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Short communication

$Ce_{0.75}Y_{0.25}O_{1.875}$: New temperature-stable microwave dielectric ceramics with high Q values for microwave application

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ABSTRACT

$Ce_{0.75}Y_{0.25}O_{1.875}$, new microwave dielectric ceramics which presented high quality factors and stable resonant frequency temperature coefficient, were prepared successfully via the method of solid-state reaction. The sintering behavior, crystal structure and microwave dielectric properties of the new ceramics had been investigated afterwards. The $Ce_{0.75}Y_{0.25}O_{1.875}$ ceramics presented a single phase indexed as CeO_2 structure which belonged to Fm-3m (225) space group, cubic system. The grain size of the $Ce_{0.75}Y_{0.25}O_{1.875}$ ceramics was calculated to evaluate the grain growth. The dielectric constant (ε_r) of the $Ce_{0.75}Y_{0.25}O_{1.875}$ ceramics, which could reflect the microwave dielectric properties, was on the dependence of relative densities. The $Q \times f$ values, which could be explained by packing fraction and grain size, had been further investigated. The resonant frequency temperature coefficient (τ_f) of the $Ce_{0.75}Y_{0.25}O_{1.875}$ ceramics was related to the dielectric constant. The excellent microwave dielectric properties of the new $Ce_{0.75}Y_{0.25}O_{1.875}$ ceramics was $\varepsilon_r = 19.75$, $Q \times f = 96600$ GHz, $\tau_f = -22.53$ ppm/°C.

1. Introduction

Cerium oxide (CeO_2), which was an excellent modifier in improving microwave dielectric properties, had attracted the attentions of many researchers [1–5]. In 2002, the CeO_2 ceramics with $\varepsilon_r = 24$, $Q \times f = 57000$ GHz, $\tau_f = -104$ ppm/°C had been reported. Owing to the large negative τ_f values, Kim et al. studied to adjust the τ_f values of TiO_2 to obtain temperature-stable microwave dielectric ceramics through the use of CeO_2 [1]. In addition, CeO_2 addition could also be utilized to optimize the phase composition or grain growth of ceramics for the sake of improving microwave dielectric performance [2–5]. For grain growth optimizing, the properties of the $Ca_{0.6}La_{0.8/3}(Sn_{0.02}Ti_{0.98})O_3$, $Na_{1/2}Sm_{1/2}TiO_3$ and Mg_2TiO_4 ceramics had been enhanced by CeO_2 additive [2–4]. In 2018, the properties of $LaGaO_3$-$SrTiO_3$ ceramics had been reported to be promoted through CeO_2 additive since the secondary phase had been effectively suppressed [5].

Obviously, CeO_2 was an effective additive to improve microwave dielectric properties. Therefore, it was really necessary to establish researches on CeO_2 ceramics and its microwave dielectric properties. In 2010, CeO_2 ceramics with Rare earth ion substitution had been reported, accompanied with the analysis of solid solution limit and microwave dielectric properties [6]. However, the performances of Y-substituted CeO_2 ceramics were not satisfactory, which had not been studied in depth yet.

In this paper, the $Ce_{0.75}Y_{0.25}O_{1.875}$ ceramics, which had been successfully synthesized using Y ion to substituted for Ce ion, had been reported with higher Q values and better τ_f values. In addition, the crystal structure, grain growth and microwave dielectric properties had also been further studied.

2. Experimental procedure

The $Ce_{0.75}Y_{0.25}O_{1.875}$ ceramics were compounded utilizing solid-state reaction method, with the raw materials being selected as high purity CeO_2 and Y_2O_3 powders. After weighted according to the designed stoichiometric ratio, the powders were all put into the ball mill jar and ball milled for 6 h with distilled water as a milling medium. Then, the mixture was desiccated, crushed, sifted and next sintered at 1200 °C for 4 h. The sintered powders were poured into a ball mill jar and milled for 24 h, then repeated steps of drying, crushing and sieving. The final powders were pressed into a cylinder with the diameter of 10 mm and thickness of 5 mm. The cylindrical samples were calcined at 1400 °C to 1500 °C for 4 h and the heating rate was 5 °C per minute.

The X-ray diffraction (XRD, Model D/Max-B, Rigaku Co., Japan) was engaged as a tool to analyze the phase composition and crystal structure of the samples. The scanning electron microscopy (SEM, FEI

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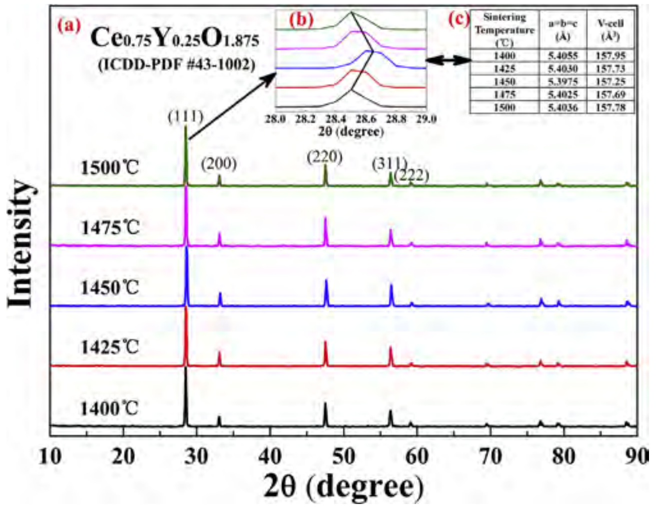

Fig. 1. The XRD patterns and lattice constant of $Ce_{0.75}Y_{0.25}O_{1.875}$ ceramics with different sintering temperature.

Quanta 250, USA) was employed to characterize the surface topography of the samples. The relative densities of the samples were calculated with the apparent densities being measured using Archimedes drainage method. Hakki-Coleman's resonator method (N5234A, Agilent Co., USA) was chosen to measure the microwave dielectric properties [7,8].

3. Results and discussion

Fig. 1 showed the XRD patterns of the $Ce_{0.75}Y_{0.25}O_{1.875}$ ceramics under different sintering temperature. As what could be seen from Fig. 1(a), only one phase, which was marked as CeO_2 with the cubic system Fm-3m (225) group, was detected and there was no second phase within the designed sintering temperature range. Therefore, in $Ce_{0.75}Y_{0.25}O_{1.875}$ ceramics, Y^{3+} ion entered into the CeO_2 lattice and occupied the Ce site to form a solid solution, owing to the analogical ionic radius between Y^{3+} and Ce^{4+} ion (Y^{3+}: 1.159 Å, Ce^{4+}: 1.11 Å) [9]. Although a solid solution was formed in $Ce_{0.75}Y_{0.25}O_{1.875}$ ceramics, the crystal structure thereof changed with the sintering temperature. Fig. 1(b) showed the movement of the strongest peak position as the changing sintering temperature. Obviously, the peak position shifted first to a high angle and then to a low angle, manifesting that the unit cell volume of the phase had been changed. In order to quantify the change, the lattice constant was extracted through the Rietveld refinement method, listed in Fig. 1(c). When the sintering temperature increased to 1450 °C, the unit-cell volume (V-cell) decreased to the minimum value, and increased afterwards, which was in accordance with the analysis of the peak position shift. As a result, a kind of solid solution was formed in $Ce_{0.75}Y_{0.25}O_{1.875}$ ceramics based on the CeO_2 structure, and its unit-cell volume was enslaved to the sintering temperature.

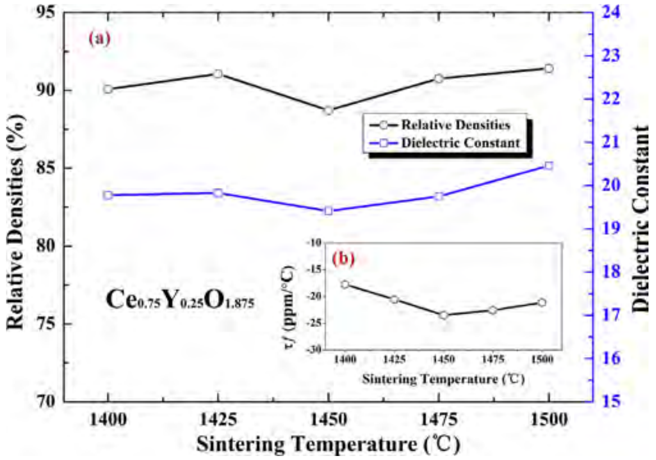

Fig. 3. The relative densities, dielectric constant and τ_f values of $Ce_{0.75}Y_{0.25}O_{1.875}$ ceramics as a function of sintering temperature.

The apparent morphology of the $Ce_{0.75}Y_{0.25}O_{1.875}$ ceramics under different sintering temperature were shown in Fig. 2. The straight grain boundaries without pores could be clearly seen, which obviously meant that dense ceramics had been obtained among the experiment temperature ranged of 1400 °C to 1500 °C. To evaluate the grain growth, the grain size (gz) of the samples at different sintering temperature was additionally calculated, listed in Fig. 2. When the experiment temperature rose to 1475 °C, the gz values increased to a maximum value (1.68), and decreased afterwards. Moreover, the grain size increased slowly in the temperature interval of 1400 °C to 1450 °C, which nevertheless rapidly increased in the interval of 1450 °C to 1475 °C. The apparent characteristics of the $Ce_{0.75}Y_{0.25}O_{1.875}$ ceramics were closely related to their properties.

Fig. 3 showed the relative densities, dielectric constant and τ_f values of $Ce_{0.75}Y_{0.25}O_{1.875}$ ceramics as the variation of sintering temperature. Relative density was a physical quantity measured density of ceramics, which reflected the numbers of pores. Obviously, the relative densities of $Ce_{0.75}Y_{0.25}O_{1.875}$ ceramics did not change much in the designed sintering temperature zone, which was consistent with the analysis of the apparent morphology. In general, the sintering characteristics of the

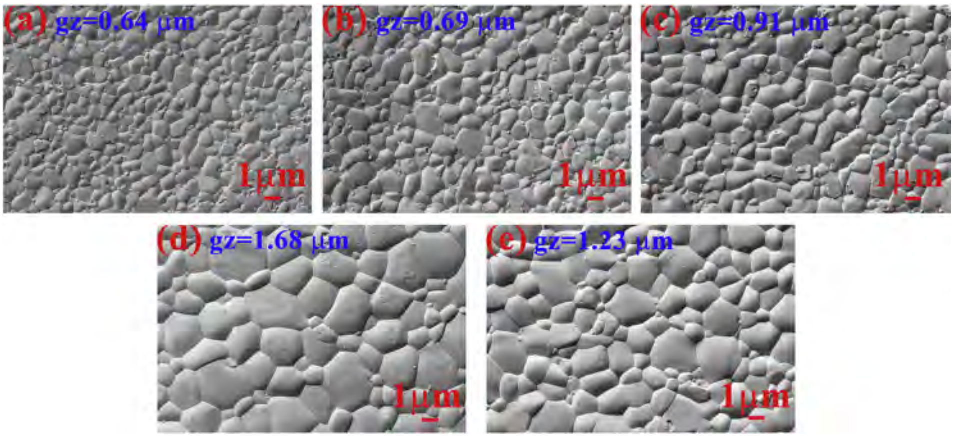

Fig. 2. The apparent morphology and grain size of $Ce_{0.75}Y_{0.25}O_{1.875}$ ceramics with different sintering temperature (a: 1400 °C, b: 1425 °C, c:1450 °C, d:1475 °C, e:1500 °C).

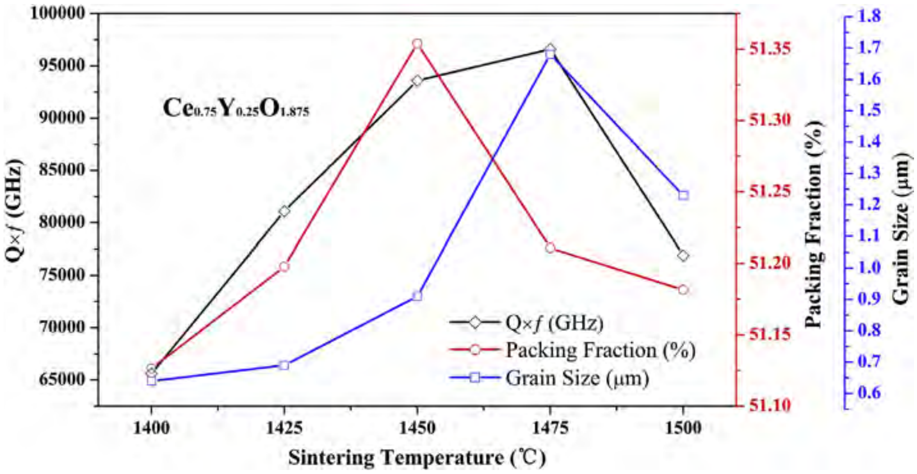

Fig. 4. The Q × *f* values of $Ce_{0.75}Y_{0.25}O_{1.875}$ ceramics as a function of sintering temperature.

dielectric constant were related to the relative densities due to the invariant chemical formula. Therefore, the curve of the dielectric constant of $Ce_{0.75}Y_{0.25}O_{1.875}$ ceramics was similar to that of the relative densities, as shown in Fig. 3(a). In addition, it was known that τ_f values and ε_r had the following relationship [10]:

$$\tau_f = \alpha_L \times \left(\frac{\varepsilon_r}{2} - 1\right) \propto \varepsilon_r \tag{1}$$

where α_L was the linear thermal expansion coefficient. It was easy to get a conclusion that τ_f values and ε_r had the similar variations, which was also well represented in this work, demonstrated in Fig. 3(b). Importantly, the τ_f values varied from −17.73 ppm/°C to −23.47 ppm/°C, suggesting that $Ce_{0.75}Y_{0.25}O_{1.875}$ ceramics were belonged to the temperature-stable microwave dielectric ceramics.

The Q × *f* values, packing fraction and grain size of $Ce_{0.75}Y_{0.25}O_{1.875}$ ceramics at different sintering temperature had been exhibited in Fig. 4. Through the range of 1400 °C to 1450 °C, the Q × *f* values increased rapidly, and accompanied with the temperature being further increased, the rate of increasing slowed down, which even changed to a decrease trend when the temperature was greater than 1475 °C. The influencing factors to Q × *f* values were complex which vested in two parts, namely intrinsic and extrinsic factors. In this paper, the variation of Q × *f* values was also considered from the two parts, where packing fraction and grain size represented the intrinsic factor and extrinsic factor, respectively. As shown in Fig. 4, in the temperature range that the Q × *f* values rapidly increased, the grain size and packing fraction increased. Subsequently, the increase of the Q × *f* values became slow, due to the general effect of decrease in packing fraction and rapid increase in grain size. After the increasing temperature point of 1475 °C, the Q × *f* values decreased because the packing fraction and grain size both decreased. Therefore, the Q × *f* values of $Ce_{0.75}Y_{0.25}O_{1.875}$ ceramics were enslaved to packing fraction and grain size.

4. Conclusion

A new kind of low dielectric constant microwave dielectric ceramic of $Ce_{0.75}Y_{0.25}O_{1.875}$ had been successfully prepared, which was a temperature-stable microwave ceramic with high Q × *f* values. The $Ce_{0.75}Y_{0.25}O_{1.875}$ ceramics had the similar structural characteristics to CeO_2 and their unit-cell volume was enslaved to the sintering temperature. Temperature zone of 1400 °C to 1500 °C was suitable for the sintering process, and the grain size reached a maximum at 1475 °C. The ε_r value was governed by the relative density and did not vary much within the suitable sintering temperature range. Also, the τ_f values associated with the dielectric constant did not change much. The Q × *f* values which influenced by grain size and packing fraction had the maximum value (96600 GHz) at 1475 °C.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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