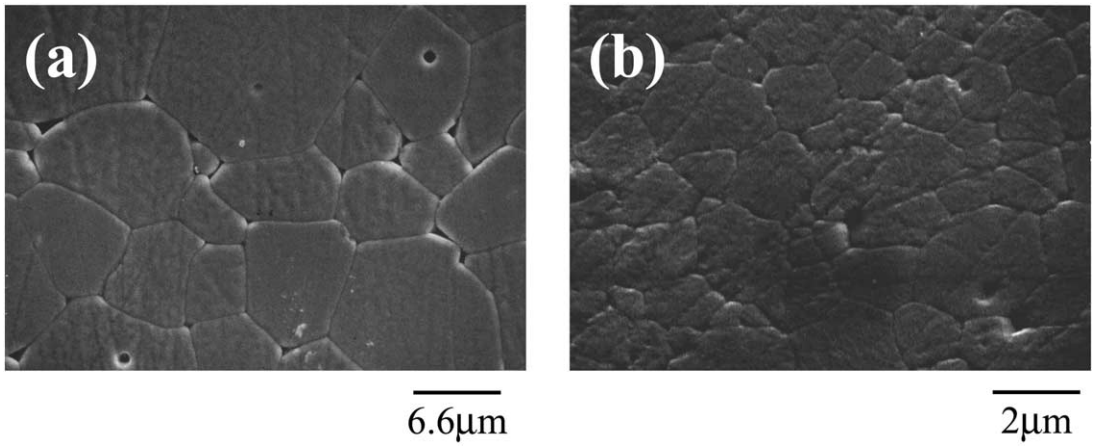

Fig. 4. SEM photographs of $(Pb_{0.4}Ca_{0.6})(Fe_{0.5}Ta_{0.5})O_3$ specimens sintered at (a) 1250 °C for 3 h prepared by conventional mixed-oxide method, and sintered at (b) 1100 °C for 3 h prepared by mechanochemical processing.

as well as the powders calcined at 900 °C for 3 h. From the XRD patterns, the particle size could be calculated by the Scherrer formula, as in Eq. (1).[9]

$$D = \frac{K \cdot \lambda}{\beta_s \cdot \cos\theta} \quad (1)$$

where, D: Particle size; β_s: Full width at half maximum (angular width, in rad.); K: Constant (0.9 in this case).

The particle size calculated from this equation was about 7.1 nm for MP and 5.3 μm for CMO. Therefore, the single phase PCFT could be obtained by MP at sintering temperature of 100 °C lower than that of CMO, which could be attributed to the reduction of particle size by MP.

Fig. 3 shows the relative density of specimens as a function of a sintering temperature. The density of specimens by CMO increased with an increase of sinteiring temperature, and the specimen sintered at 1250 °C for 3 h showed 96% of relative density. On the other hand, the relative density showed a maximum value of 95% for the specimen sintered at 1100 °C for 3 h prepared by the powders from MP. Microstructures of the sintered specimens which were prepared by two different methods but had similar densities are shown in Fig. 4. The grain size of the specimen by CMO sintered at 1250 °C for 3 h was about 10 μm, which was three times larger than that of specimen by MP (3 μm). It was reported that there was strong possibility of exaggerated grain growth in case of the fine particle sizes,[10] but in this study, the uniform grains without abnormal grain growth were obtained from the nanometer-size particles prepared by MP.

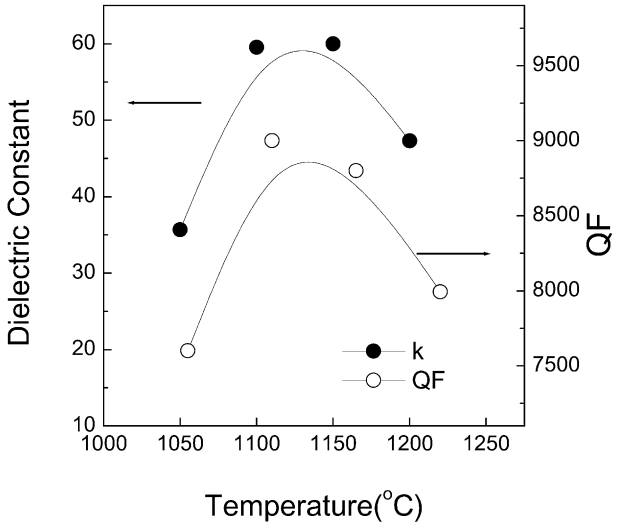

Fig. 5. Microwave dielectric properties of $(Pb_{0.4}Ca_{0.6})(Fe_{0.5}Ta_{0.5})O_3$ specimens prepared by mechanochemical processing sintered at different temperatures.

Fig. 5 shows the microwave dielectric properties of the specimens prepared by MP as a function of sintering temperature. The dielectric properties of specimens prepared by MP were proportional to the change of relative density,[11,12] and the MP specimens sintered at 1100 °C for 3 h showed similar properties compared to the properties of specimens prepared by CMO sintered at 1250 °C for 3 h ($k = 63$, $Q \cdot f = 10{,}000$), even though the specimen prepared by MP was not calcined and heat treated at 150 °C lower sintering temperature than CMO.

Generally, the sintering temperature of the specimens prepared by CMO could be lowered by the addition of suitable sintering aids. In our preliminary experiment, three kinds of sintering aids CuV_2O_5 (CV), B_2O_3–Li_2O (BL) and borosilicate glass frit (GF) were available to lower the sintering temperature of PCFT. The sintering temperature of PCFT was dependent on the amount of the sintering aids as well as the kinds of sintering aids. In Fig. 6, the sintering temperature for each sintering aid was taken from the minimum sintering temperature in which 95% of relative density could be obtained. The sintering temperature of PCFT was effectively lowered by the addition of each sintering aid. With 0.4 wt.% of CuV_2O_6 or B_2O_3–Li_2O, the sintering temperature of PCFT by CMO was lowered to the 1100 °C for 3 h,

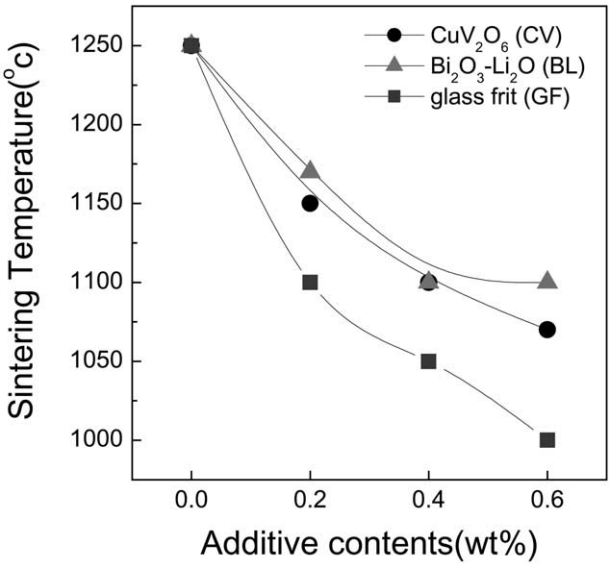

Fig. 6. The change in sintering temperature of $(Pb_{0.4}Ca_{0.6})(Fe_{0.5}Ta_{0.5})O_3$ specimens with various low-firing additives.

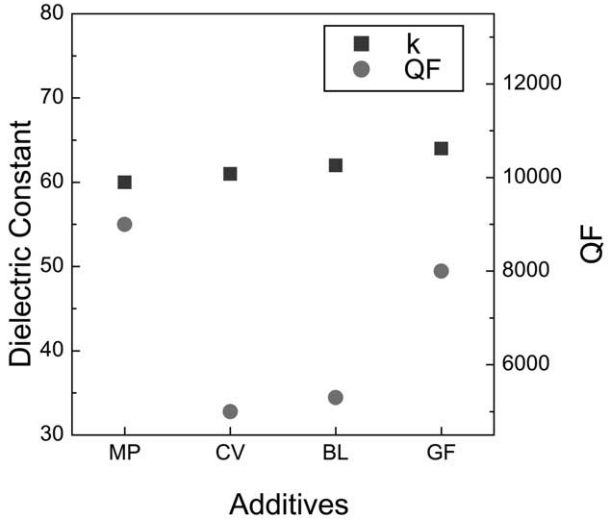

Fig. 7. Dielectric constant and Qf value of $(Pb_{0.4}Ca_{0.6})(Fe_{0.5}Ta_{0.5})O_3$ specimens prepared by mechanochemical processing and by conventional mixed-oxide method with various low-firing additives.

which was the same sintering temperature of the specimen by MP. There is a comparison of the microwave dielectric properties of the PCFT prepared by MP with those of specimens by CMO with the sintering aids in Fig. 7. The sintering condition was taken as 1100 °C for 3 h that showed about 95% of relative density in all specimens. Dielectric constants were not changed significantly in any case. However, the Qf values of the PCFT prepared by CMO with the sintering aids decreased remarkably compared with that of the specimen prepared by MP. The sintering temperature of PCFT was effectively lowered by MP without the degradation of the microwave dielectric properties.

4. Conclusion

By mechanochemical process (MP) for 60 h without calcination process, nanometer-size particles were obtained, and single phase complex perovskite $(Pb_{0.4}Ca_{0.6})(Fe_{0.5}Ta_{0.5})O_3$ (PCFT) was formed at 100 °C lower than the temperature for the conventional mixed-oxide method (CMO). Uniform grains of about 3 μm were observed without abnormal grain growth. Due to the reduction of particle size by MP, the sintering temperature of PCFT could be lowered from 1250 to 1100 °C. MP can lower the sintering temperature of PCFT without degradation of the microwave dielectric properties.

Acknowledgements

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