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Structure and properties of low temperature sintered $ZnTa_2O_6$ microwave dielectric ceramics

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Abstract

$ZnTa_2O_6$ microwave dielectric ceramics have been prepared using $ZnTa_2O_6$ nano-powders synthesized by sol–gel processing in this study. The crystal structure and microstructure of the $ZnTa_2O_6$ powders and ceramics were characterized by XRD and SEM techniques. $ZnTa_2O_6$ ceramics can be densified at a lower sintering temperature of 1200 °C. Microwave dielectric properties show that both of $Q \times f$ and ε_r values are lower than those of ceramics prepared by solid state route, and the τ_f values do not show different from that of solid state route. $ZnTa_2O_6$ ceramics sintered at 1200 °C exhibit good microwave dielectric properties: $Q \times f = 50{,}600$ GHz, $\varepsilon_r = 35.12$ and $\tau_f = 9.69$ ppm/°C.

Keywords: A. Sol–gel processes; C. Dielectric properties; D. $ZnTa_2O_6$; Nano-powder

1. Introduction

With the rapid progress of mobile and satellite communication systems such as cellular phones, and global positioning systems, the dielectric ceramics with high Q values have been paid much attention for their applications in microwave resonators, filters, microstrip antennas and wave guides in the past decade [1,2]. Recently, $ZnTa_2O_6$ ceramics were found to be promising candidates with high Q values for application in microwave devices due to its excellent microwave dielectric properties: $Q \times f = 87{,}580$ GHz, $\varepsilon_r = 30.3$ and $\tau_f = 9$ ppm/°C [3–5]. However, the sintering temperature of $ZnTa_2O_6$ ceramics prepared by traditional solid state route is too high (1400 °C), which limited its' applications in low-fired microwave dielectric ceramics and multilayer microwave devices. Therefore, many researchers have focused their interesting on lowing sintering temperature of $ZnTa_2O_6$ ceramics. Huang et al. investigated the dielectric behavior of CuO-doped $ZnTa_2O_6$ ceramics prepared by traditional solid-state method, and found that 0.25 wt% addition of CuO can effectively reduce the sintering temperature of $ZnTa_2O_6$ ceramics from 1350 °C to 1230 °C [6]. In general, the wet chemical preparation routes have been found to be a more effective method to lower the sintering temperature of ceramics because it is possible to produce very pure, homogeneous, and extremely fine powders with good sintering properties by those techniques [7–9]. Therefore, we prepared $ZnTa_2O_6$ ceramics using $ZnTa_2O_6$ nano-powders synthesized by sol–gel method in this paper, and the microstructures and microwave dielectric properties of $ZnTa_2O_6$ ceramics were also investigated systematically.

2. Experimental

High purity Ta_2O_5 powders, HF (40%), $Zn(NO_3)_2$ and ammonia were used as raw materials, and citric acid monohydrate (CA) was used as a chelating agent and reaction medium. Firstly, $Ta(OH)_5$ obtained by dissolving Ta_2O_5 in HF (40%) was dissolved in different amount of citric acid to form the Ta-citric solution. Then, $Zn(NO_3)_2$ solution was added to this solution and then the polymeric precursors were obtained by heating this sol–gel at 120 °C. Finally, the $ZnTa_2O_6$ powders can be obtained by heating the polymeric precursor at 900 °C. $ZnTa_2O_6$ nano-powders were ball-milled in a polyethylene

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bottle with agate balls using ethanol as a medium. After drying and sieving, the powders were uniaxially pressed into pellets with the size of 10 mm in diameter and 4 mm in thickness under the pressure of 100 MPa. The samples were sintered at 1100–1300 °C with a heating rate of 5 °C/min, and then cooled to room temperature.

The bulk densities of the sintered ceramics were measured by Archimedes method. The crystal structures of sintered samples were analyzed by X-ray diffractometry with a graphite monochromator, and CuKα radiation with step scanning. The microstructure analyses were observed by a scanning electron microscopy (SEM). The microwave dielectric properties of sintered samples were measured by HP8720ES network analyzer in the frequency range of 6–8 GHz.

3. Results and discussion

Fig. 1 shows the XRD patterns of $ZnTa_2O_6$ nano-powders and ceramics. For $ZnTa_2O_6$ nano-powders synthesized at 900 °C, the main diffraction peaks of $ZnTa_2O_6$ crystal phase can be observed, and can be good indexed in accord with single phase of $ZnTa_2O_6$ (JCPDF#76-1826) with the lattice parameters: a = 4.702 Å, b = 17.09 Å and c = 5.070 Å. The average particle size calculated from Scherrer's formula is 30 nm. For $ZnTa_2O_6$ ceramics prepared at 1200 °C, XRD patterns also show a single phase of $ZnTa_2O_6$, however, the diffraction peaks are sharper than that of $ZnTa_2O_6$ nano-powders. This phenomenon can be attributed to the growth of grain size in ceramics.

The bulk density curves of $ZnTa_2O_6$ ceramics as a function of sintering temperature are shown in Fig. 2. It can be seen that the densities of sample increase steady with increasing sintering temperature, after 1150 °C, the density increases rapidly, and reaches a maximum at 1200 °C, then decreases. The reason for rapidly change of densities at 1200 °C may be attributed to two factors, one is that the ceramics will be densitified rapidly with increasing sintering temperature as the starting materials are

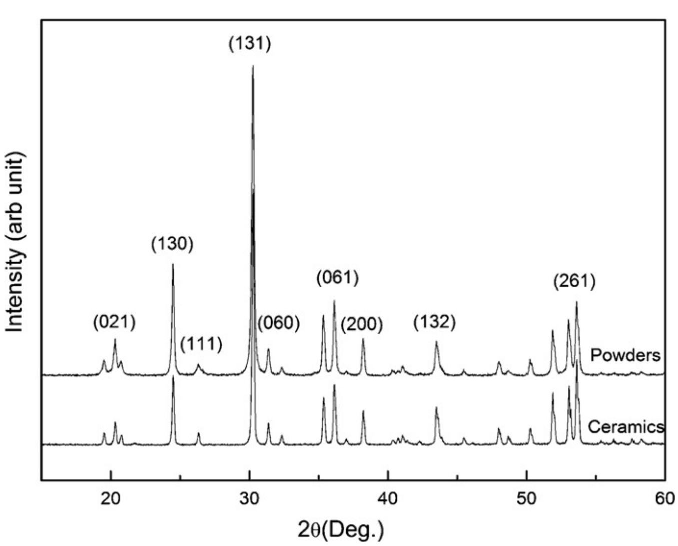

Fig. 1. XRD patterns of $ZnTa_2O_6$ nano-powders and ceramics.

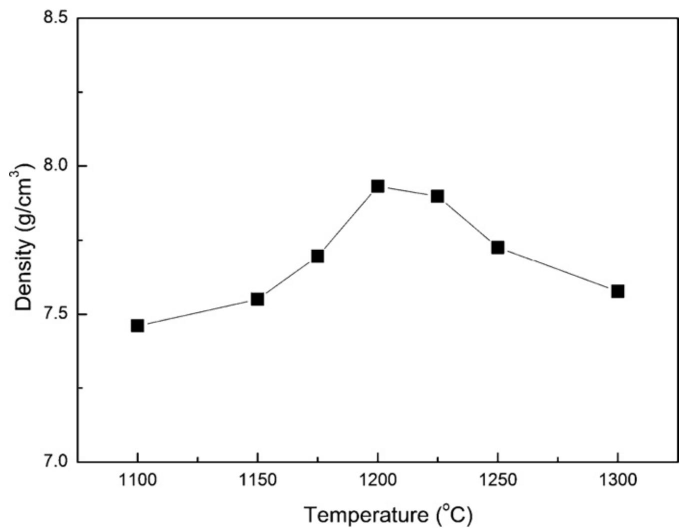

Fig. 2. Bulk density curves of $ZnTa_2O_6$ ceramics as a function of sintering temperature.

nano-powders, because that nano-powders have more higher specific surface area and surface free energy. Another one is abnormal grain growth, melting ablation and glass phase or pores will appear rapidly as the temperature is higher than sintering temperature of ceramics. These two factors make the range of sintering temperature become very narrow, which results in the remarkable change of density at 1200 °C. This result illuminates that the densification temperature of $ZnTa_2O_6$ ceramics is 1200 °C, and 93% of theoretical density can be obtained. In general, the densification temperature of $ZnTa_2O_6$ ceramics prepared by solid state route ranged from 1400 °C to 1500 °C [3,4]. Therefore, the sintering temperature of $ZnTa_2O_6$ ceramics can be lowed from 1400 °C to 1200 °C by using $ZnTa_2O_6$ nano-powders synthesized by sol–gel method.

The SEM micrographs of $ZnTa_2O_6$ ceramics sintered at different temperature are shown in Fig. 3. It can be seen that a much easier densification of $ZnTa_2O_6$ ceramics is evident at a lower sintering temperature. However, for ceramics sintered at 1100 °C (Fig. 3(a)), some pores and inhomogeneous microstructure were observed. With increasing sintering temperature to 1200 °C, the grains are uniform in size, and a few pores can be observed in surface for sintered ceramics (Fig. 3(b)). Further increasing sintering temperature to 1300 °C, some pores appear again, and abnormity growth and melting of grain can be observed from the surface of sintered ceramics (Fig. 3(c)). SEM results demonstrate that densified $ZnTa_2O_6$ ceramics can be obtained at 1200 °C, and agree with those of bulk density curves of $ZnTa_2O_6$.

The microwave dielectric properties of sintered $ZnTa_2O_6$ ceramics were measured at 6–10 GHz, and demonstrated in Fig. 4. The ε_r values of sintered $ZnTa_2O_6$ ceramics increased with increasing sintering temperature, and then reached a saturation value at 1200 °C. However, ε_r values decreased with further increasing sintering temperature. This phenomenon was attributed to the increase of relative density which depends on the sintering temperature. The relationships between $Q \times f$ values and sintering temperatures show the same trend with

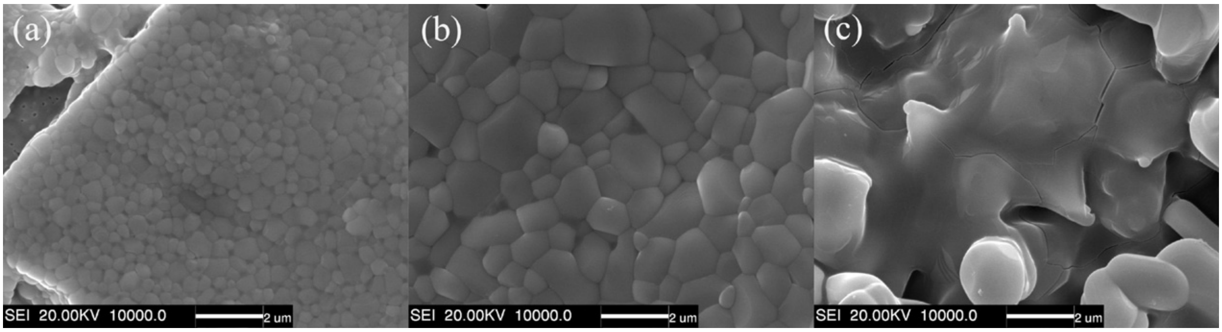

Fig. 3. SEM micrographs of $ZnTa_2O_6$ ceramics sintered at different temperature: (a) 1100 °C, (b) 1200 °C and (c) 1300 °C.

those between ε_r and sintering temperatures. As shown in Fig. 4, the $Q \times f$ values of $ZnTa_2O_6$ ceramics increased with increasing the sintering temperature, after reached the maximum value at 1200 °C, and then decreased. The highest ε_r and $Q \times f$ values of sintered $ZnTa_2O_6$ ceramics in this study were 35.72 and 50,600 GHz, respectively. However, these two values were lower than those of $ZnTa_2O_6$ ceramics reported by Lee et al. and Kan et al. [3,4]. In general, microwave dielectric loss could be divided into two fields: the intrinsic loss and extrinsic loss. The intrinsic loss was mainly caused by lattice variation modes while the extrinsic loss was mainly dominated by secondary phase, oxygen vacancies, grains sizes and densification [10]. And many researches also suggest that high $Q \times f$ values can be obtained for the ceramics with large grain size due to large grains resulted in less grain boundary, which meant less lattice mismatch and lower dielectric loss [10]. This effect of grain size on $Q \times f$ values can be also observed in this study, such as the sample sintered at 1100 °C has a smaller grain size (0.5–1 μm) and a lower $Q \times f$ value (38,400 GHz), while the grain size of ceramics sintered at 1200 °C increases to 1–2 μm, and its $Q \times f$ value also increases to the highest (50,600 GHz). Though the ceramic sintered at 1300 °C has more larger grain size, too much pores and abnormal grain growth result in the decrease of $Q \times f$ value. Therefore, the lower $Q \times f$ values may be attributed to two factors, one is lower densities of sintered ceramics compared that prepared by solid state route, another one is the smaller grain size of ceramics due to the sol–gel process.

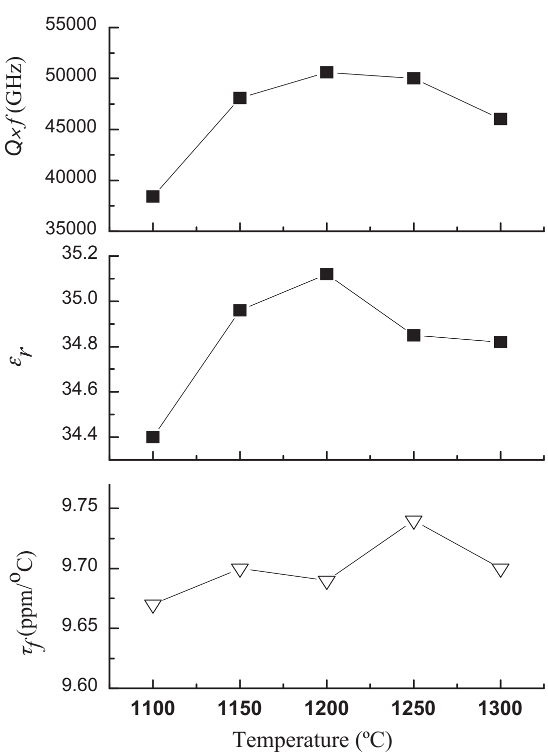

Fig. 4. Microwave dielectric properties of sintered $ZnTa_2O_6$ ceramics.

However, the temperature coefficients of resonant frequency of $ZnTa_2O_6$ ceramics show a different trend compared with ε_r and $Q \times f$ values. The τ_f values of $ZnTa_2O_6$ ceramics range from 9.67 to 9.74 ppm/°C as sintering temperatures range from 1100 °C to 1300 °C, and show a very little change for all sintering temperatures. This result suggests that sintering temperatures have no obvious effects on the τ_f values of $ZnTa_2O_6$ ceramics prepared by chemical route.

4. Conclusions

$ZnTa_2O_6$ microwave dielectric ceramics have been prepared using $ZnTa_2O_6$ nano-powders synthesized by citrate sol–gel method. XRD results reveal that a single phase of $ZnTa_2O_6$ nano-powders and ceramics can be obtained at a low temperature of 900 °C and 1200 °C, respectively. The densification temperature of $ZnTa_2O_6$ ceramics is 1200 °C, and 93% of theoretical density can be obtained. Good homogeneity microstructure with an average grain size of 1 μm can be obtained for $ZnTa_2O_6$ ceramics sintered at 1200 °C. Those results suggest that the smaller grain size of $ZnTa_2O_6$ powders caused by sol–gel process can significantly lower the sintering temperature of $ZnTa_2O_6$ ceramics. Both of $Q \times f$ and ε_r values are lower than those of ceramics prepared by solid state route, and the τ_f values do not show different from that of solid state route. $ZnTa_2O_6$ ceramics sintered at 1200 °C exhibit good microwave dielectric properties: $Q \times f$ = 50,600 GHz, ε_r = 35.12 and τ_f = 9.69 ppm/°C.

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