Investigation on microwave dielectric properties of new low-loss $CoZrTa_2O_8$ ceramics

Ying Wang, Shao-Bo Zhang, Tian-Liang Tang, Wang-Suo Xia, Li-Wei Shi

PII: S0167-577X(18)31178-9
DOI: https://doi.org/10.1016/j.matlet.2018.07.136
Reference: MLBLUE 24702

To appear in: *Materials Letters*

Received Date: 20 May 2018
Revised Date: 12 July 2018
Accepted Date: 29 July 2018

Please cite this article as: Y. Wang, S-B. Zhang, T-L. Tang, W-S. Xia, L-W. Shi, Investigation on microwave dielectric properties of new low-loss $CoZrTa_2O_8$ ceramics, *Materials Letters* (2018), doi: https://doi.org/10.1016/j.matlet.2018.07.136

Investigation on microwave dielectric properties of new low-loss $CoZrTa_2O_8$ ceramics

Ying Wang†, Shao-Bo Zhang, Tian-Liang Tang, Wang-Suo Xia, Li-Wei Shi†

School of Physical science and technology, China University of Mining and Technology, Xuzhou 221116, China

Abstract

New ceramics with $CoZrTa_2O_8$ formula were prepared by conventional solid-state reaction method. The phase composition of all sintered samples was confirmed as a single phase with monoclinic wolframite structure belonged to the *P2/c* space group. The grain growth was analyzed through the investigation of relative density and grain size. The dielectric constant (ε_r) was discussed with relative density, polarizability and porosity. The quality factors ($Q\times f$) were analyzed by considering grain growth and atomic packing fraction. The temperature coefficient of resonant frequency (τ_f) had no significant change under different sintering temperature. The typical microwave dielectric properties of $CoZrTa_2O_8$ ceramics were ε_r=23.54, $Q\times f$=20100GHz, and τ_f=-8.72ppm/℃, sintered at 1250℃ for 4h. Considering the low dielectric loss and near-zero τ_f value, $CoZrTa_2O_8$ ceramics should be good candidates for microwave device application.

Keywords: Ceramics; Microwave dielectric properties; Sintering; Structural feature

1. Introduction

With the ongoing revolution in wireless communication, microwave dielectric ceramics, which play an important role in microwave devices, have attracted increasing research interests [1-4]. Under this background, many researchers have been committed to research and develop new microwave dielectric

† Corresponding author. Tel./fax:+86 18852140230

E-mail address: wangy@cumt.edu.cn (Y. Wang), liwei5450@cumt.edu.cn (L. W. Shi)

ceramics.

Zn-AO_2-Nb_2O_5 (A= Ti, Zr, Sn) system had been studied firstly by A. Baumgarte and R. Blachnik in 1994 [5]. In that paper, the crystalline structure of $ZnTiNb_2O_8$ had been reported with orthorhombic, space group *PBCN*. Then, the phase composition and microwave dielectric properties of $Zn_3Nb_2O_8$-TiO_2 and $ZnNb_2O_6$-TiO_2 had been studied by D. W. Kim *et al* [6, 7]. In 2011, $ZnTiNb_2O_8$ ceramics, as a new microwave dielectric material, had drawn a great of interests owing to the excellent microwave dielectric properties: ε_r~34, $Q\times f$~50000GHz, τ_f~-45ppm/℃ [8]. Thereafter, a series of novel microwave dielectric ceramics, which had similar formulate to $ZnTiNb_2O_8$, had been reported for their possible use in microwave application [9-12]. Among the researches, it was important to note that those new ceramics were almost obtained by ionic substitution on Zn-site, Ti-site or Nb-site of $ZnTiNb_2O_8$ ceramics. However, what was noteworthy was that there were less investigations on $A^{2+}ZrTa_2O_8$ system, which obtained by employing Zr and Ta ions as substitution ions. Especially, there were no report on $A^{2+}ZrTa_2O_8$ ceramics with A=Mn, Co, Ni. To develop a new-type microwave dielectric ceramic with excellent properties, and considering that Co ion was a good substitution in the type of bivalent ions, high-Q microwave dielectric ceramics $CoZrTa_2O_8$, which were made by utilizing Co to occupy A-site of $A^{2+}ZrTa_2O_8$ ceramics, had been prepared and investigated.

In this work, $CoZrTa_2O_8$ ceramics, which exhibited a pure phase with monoclinic wolframite structure, were successfully prepared for the first time up to now. Moreover, microwave dielectric properties of $CoZrTa_2O_8$ ceramics had been reported, with the influence of intrinsic factors and extrinsic factors on microwave dielectric properties being taken into overall consideration.

2. Experimental procedure

$CoZrTa_2O_8$ ceramics were synthesized using conventional mixed-oxide methods with high-purity

oxide powders including CoO (99%), ZrO_2 (99%) and Ta_2O_5 (99.9%). These powders were milled under distilled water for 12h with zirconia ball. After milling, the slurries were dried using a dry oven and sieved with a 40 mesh screen. The powders were calcined at 1000℃ for 4h in an alumina crucible. Then the calcined powders were re-milled for 24h in distilled water. Next, the slurries were dried and sieved again with an 80 mesh screen. The final powders were pressed into pellets with 10 mm in diameter and 5 mm in thickness. Ultimately, these pellets were sintered between 1175℃ and 1275 ℃ for 4h in air.

Crystalline phases of $CoZrTa_2O_8$ ceramics were analyzed by powder X-ray diffraction analysis using a Rigaku diffractometer (Model D/Max-B, Rigaku Co., Japan) with Ni filtered Cu Kα radiation (λ=0.1542nm) in the 2θ range of 10-90°. The ceramic surface was observed and analyzed using a scanning electron microscopy (SEM, FEI Quanta 250, USA). Densities of the sintered specimens were measured using the liquid Archimedes method (Mettler Toledo XS64) with distilled water. Moreover, the microwave dielectric properties were measured via Hakki-Coleman's dielectric resonator method using a network analyzer (N5234A, Agilent Co., USA) in the frequency range of 7-10 GHz [13, 14]. The τ_f values were calculated with temperature variation of the $TE_{01\delta}$ mode (temperature range from 25℃ to 85℃). The τ_f (ppm/℃) was defined as the following formula:

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \qquad (4)$$

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

3. Result and discussion

Fig. 1 showed the SEM images of $CoZrTa_2O_8$ ceramics sintered at different temperatures. There was no pore observed in all images, suggesting that the well-developed microstructure was obtained. The grain size of $CoZrTa_2O_8$ ceramics increased from 0.45μm to 1.76μm with the increase of sintering

temperature, and uniform grain morphology was produced at 1250℃ with the grain size of 0.94μm. As shown in Fig. 1(d), the abnormal grain growth occurred for $CoZrTa_2O_8$ ceramics sintered at 1275℃, implying that excessive sintering temperature was unfavorable. As a result, the grain growth of $CoZrTa_2O_8$ ceramics was good for their microwave dielectric properties when the sintering temperature ranged from 1175℃ to 1250℃. When further increasing the sintering temperature, abnormal grain growth appeared, which had no benefit to microwave dielectric properties.

Fig. 2 showed the XRD patterns for the $CoZrTa_2O_8$ ceramics sintered at 1175-1275℃ for 4h. The diffraction patterns of $CoZrTa_2O_8$ ceramics were indexed by wolframite structure type belonged to the space group *P2/c* (C_{2h}^4), and no secondary phase was observed in all samples during the sintering process. In details, the peak position shifted to a lower angle when the sintering temperature increased, suggesting that the lattice parameters were affected by sintering temperature. Accordingly, the unit-cell volume of $CoZrTa_2O_8$ ceramics was carried out by XRD data to investigate the effect of different sintering temperature. As shown in the illustrations of Fig. 2, the unit-cell volume of $CoZrTa_2O_8$ ceramics increased obviously when the sintering temperature increased, which would affect the $Q \times f$ values of $CoZrTa_2O_8$ ceramics.

Fig. 3 illustrated the dielectric constant and relative density of $CoZrTa_2O_8$ ceramics sintered at 1175-1275℃ for 4h. Considering the sintering temperature effects, the dielectric constant of $CoZrTa_2O_8$ ceramics was dependent on the relative density and phase composition. Refer to the analysis of XRD results, the relative density here was owed to pure crystalline phase. As shown in Fig. 3, the dielectric constant of $CoZrTa_2O_8$ ceramics increased from 22.57 to 23.54 and then tended to be gentle, which was consistent with the variation of relative densities. In addition, it was known that the dielectric constant in microwave frequency was dependent on ionic polarizability as well. As shown in the inset of Fig. 3,

the molecular polarizability (α-pc) of $CoZrTa_2O_8$ ceramics was calculated according to the Clausius-Mosotti equation [15]:

$$\alpha_{-pc} = \frac{3V_m}{4\pi} \cdot \frac{K-1}{K+2}$$

where V_m was the molar volume, K was the porosity-corrected dielectric constant, which was calculated using the following formula [16]:

$$\frac{\boldsymbol{\varepsilon_r - K}}{\boldsymbol{3\varepsilon_r}} = \frac{\boldsymbol{\delta(\varepsilon_1 - K)}}{\boldsymbol{\varepsilon_1 + 2\varepsilon_r}}$$

where ε_r was the measured dielectric constant, ε_1 was dielectric constant of porosity, δ was the fractional porosity. It was noted that there was no obvious change in the molecular polarizability under different sintering temperature, implying that sintering temperature had almost no influence to ionic polarizability. The average value (avg(α-pc)) of $CoZrTa_2O_8$ ceramics was 29.37 $Å^3$, which was smaller than the theoretical molecular polarizability calculated as follows:

$\alpha(CoZrTa_2O_8)=\alpha(Co^{2+})+\alpha(Zr^{4+})+2\alpha(Ta^{5+})+8\alpha(O^{2-})$

where $\alpha(Co^{2+})=1.65Å^3$, $\alpha(Zr^{4+})=3.25Å^3$, $\alpha(Ta^{5+})=4.73Å^3$, $\alpha(O^{2-})=2.01Å^3$ [15]. Differences could been found between avg(α-pc) and α-theo, suggesting that there was a slight change in ionic polarizability owing to different coordinated environment.

Fig. 4 showed the $Q\times f$ values and packing fraction of $CoZrTa_2O_8$ ceramics sintered at 1150-1275℃ for 4h. The quality factor of ceramics at microwave frequency was mainly caused by both the intrinsic loss as lattice vibration and the extrinsic loss such as the pore, density, grain size and impurities. In this work, the packing fractions were carried out to investigate the intrinsic loss. As shown in Fig.4, the curve of packing fraction presented a downward trend as the sintering temperature increased. It was important to note that the variation trend of $Q\times f$ values and packing fraction of

$CoZrTa_2O_8$ ceramics were inconsistent with each other at the sintering temperature range from 1175℃ to 1250℃, implying that some extrinsic factors should be considered to analyze the change of $Q\times f$ values. Here, grain size, as an extrinsic factor, was considered to be the main factor affected the $Q\times f$ values. According to the analysis of SEM, when the sintering temperature increased, the grain size also increased while the grain boundary decreased, which resulted in the increasing of $Q\times f$ values shown in Fig. 4. With further increase of sintering temperature, the $Q\times f$ values decreased, owing to the abnormal grain growth and packing fraction. In addition, the τ_f values of $CoZrTa_2O_8$ ceramics changed from -17.1 ppm/℃ to -8.7 ppm/℃, and no significant change in τ_f values was found under different sintering temperature.

4. Conclusion

High-Q $CoZrTa_2O_8$ ceramics were prepared by solid-state reaction and the microwave dielectric properties were investigated. The crystal structure of $CoZrTa_2O_8$ ceramics was indexed as wolframite structure belonged to the space group *P2/c* (C_{2h}^4), with only one single-phase being detected from the XRD patterns under different sintering temperature. The dielectric constant of $CoZrTa_2O_8$ ceramics was dependent on the relative densities and ion polarizability. The $Q\times f$ values of $CoZrTa_2O_8$ ceramics were affected by grain size and packing fraction. The τ_f values of $CoZrTa_2O_8$ ceramics had no significant change under different sintering temperature. The promising microwave dielectric properties were reported with ε_r=23.54, $Q\times f$=20100 GHz, τ_f=-8.72 ppm/℃ for $CoZrTa_2O_8$ ceramics sintered at 1250℃.

Acknowledgments

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.

References

[1] I. M. Reaney, D. Iddles, J. Am. Ceram. Soc. 89 (2006) 2063-2072.

[2] Z. X. Fang, B. Tang, F. Si, E. Z. Li, H. Y. Yang, S. R. Zhang, Ceram. Int. 43 (2017) 13645-13652.

[3] Z. X. Fang, B. Tang, Y. Yuan, X. Zhang, S. R. Zhang, J. Am. Ceram. Soc. 101 (2018) 252-264.

[4] C. H. Yang, Y. J. Han, X. S. Sun, J. Chen. J. Qian, L. X. Chen, Ceram. Int. 44 (2018) 6330-6336.

[5] A. Baumgarte, R. Blachnik, J. Alloy. Compd. 210 (1994) 75-81.

[6] D. W. Kim, D. Y. Kim, K. S. Hong, J. Mater. Res. 15 (2000) 1331-1335.

[7] D. W. Kim, J. H. Kim, J. R. Kim, K. S. Hong, Jpn. J. Appl. Phys. 40 (2001) 5994-5998.

[8] M. Guo, S. P. Gong, G. Dou, D. X. Zhou, J. Alloy. Compd. 509 (2011) 5988-5995.

[9] S. D. Ramarao, V. R. K. Murthy, Scripta Mater. 69 (2013) 274-277.

[10] H. T. Wu, Z. B. Feng, Q. J. Mei, J. D. Guo, J. X. Bi, J. Alloy. Compd. 648 (2015) 368-373.

[11] X. S. Lyu, L. X. Li, H. Sun, S. Zhang, S. Li, Ceram. Int. 42 (2016) 2036-2040.

[12] W. S. Xia, F. Y. Yang, G. Y. Zhang, K. Han, D. C. Guo, J. Alloy. Compd. 656 (2016) 470-475.

[13] B. W. Hakki, P. D. Coleman, IEEE Trans. Microwave Theory Tech. 8 (1960) 402-410.

[14] W. E. Courtney, IEEE Trans. Microwave Theory Tech. 18 (1970) 476-485.

[15] R. D. Shannon, J. Appl. Phys. 73 (1993) 348-366.

[16] K. M. Manu, C. Karthik, R. Ubic, M. T. Sebastian, J. Am.Ceram. Soc. 96 (2013) 3842-3848.

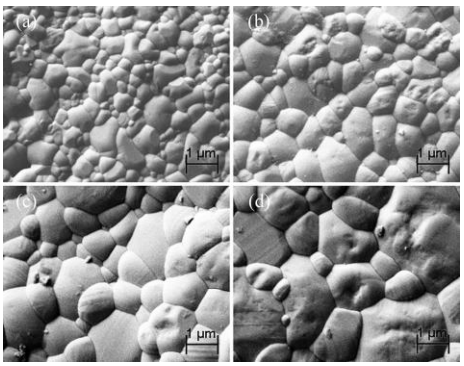

Fig. 1. SEM micrographs of $CoZrTa_2O_8$ ceramics sintered at (a) 1175℃, (b) 1225℃, (c) 1250℃, (d)

1275℃

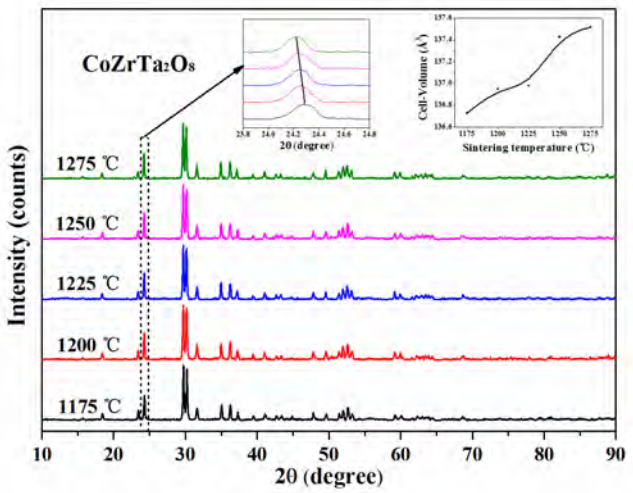

Fig. 2. XRD patterns of $CoZrTa_2O_8$ ceramics sintered at 1175-1275℃ for 4h

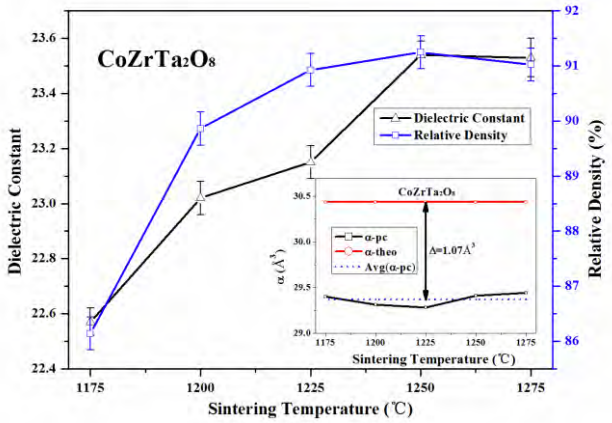

Fig. 3. Dielectric constant, relative density and polarizability of $CoZrTa_2O_8$ ceramics

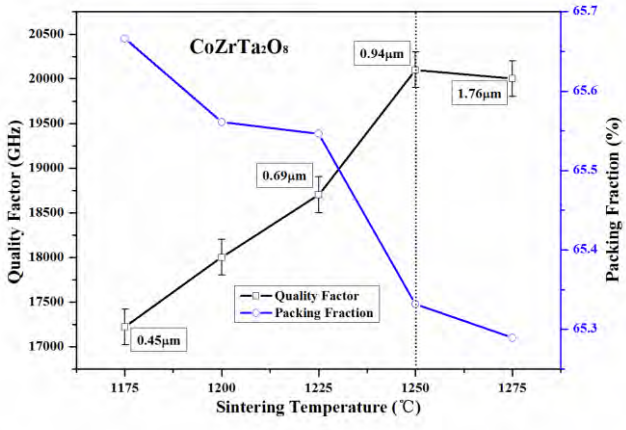

Fig. 4. Q×f values and packing fraction of $CoZrTa_2O_8$ ceramics

Highlights:

1. $CoZrTa_2O_8$ ceramics are designed for the first time according to ionic substitution on $ZnTiNb_2O_8$ ceramics.
2. The new materials of $CoZrTa_2O_8$ were successfully prepared by a conventional mixed-oxide route.
3. The crystal structure, ionic polarizability and microwave dielectric properties were investigated.