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PII: S0167-577X(18)30257-X
DOI: https://doi.org/10.1016/j.matlet.2018.02.051
Reference: MLBLUE 23877

To appear in: *Materials Letters*

Received Date: 3 July 2017
Revised Date: 25 January 2018
Accepted Date: 11 February 2018

Please cite this article as: Y. Wang, L-Y. Zhang, S-B. Zhang, W-S. Xia, L-W. Shi, Sintering behavior and microwave dielectric properties of $MgZrTa_2O_8$ ceramics with fluoride addition, *Materials Letters* (2018), doi: https://doi.org/10.1016/j.matlet.2018.02.051

Sintering behavior and microwave dielectric properties of $MgZrTa_2O_8$ ceramics with fluoride addition

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Abstract

$MgZrTa_2O_8$ ceramics with CaF_2 addition were synthesized by solid-state reaction, and the effects of CaF_2 addition on sintering behavior and microwave dielectric properties were investigated. The densification of $MgZrTa_2O_8$ ceramics could be effectively accelerated with CaF_2 addition and the sintering temperature of CaF_2-doped $MgZrTa_2O_8$ ceramics was lowered from 1475℃ to 1375℃ due to liquid phase effect. The phase composition of $MgZrTa_2O_8$ ceramics with CaF_2 addition varied from single phase to three phases because of the reaction between $MgZrTa_2O_8$ and CaF_2. Well-developed microstructure was observed with 0.5 wt.% CaF_2 addition owing to the single phase. The microwave dielectric properties presented a significant dependence on extrinsic effects. The dielectric constant (ε_r) of CaF_2-doped $MgZrTa_2O_8$ ceramics had no significant difference for all levels of CaF_2 addition. The quality factors $Q\times f$ were strongly affected by the content of CaF_2 owing to the density, grain size and phase composition. The temperature coefficients of resonant frequency (τ_f) were correlated with the dielectric constant, which could be optimized to -2.86 ppm/℃ with CaF_2 addition. In this work, the $MgZrTa_2O_8$ ceramics could be optimized to the temperature-stable dielectric material for microwave application.

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Keywords: ceramics; CaF_2 addition; sintering behavior; microwave dielectric properties

1. Introduction

Recently, monoclinic structure material of $MgZrTa_2O_8$ ceramics had received much more attention because of its excellent microwave dielectric properties with ε_r=29.5, Q×f=140900 GHz, τ_f~-44.3 ppm/℃, sintered at 1450℃ [1] and ε_r=22.76, Q×f=131500 GHz, and τ_f~-33.81 ppm/℃, sintered at 1475℃ [2]. However, it was important to note that the sintering temperature of pure $MgZrTa_2O_8$ ceramics was higher than 1450℃ and its temperature coefficient of resonator frequency was also too large (τ_f<-33 ppm/℃), which limited its application in microwave frequencies. Therefore, the purpose of this paper was to lower the sintering temperature and optimize the τ_f values.

In addition, fluorides, such as LiF, MgF_2 and CaF_2 with low melting point, were the well-known sintering aids for microwave ceramics utilizing to lower the sintering temperature [3-5]. In this paper, CaF_2 was chosen as the sintering aid to lower the sintering temperature and optimize the τ_f values. Moreover, the effects of CaF_2 addition on microstructure and microwave dielectric properties were also investigated.

2. Experimental procedure

$MgZrTa_2O_8$ powders were synthesized from the raw materials including MgO (99%), ZrO_2 (99%) and Ta_2O_5 (99.9%). The raw materials were mixed according to the formula of $MgZrTa_2O_8$ and ball-milled in distilled water for 24 h. After milling, all mixtures were dried and calcined at 1000℃ for 4h. Then calcined powders were prepared with various amount of CaF_2 (99%) addition. Next, the mixtures were re-milled for 24 h. After milling, the slurries were dried, crushed and sieved with an 80 mesh screen. The mixtures were pressed into 10 mm diameter and 5 mm thickness pellets. Then these pellets were sintered between 1350℃ and 1450 ℃ for 4h. The heating rate was 5℃/min.

The crystal structure of the sintered pellets were analyzed by powder X-ray diffraction analysis using Rigaku diffractometer (Model D/Max-B, Rigaku Co., Japan). Bulk densities of the samples were measured by using the Archimedes method (Mettler Toledo XS64). The microstructure on ceramic surfaces was performed and analyzed by a scanning electron microscopy (SEM, FEI Quanta 250, USA), and the compositions of the ceramics were characterized by Energy Dispersive Spectrometer (EDS, Bruker Quantax 400-10, Germany). Microwave dielectric properties of the sintered pellets were measured by a network analyzer (N5234A, Agilent Co., USA) in the frequency range of 7-10 GHz using Hakki-Coleman's dielectric resonator method [6, 7]. The τ_f values could be obtained by measuring the $TE_{01\delta}$ resonant frequency from 25℃ to 85℃ and calculated by noting the changes in resonant frequency (Δf),

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \qquad (1)$$

where f_1 was resonant frequency at T_1, and f_2 was the resonant frequency at T_2.

3. Result and discussion

Fig. 1 showed the apparent density of $MgZrTa_2O_8$-x wt.% CaF_2 ($0.5 \le x \le 2.0$) ceramics at different sintering temperature. The apparent densities of all samples increased to a maximum value and then tended to be gentle. The density curve suggested that the optimal sintering temperature of $MgZrTa_2O_8$ ceramics with 0.5-2.0 wt.% CaF_2 addition were 1375℃. In addition, the apparent densities of sintered samples decreased with the increase of CaF_2 content when the sintering temperature was fixed, implying that excessive CaF_2 addition was not conducive to densification of $MgZrTa_2O_8$ ceramics. However, the results of apparent density curve indicated that the sintering characteristic of $MgZrTa_2O_8$ ceramics could be optimized with CaF_2 addition.

Fig. 2 showed the results of the X-ray diffraction measurements for $MgZrTa_2O_8$-x wt.% CaF_2

(0.5≤x≤2.0) ceramics sintered at 1375℃. The diffraction patterns for $MgZrTa_2O_8$-0.5 wt.% CaF_2 ceramics were indexed by wolframite structure type belonged to *P2/c* (C_{2h}^4) space group (orthorhombic: ICDD-PDF #00-039-1484) with no second phase being observed. When x≥1.0, the main crystal phase was also matched with $MgZrTa_2O_8$ phase, however other phases, which were indexed by $CaTa_2O_6$ and $Ca_2Ta_2O_7$ phase, were observed. It was noted that the peak intensities of the two phases increased with the increasing of CaF_2 addition, which suggested that the proportion of $CaTa_2O_6$ and $Ca_2Ta_2O_7$ phase increased. These results of the XRD measurements indicated that the $MgZrTa_2O_8$ ceramics sintered at 1375℃ exhibited almost a single phase with less CaF_2 addition, excessive CaF_2 addition would result in the formation of other phases.

Fig. 3 illustrated the SEM images of $MgZrTa_2O_8$-x wt.% CaF_2 (0.5≤x≤2.0) ceramics sintered at 1375℃. Significant differences in grain growth were observed between x=0.5 and 1.0≤x≤2.0. The well-developed microstructure of the ceramics could be achieved with x=0.5 at 1375℃, and the morphologies of $MgZrTa_2O_8$ ceramics were homogeneous. However, with CaF_2 content increased, the grains grew abnormally and the grain shapes tended to ruleless, as shown in Fig. 3b-3d. In addition, the average grain size of the samples were decreased and more than two kinds of grain shapes were observed, which had different elemental ratios (Spot A: Mg:Ta=10.27:25.05 at.%, Spot B: Mg:Ta=0.26:33.22 at.%, Spot C: Mg:Ta=0.00:22.45 at.%). Together with the density and XRD analysis, it could be seen that the well-developed microstructure of $MgZrTa_2O_8$ ceramics with a single phase could be achieved with CaF_2 addition (x=0.5), sintered at 1375℃, and exceeded CaF_2 addition had no benefits to the densification and phase composition of $MgZrTa_2O_8$ ceramics.

The microwave dielectric properties of $MgZrTa_2O_8$-x wt.% CaF_2 (0.5≤x≤2.0) ceramics were illustrated in Table 1. The microwave dielectric properties of these samples varied regularly with the variation of CaF_2 content, because the grain growth, densification and phase composition of microwave dielectric ceramics, which affected the microwave dielectric properties, were changed with different content of CaF_2 addition.

It was known that the dielectric constant was depended on apparent density and phase composition. Allow for the analysis of XRD results, the dielectric constant of the samples were related to $CaTa_2O_6$ (ε_r=21.2) and $Ca_2Ta_2O_7$ (ε_r=23.53) phase. Compared the dielectric constant of $MgZrTa_2O_8$, $CaTa_2O_6$ and $Ca_2Ta_2O_7$ ceramics [8, 9], the dielectric constant of the samples should have no significant variation according to the Lichtenecker logarithmic mixing rule. It suggested that the phase composition was not the main factor influencing the dielectric constant. In addition, the variation of dielectric constant was consistent with that of density, and a maximum ε_r value of 23.63 was obtained for $MgZrTa_2O_8$ ceramics with a 0.5 wt.% CaF_2 addition sintered at 1375℃, as shown in table 1. It is known that higher density would lead to higher dielectric constant owing to lower porosity. It suggested that 1375℃ was a suitable sintering temperature when CaF_2 was added, which was lower than that of pure $MgZrTa_2O_8$ ceramics (the sintering temperature of pure $MgZrTa_2O_8$ ceramics was 1475℃).

The τ_f values were governed by the composition, additives and second phase of the materials and satisfied with the Lichtenecker logarithmic mixing rule. According to the analysis of dielectric constant, these factors were considered to explain the variation of dielectric constant. Here, the changes of τ_f values were consistent with those of dielectric constant. The relationship between τ_f values and ε was founded as shown follows [10]:

$$\boldsymbol{\tau_f = \alpha_L \times \left(\frac{\varepsilon}{2} - 1\right) \propto \varepsilon} \qquad (2)$$

Thus, the change rules of τ_f values and ε_r were consistent. The best τ_f value of -2.86 ppm/℃ was obtained in 0.5 wt.% CaF_2-doped $MgZrTa_2O_8$ ceramics sintered at 1375℃ (for pure $MgZrTa_2O_8$ ceramics, τ_f~-34ppm/℃ sintered at 1475℃).

As shown in Table 1, the $Q\times f$ values of the ceramics decreased quickly with an increase of CaF_2 content. It is known that the quality factor of ceramics at microwave frequency was governed by density, grain size and phase composition. With the increasing CaF_2 content, the density and grain size decreased according to the analysis of sample density and SEM images, which resulted in deterioration of $Q\times f$ values. Moreover, the phase composition changed from single phase to three phases with the dielectric loss of $CaTa_2O_6$ and $Ca_2Ta_2O_7$ ceramics being larger, which exacerbated degradation of $Q\times f$ values.

4. Conclusion

The effects of CaF_2 addition on the densification and microwave dielectric properties of $MgZrTa_2O_8$ ceramics were investigated. The added CaF_2 effectively lowered the sintering temperature of $MgZrTa_2O_8$ ceramics from 1475°C to 1375°C due to the liquid-phase effect. The grain growth, densification and phase composition of microwave dielectric ceramics, which affected the microwave dielectric properties, were changed with different content of CaF_2 addition owing to the reaction with CaF_2. The variation of dielectric constant was consisted with that of the density. The $Q\times f$ values decreased due to the deterioration of density, grain size and phase composition. The τ_f values were correlated with the dielectric constant, which could be optimized to -2.86 ppm/℃ with CaF_2 addition.

Acknowledgements

This work is supported by the National Natural Science Foundation of China under Grant No. 51702359 and the projects from the Fundamental Research Funds for the Central Universities of China University of Mining and Technology under Grant No. 2017XKQY016.

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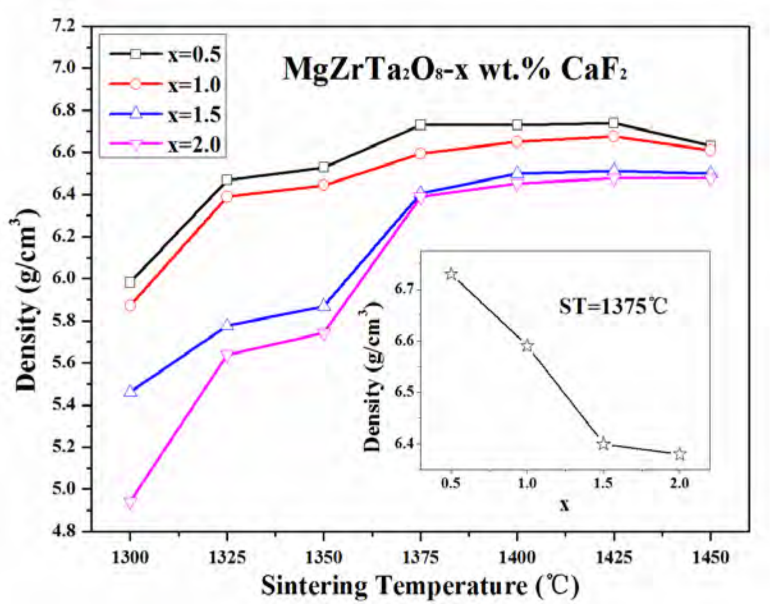


Fig. 1. Densities of $MgZrTa_2O_8$-x wt.% CaF_2 (0.5≤x≤2.0) ceramics sintered at different temperatures

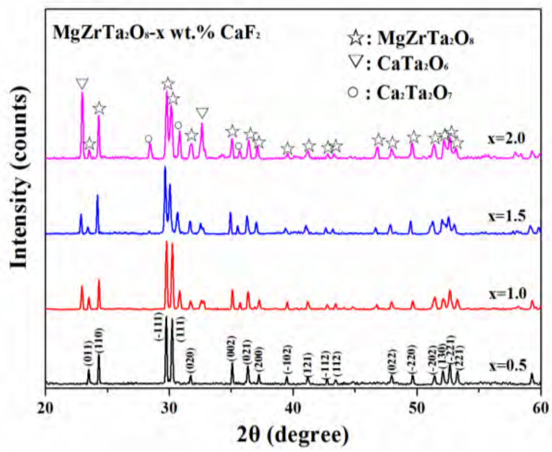


Fig. 2. XRD patterns of $MgZrTa_2O_8$-x wt.% CaF_2 (0.5≤x≤2.0) ceramics sintered at 1375℃

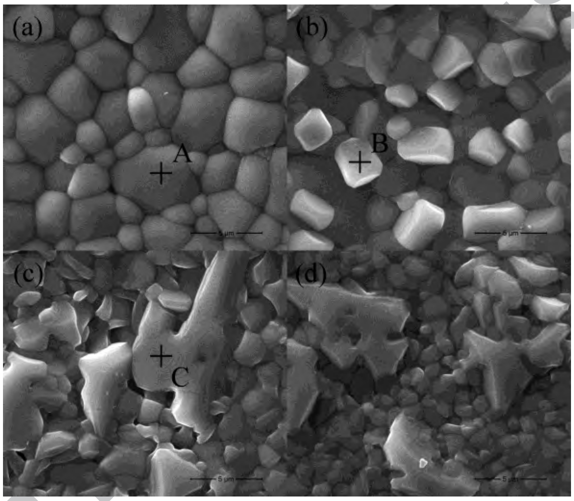
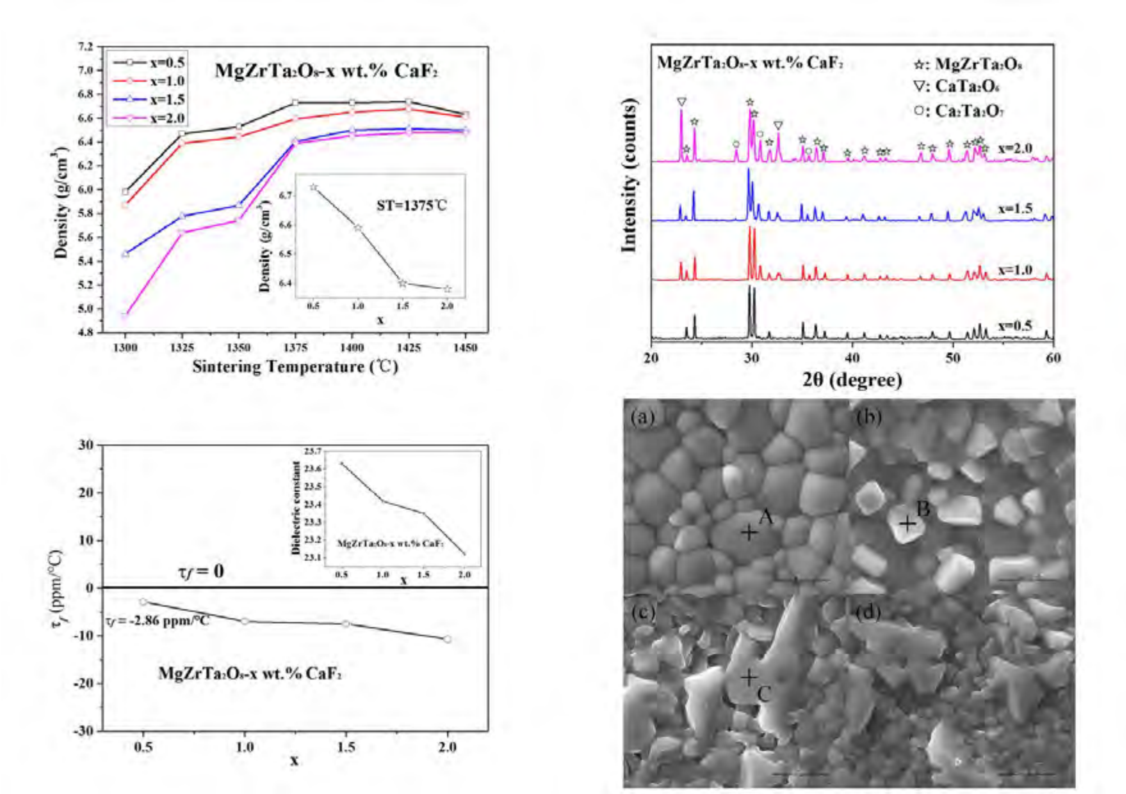


Fig. 3. SEM micrographs of $MgZrTa_2O_8$-x wt.% CaF_2 (0.5≤x≤2.0) ceramics sintered at 1375℃ with (a) x=0.5, (b) x=1.0, (c) x=1.5, (d) x=2.0

Table 1. Microwave dielectric properties and phase composition of $MgZrTa_2O_8$-x wt.% CaF_2 (0.5≤x≤2.0) ceramics

Composition x	**Phase composition**	**Density (g/cm^3)**	**ε_r**	**Q×*f* (GHz)**	**τ_f (ppm/℃)**
0.5	$MgZrTa_2O_8$	6.73	23.63	39000	-2.86
1.0	$MgZrTa_2O_8$ +$CaTa_2O_6$ +$Ca_2Ta_2O_7$	6.59	23.42	20000	-6.92
1.5	$MgZrTa_2O_8$ +$CaTa_2O_6$ +$Ca_2Ta_2O_7$	6.40	23.35	11400	-7.47
2.0	$MgZrTa_2O_8$ +$CaTa_2O_6$ +$Ca_2Ta_2O_7$	6.38	23.12	9000	-10.7

Graphical Abstract



Sintering temperature of $MgZrTa_2O_8$ ceramics was effectively lowered from 1475℃ to 1375℃. The temperature coefficients of resonant frequency of $MgZrTa_2O_8$ ceramics was optimized to -2.86 ppm/℃. The microstructure and crystal structure were analyzed to investigate the microwave dielectric properties.

Highlights:

1. The sintering temperature of $MgZrTa_2O_8$ ceramics was effectively lowered.
2. The densification of $MgZrTa_2O_8$ ceramics could be accelerated with CaF_2 addition.
3. The τ_f values of $MgZrTa_2O_8$ ceramics have been optimized to a near-zero level.
4. The extrinsic factors were the main factors affected the microwave dielectric properties.