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Effects of aqueous gelcasting and dry pressing on the sinterability and microwave dielectric properties of $ZnAl_2O_4$-based ceramics

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Abstract

The effects of aqueous gelcasting and dry pressing on the sinterability and microwave dielectric properties of 90 wt.% ($0.75ZnAl_2O_4$–$0.25TiO_2$)–10 wt.% $MgTiO_3$(ZTM) ceramics have been investigated. It is found that aqueous gelcasting could effectively decrease the sintering temperature of ZTM ceramics by 100 °C and acquire more excellent microwave dielectric properties of ZTM ceramics compared with conventional dry pressing. X-ray diffraction (XRD), environment scanning electron microscope (ESEM) and energy-dispersive X-ray spectroscopy (EDX) were used to analyze the phase compositions and microstructures of ZTM ceramics. The results illustrate that the phase compositions are completely uniform no matter what sintering temperature and forming method are adopted. However, the densities, ε_r and $Q \times f$ values are greatly affected by different forming methods, whereas there are few effects on the τ_f values. It is observed that ZTM ceramics prepared by aqueous gelcasting exhibit greater densities, more excellent and stable microwave dielectric properties compared with that prepared by dry pressing at the relative low sintering temperatures. However, when the sintering temperature becomes higher, the opposite phenomenon would gradually appear.

Keywords: Aqueous gelcasting; Dry pressing; Sinterability; Microwave dielectric properties; $ZnAl_2O_4$

1. Introduction

With the rapid development of microwave application in the area of microwave substrate and antenna, high performance microwave dielectric ceramics with low dielectric constant (ε_r), high quality factor ($Q \times f$) and near-zero temperature coefficient of resonator frequency (τ_f) are required. Recently, Surendran et al. [1,2] had found that $ZnAl_2O_4$ ceramics present low dielectric constant ($\varepsilon_r = 8.5$) and high quality factor ($Q \times f = 56300$ GHz). However, the sintering temperature of $ZnAl_2O_4$ is so high (1650 °C) that they could not be used in real application. Meanwhile, the τ_f value of $ZnAl_2O_4$ ceramics is too negative ($\tau_f = -79$ ppm/°C) [1]. TiO_2, which has high positive τ_f value ($\tau_f = +398$ ppm/°C) [2], has often been used to adjust the τ_f value of microwave dielectric materials with negative τ_f value and lower the sintering temperature of ceramics [3–7]. In addition, it had been reported that gelcasting could decrease the sintering temperature for Al_2O_3 ceramics [8]. Therefore, gelcasting would be another promising method to decrease the sintering temperature of $ZnAl_2O_4$ ceramics.

Gelcasting, which was invented by researchers of Oak Ridge National Laboratory [9], has been successfully used to form various ceramics including Si_3N_4-SiC [10], SiC [11], and Al_2O_3 [12], etc. In this process, the high solids loading slurry is solidified by the polymerization of monomers to form green bodies. This forming method has many outstanding advantages, such as high strength of the dried green body, facile fabrication of devices with complicated shape and comprehensive application in a wide range of materials, etc. Generally, non-aqueous solvents and aqueous solvents are used in gelcasting. Non-aqueous gelcasting has several disadvantages such as health problems, environmental hazards and high cost, so aqueous gelcasting, which has the advantages of low toxicity and low cost, has been widely used to gradually substitute non-aqueous gelcasting to form various materials.

So far, some researches have been done on the microwave dielectric properties of $ZnAl_2O_4$-based ceramics prepared by conventional dry pressing method. However, there are few researches about the effects of different forming methods on the sinterability and microwave dielectric properties of microwave

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dielectric ceramics. In this paper, aqueous gelcasting and dry pressing were used to prepare 90 wt.% (0.75$ZnAl_2O_4$–0.25TiO_2)–10 wt.% $MgTiO_3$(ZTM) ceramics. In order to satisfy the requirements of our project, $MgTiO_3$ was used to adjust the ε_r and τ_f values of 0.75$ZnAl_2O_4$–0.25TiO_2 ceramics. The effects of different forming methods on the sinterability, phase compositions, microstructures and microwave dielectric properties of ZTM ceramics were investigated.

2. Experimental procedure

The monomer used in aqueous gelcasting was acrylamide (AM) and cross-linker was *N*,*N*′-methylenebisacrylamide (MBAM). 3 wt.% ammonium persulfate (APS) aqueous solution and *N*,*N*,*N*′,*N*′-tetramethyl ethylenediamine (TEMED) were used as initiator and catalyst, respectively. The dispersant used in aqueous gelcasting was ammonium polyacrylate (PAA-NH_4). The ZTM powder was prepared by the conventional solid state reaction method. Reagent grade ceramic powders ZnO (99.5%), Al_2O_3 (98.5%), TiO_2 (rutile, 99.6%) and MgO (98.5%) were used as raw materials. TiO_2 and MgO in a molar ratio of 1:1 were milled with zirconia balls and alcohol for 5 h at a speed of 365 r/min. After the slurry was dried, the mixture was calcined at 1190 °C for 3 h to synthesize $MgTiO_3$. Stoichiometric starting powders according to the compositions of 0.75$ZnAl_2O_4$–0.25TiO_2 were also milled with zirconia balls and alcohol for 5 h at a speed of 365 r/min and then dried. The powders were calcined at 1130 °C for 3 h. Afterwards, 10 wt.% $MgTiO_3$ prepared before was added into 90 wt.% 0.75$ZnAl_2O_4$–0.25TiO_2 calcined powder. After mixing and drying, some dried powders were uniaxially pressed into samples with dimensions of 20 mm diameter and 10 mm height under a pressure of 150 MPa, the other powders were used to prepare the same samples by aqueous gelcasting. The flow chart of aqueous gelcasting is shown in Fig. 1. The premix solution was prepared by mixing the monomer, cross-linker and deionized water. The concentration of the premix solution was about 14 wt.% and the ratio of AM and MBAM was 20:1. The ZTM powder and dispersant were added into the premix solution to make slurry with solids loading of about 50 vol.%. Strong aqua ammonia was used to adjust the pH value of the slurry at about 8–10 [13]. After ball milling for 1 h, the high solids loading slurry was obtained, then degassing was subsequently carried out for 10 min under vacuum. Afterwards, the catalyst and initiator were added into the slurry to initiate the gelation. After casting, demolding and drying, the green samples were removed binder at 600 °C for 1 h and then all the samples prepared by two forming methods were sintered at 1370–1470 °C for 3 h to form ceramics.

The densities of the sintered samples were measured with Archimedes method. The crystalline phase analysis of the sintered samples was achieved with X-ray diffraction (XRD) (X'Pert PRO, PANalytical B.V., Holland). The microstructure observation and quantitative analysis of the sintered samples were performed using environment scanning electron microscope (ESEM) (Quanta 200, FEI, Holland) and energy-dispersive X-ray spectroscopy (EDX) (Genesis 7000, EDAX

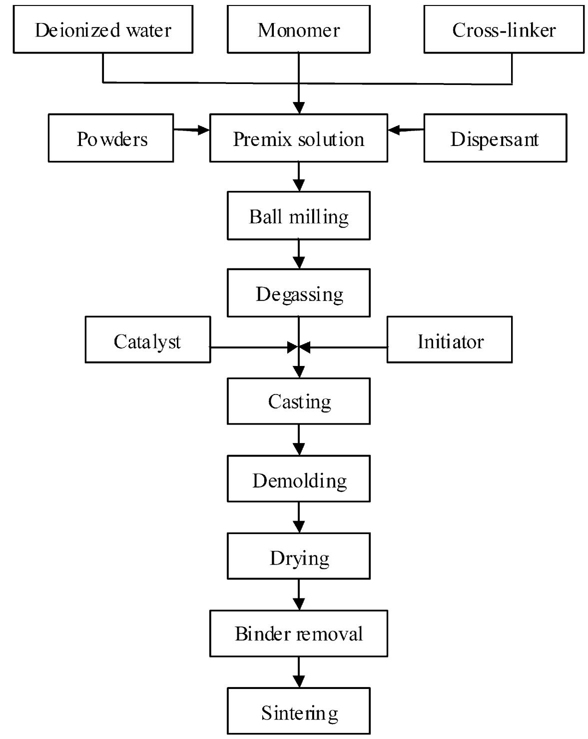

Fig. 1. The flow chart of aqueous gelcasting.

Inc., USA), respectively. The ε_r and the $Q \times f$ values were measured in the TE_{011} mode with the Hakki and Coleman method [14], a vector network analyzer (Advantest R3767C, Advantest Corporation, Japan) and parallel silver boards were used for the measurement. The temperature coefficient of resonant frequency (τ_f) was calculated with the following formula in the temperatures ranging from 25 °C to 75 °C:

$$\tau_f = \frac{1}{f(25)} \times \frac{f(75) - f(25)}{75 - 25} \quad (1)$$

where $f(25)$ and $f(75)$ represent the resonant frequency at 25 °C and 75 °C, respectively.

3. Results and discussion

The densities of ZTM ceramics prepared by aqueous gelcasting and dry pressing are shown as a function of sintering temperature in Fig. 2. With the increase of sintering temperature, the densities of ZTM ceramics prepared by aqueous gelcasting increase firstly and then decrease slightly. The densities of ZTM ceramics prepared by dry pressing increase with the increase of sintering temperature until 1420 °C, and then decrease slightly until 1445 °C. Afterwards, the densities increase again. The anomalous phenomenon appearing at 1445 °C is attributed to the increase of the volume ratio of TiO_2 phase and decrease of the volume ratio of $ZnAl_2O_4$ phase, which will be pointed out in the XRD results shown in Fig. 3. Because the theoretical density of TiO_2 (4.26 g/cm^3) is lower than that of $ZnAl_2O_4$ (4.58 g/cm^3) [1], the densities of ZTM ceramics prepared by dry pressing and sintered at

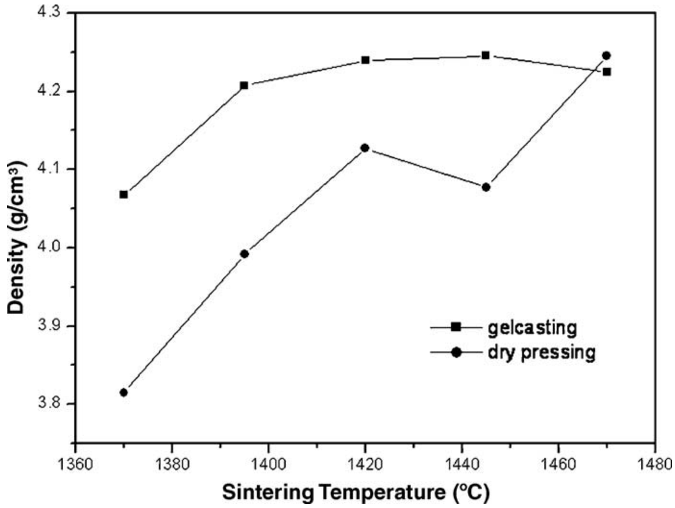

Fig. 2. Densities of ZTM ceramics prepared by aqueous gelcasting and dry pressing as a function of sintering temperature.

1445 °C decrease slightly. Meanwhile, it is obvious that the densities of ZTM ceramics prepared by aqueous gelcasting are much greater than that of ZTM ceramics prepared by dry pressing at the same sintering temperature below 1470 °C, which means that ZTM ceramics prepared by aqueous gelcasting are much denser than that prepared by dry pressing. Particles in the ZTM ceramics prepared by aqueous gelcasting are more compact and uniform, which is helpful for the mass transfer in the sintering process. Meanwhile, the increase of sintering temperature is beneficial for the diffusion of ions and could give rise to the increase of densities. Whereas, when the sintering temperature becomes too high, the abnormal grains growth, ions volatilization and other defects would appear in the sintered ceramics, which could lead to the decrease of densities.

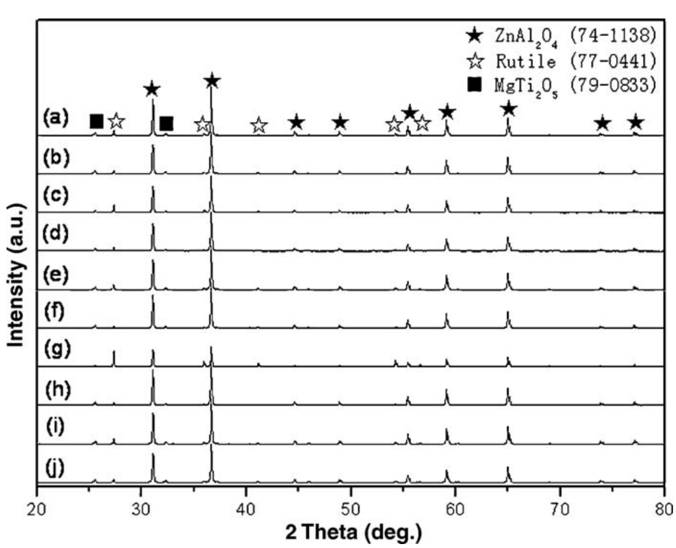

Fig. 3. X-ray diffraction patterns of ZTM ceramics sintered at (a) 1370 °C, (c) 1395 °C, (e) 1420 °C, (g)1445 °C, and (i) 1470 °C, respectively, prepared by dry pressing; (b) 1370 °C, (d) 1395 °C, (f) 1420 °C, (h)1445 °C, and (j) 1470 °C, respectively, prepared by aqueous gelcasting.

Fig. 3 shows the X-ray diffraction patterns of the ZTM ceramics prepared by aqueous gelcasting and dry pressing and sintered at different temperatures. The sintered ceramics include $ZnAl_2O_4$, rutile (TiO_2) and $MgTi_2O_5$ phases indexed in JCPDS card Nos. 74-1138, 77-0441 and 79-0833, respectively, and the X-ray diffraction intensities of all the phases are nearly the same whatever the sintering temperature and forming method are chosen, which means that the sintering temperature and forming method could not change the phase compositions and X-ray diffraction intensities of each phase. However, the X-ray diffraction intensities of TiO_2 enhance and that of $ZnAl_2O_4$ weaken greatly in the ZTM ceramics prepared by dry pressing and sintered at 1445 °C (Fig. 3(g)), which would be investigated in the future.

Fig. 4 shows the SEM micrographs of ZTM ceramics prepared by aqueous gelcasting and dry pressing at the sintering temperatures ranging from 1420 °C to 1470 °C and EDX micrographs of grains. The grains grow obviously with the increase of sintering temperature for the ZTM ceramics prepared by aqueous gelcasting and dry pressing, as shown in Fig. 4. Meanwhile, at the same sintering temperature, it could be found that the grains of ZTM ceramics prepared by aqueous gelcasting are bigger than that of ZTM ceramics prepared by dry pressing (Fig. 4(a) and (b)), which will be more obvious when the sintering temperature becomes higher (Fig. 4(e) and (f)). At the lower sintering temperature (such as 1420 °C), there are less pores existing in the ZTM ceramics prepared by aqueous gelcasting than that existing in the ZTM ceramics prepared by dry pressing, but when the sintering temperature becomes higher (such as 1470 °C), there are nearly no pores existing in the ZTM ceramics no matter what forming method is adopted. This phenomenon is in accordance with the trend of densities shown in Fig. 2. Obviously, there are two kinds of grains existing in the ZTM ceramics, namely big grains and small grains. Generally, grains with different shapes, dimensions and colors represent different phase compositions. In order to identify the phase compositions of different grains, EDX was used for the ZTM ceramics, as shown in Fig. 4(g) and (h). Combining the analysis of XRD, it could be found that the big grains are TiO_2, and the small grains are $ZnAl_2O_4$ and $MgTi_2O_5$. With the increase of sintering temperature, the TiO_2 grains become so big that finally the $ZnAl_2O_4$ and $MgTi_2O_5$ grains are entirely submerged by the TiO_2 grains at the sintering temperature of 1470 °C.

Fig. 5 shows the microwave dielectric properties of the ZTM ceramics prepared by aqueous gelcasting and dry pressing as a function of the sintering temperature. Fig. 5(a) illustrates the relationship between ε_r values and sintering temperatures. The ε_r values are strongly dependent on the sintering temperatures. With the increase of sintering temperature, the ε_r values of ZTM ceramics prepared by aqueous gelcasting increase firstly and then decrease slightly, whereas that of ZTM ceramics prepared by dry pressing increase all the time. Compared with ZTM ceramics prepared by dry pressing, it is obvious that ZTM ceramics prepared aqueous gelcasting exhibit higher ε_r values at the same sintering temperature below 1445 °C. The ε_r values are greatly affected by densities of ZTM ceramics, so the

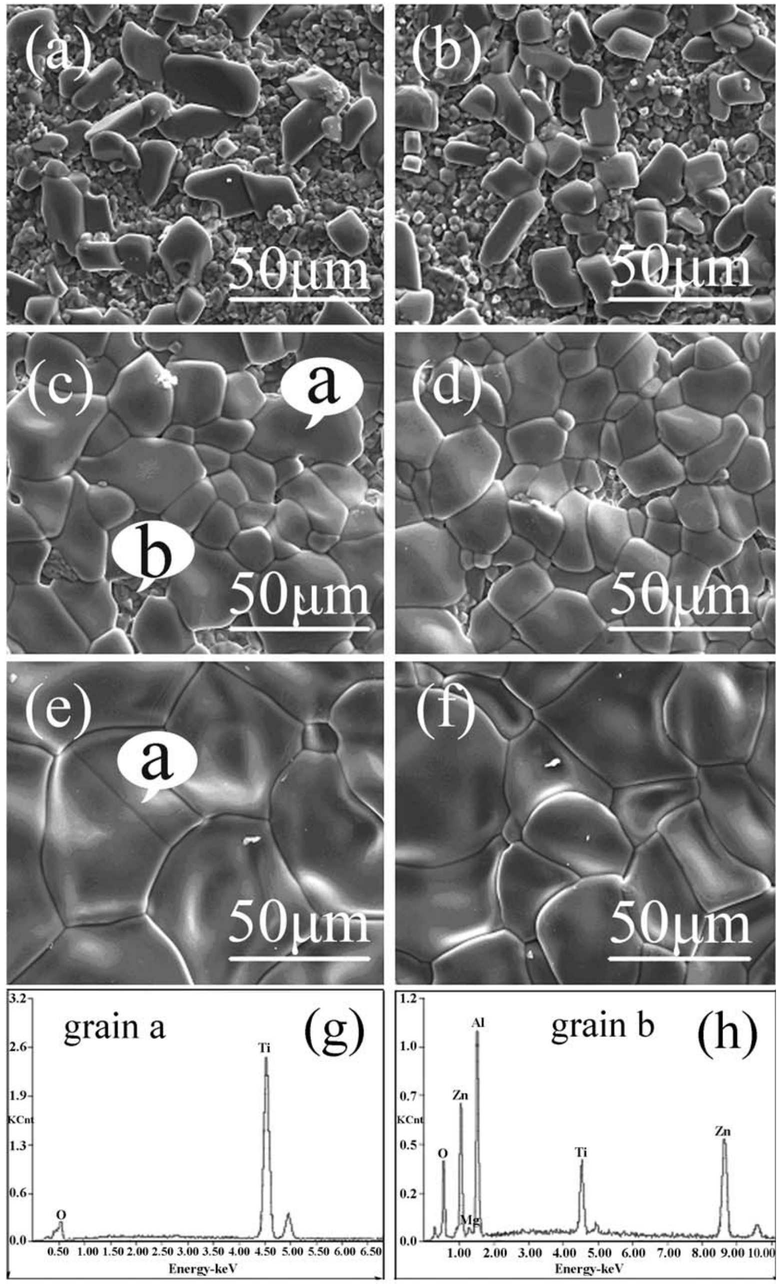

Fig. 4. The scanning electron microscope micrographs of ZTM ceramics sintered at (a) 1420 °C, (c)1445 °C, and (e) 1470 °C, respectively, prepared by aqueous gelcasting; (b) 1420 °C, (d)1445 °C, and (f) 1470 °C, respectively, prepared by dry pressing. EDX micrographs of (g) TiO_2, and (h) $ZnAl_2O_4$ and $MgTi_2O_5$ grains.

relationship between ε_r values and sintering temperatures is nearly the same as that between densities and sintering temperatures, as shown in Fig. 2. When the sintering temperature is below 1445 °C, the ZTM ceramics prepared by aqueous gelcasting are denser than that prepared by dry pressing, so less pores exist in the ZTM ceramics prepared by aqueous gelcasting. Air containing in the pores has a very low dielectric constant ($\varepsilon_r = 1$), therefore, ε_r values of ZTM ceramics prepared by dry pressing are lower.

Fig. 5(b) illustrates the relationship between $Q \times f$ values and sintering temperatures for the ZTM ceramics prepared by aqueous gelcasting and dry pressing. As shown in Fig. 5(b), no matter what forming method is chosen, the same tendency is observed that the $Q \times f$ values initially increase and then decrease after reaching the maximum at 1420 °C, whereas the ceramics' densification temperature is higher than this temperature. However, at the temperature below 1420 °C, the $Q \times f$ values of the ZTM ceramics prepared by aqueous gelcasting are much larger and more stable than that of the ZTM ceramics prepared by dry pressing. When the sintering temperature is above 1420 °C, the opposite phenomenon could be observed. Generally, it has been found that densities play an important role in controlling dielectric loss for microwave dielectric materials [15–17]. Moreover, the $Q \times f$ value is

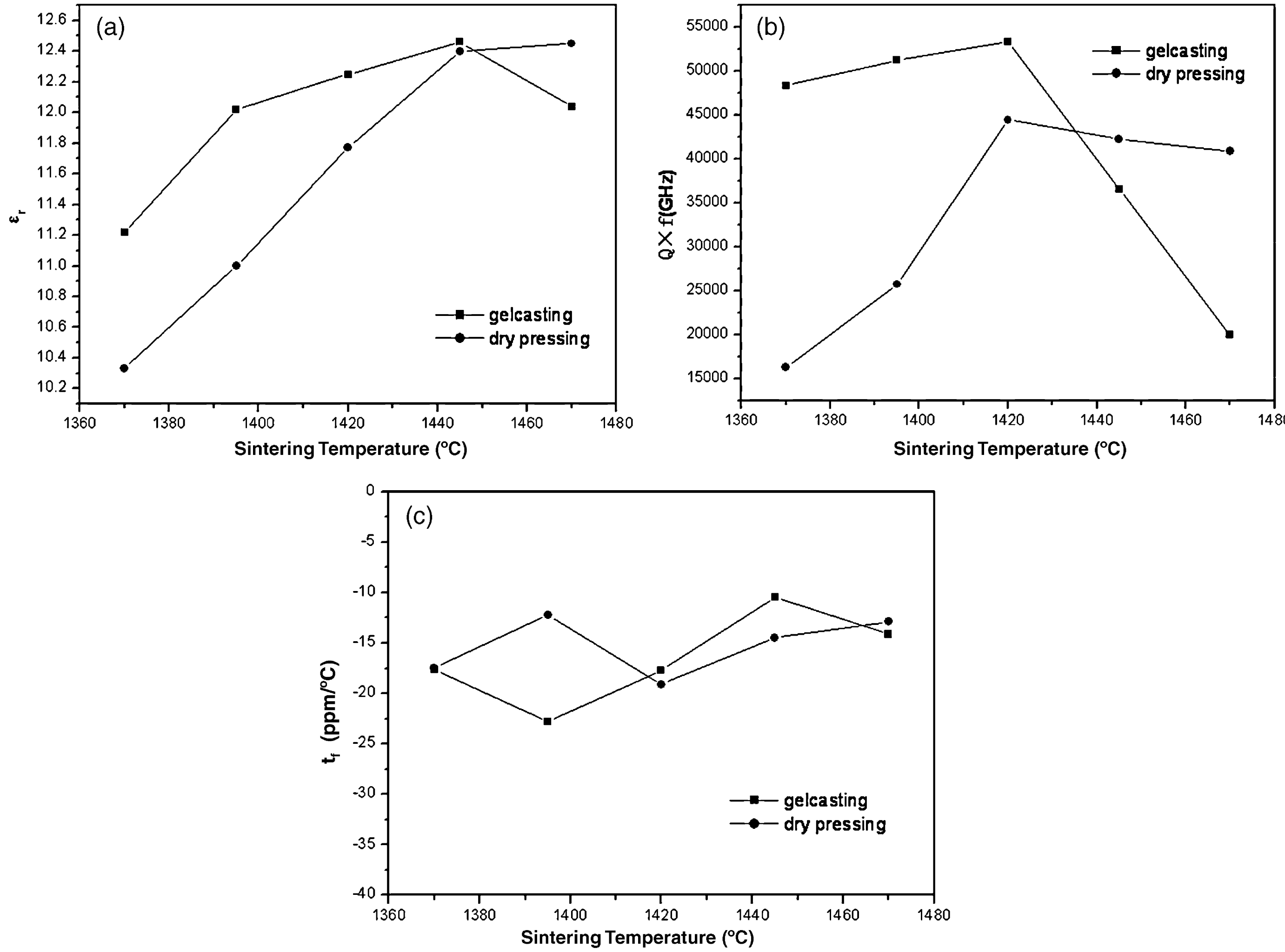

Fig. 5. Microwave dielectric properties of ZTM ceramics prepared by aqueous gelcasting and dry pressing.

affected not only by the lattice vibrational modes, but also by pores, secondary phases, impurities, lattice defect, crystallizability and inner stress [15,16]. Because particles in the ZTM ceramics prepared by aqueous gelcasting are more compact and uniform, it is helpful for the mass transfer in the sintering process. Therefore, denser ceramics and more excellent microwave dielectric properties could be obtained for the ZTM ceramics prepared by aqueous gelcasting compared with the conventional dry pressing at certain range of sintering temperature. Furthermore, the increase of sintering temperature is good for the diffusion of ions, reduction of crystal lattice defects, densification and crystallizability, which could result in the increase of $Q \times f$ values. However, when the sintering temperature is too high, ions could break away from crystal lattice and then form micro-pores, around which the deformation of lattice matrix and structural defection will appear, they could result in the decrease of $Q \times f$ values of the ZTM ceramics. Fig. 5(c) demonstrates that there are few effects on the τ_f values when different sintering temperatures and forming methods are adopted.

As shown in Fig. 5, it could also be found that using the aqueous gelcasting to prepare ZTM ceramics could decrease the sintering temperature of ZTM ceramics by 100 °C and acquire better microwave dielectric properties compared with conventional dry pressing. Therefore, it could be predicted that when the solids loading of slurry becomes higher, lower sintering temperature and more excellent microwave dielectric properties will be obtained.

4. Conclusion

The aqueous gelcasting could effectively improve the sinterability and microwave dielectric properties of ZTM ceramics compared with conventional dry pressing. With the help of XRD, ESEM and EDX, it could be found that the phase compositions are completely uniform no matter what sintering temperature and forming method are adopted. Whereas, compared with dry pressing, the aqueous gelcasting could effectively decrease the sintering temperature for ZTM ceramics by 100 °C, which is very significative for the research in the future. Moreover, the densities, ε_r and $Q \times f$ values of ZTM ceramics prepared by aqueous gelcasting could be greatly improved at the relative low sintering temperatures. With the further increase of sintering temperature, the microwave dielectric properties of ZTM ceramics prepared by aqueous gelcasting would become inferior.

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