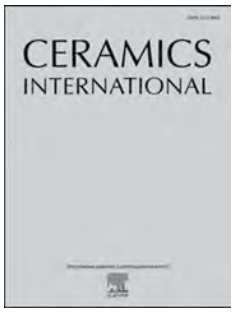
Journal Pre-proof



$MgTiTa_2O_8$: Novel middle-permittivity microwave dielectric ceramic with trirutile-type structure

Ya-Qi Chu, Li-Ping Zhao, Yuan Liu, Peng Liu

PII: S0272-8842(19)32276-X

DOI: https://doi.org/10.1016/j.ceramint.2019.08.079

Reference: CERI 22552

To appear in: *Ceramics International*

Received Date: 21 July 2019

Revised Date: 6 August 2019

Accepted Date: 8 August 2019

Please cite this article as: Y.-Q. Chu, L.-P. Zhao, Y. Liu, P. Liu, $MgTiTa_2O_8$: Novel middle-permittivity microwave dielectric ceramic with trirutile-type structure, *Ceramics International* (2019), doi: https://doi.org/10.1016/j.ceramint.2019.08.079.

$MgTiTa_2O_8$: Novel middle-permittivity microwave dielectric ceramic with trirutile-type structure

Ya-Qi Chu,[a] Li-Ping Zhao,[a] Yuan Liu,[a] Peng Liu[1a]

[a] School of Physics and Information Technology, Shaanxi Normal University, Xi'an 710062, China.

Abstract: The $MgTiTa_2O_8$ ceramics were fabricated by a conventional solid-state method, and their microwave dielectric properties were reported for the first time. The $MgTiTa_2O_8$ ceramics were well sintered over the temperature range (1150 - 1300 °C), achieving the optimized density (~ 95%) at 1225 °C. X-ray diffraction and its Rietveld refinement results confirmed that $MgTiTa_2O_8$ ceramics crystallized into a trirutile-type structure with space group $P4_2/mnm$ (136). The $MgTiTa_2O_8$ ceramic sintered at 1225 °C exhibited the optimized dielectric properties with relative permittivity of 41.6, Q×f value of 30,000 GHz (Resonant frequency = 7.6 GHz), and τ_f value of +103.9 ppm/°C.

Keywords: A. Sintering; B. Microstructure-final; C. Dielectric properties; D. Traditional ceramics;

1 Introduction

To meet the increasing need for the miniaturization of microwave devices and their applications in the 5G communication systems, it is strongly desired to develop high-performance microwave dielectric materials with a middle-to-high permittivity

[1] Corresponding author: liupeng@snnu.edu.cn

(ε_r), a high quality factor (Q×f) and a near-zero temperature coefficient of resonant frequency (τ_f) [1]. In regard to the middle-permittivity microwave dielectric materials, abundant early researches focused on the systems $BaTi_4O_9$ [2], $Ba_2Ti_9O_{20}$ [3] and (Zr, Sn)TiO_4 [4], which achieved near-zero temperature coefficient of resonant frequency and high dielectric constant ($\varepsilon_r \approx 40$). Nevertheless, relatively lower Q×f values (<10,000 GHz) are quite hard to fulfil the increasing demand for high-quality microwave devices with lower energy loss and higher selectivity [5].

Recently, the $ATiNb_2O_8$ ($A = Mg^{2+}$, Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}) family has gained much attention due to their high dielectric constant ($\varepsilon_r > 30$) and low dielectric loss. This family was reported to possess two different crystalline structures: orthorhombic ixiolite structure for $A = Mg^{2+}$ and Zn^{2+} [6-9] and tetragonal rutile structure for $A = Cu^{2+}$, Co^{2+} and Ni^{2+} [8, 10-14]. The transformation of phase structures induced by A-site ionic substitution brought significant impacts on their microwave dielectric properties. The ixiolite-structured ceramics [6-9] exhibited the permittivity of 33.8 ~ 44.4 and negative τ_f values of -19.2 ~ -75.8 ppm/°C, while the rutile-structured ceramics [8, 10-14] showed higher permittivity of 56.8 ~ 71.2 and positive τ_f values of +49.2 ~ +223.2 ppm/°C. The increased permittivity aroused from the high structural coefficient C_{21} of rutile structure [15], and the change of τ_f values may be accounted by the distortion of (A-O) oxygen octahedron originating from the phase transition according to previous researches involving systems $BiNbO_4$ [16], $(Zn_{1/3}Nb_{2/3})_{0.4}(Ti_{1-x}Sn_x)_{0.6}O_2$ ($0.15 \leq x \leq 0.3$) [17] and $(Zn_{1/3}B_{2/3}^{5+})_xTi_{1-x}O_2$ (B = Nb^{5+}, Ta^{5+}) ($0.4 \leq x \leq 0.7$) [18]. For the Q×f values, the change was not significant,

all ranging from 10,000 to 70,000 for most of these two kinds of ceramics. For a special case, among this family, the $ZnTiNb_2O_8$ ceramic displayed outstanding microwave dielectric properties (ε_r = 37.4, Q×f =194,000 GHz and τ_f = -58 ppm/°C) [8], however, as far as we know, nobody afterwards repeated the similar results. Furthermore, J. H. Park et al. [19] prepared the $ZnTiTa_2O_8$ ceramics with trirutile-type structure and investigated their dielectric properties: ε_r ~ 46.2, Q×f ~ 36,700 GHz and τ_f ~ +74 ppm/°C. One may wonder whether the $ATiTa_2O_8$ (A = Mg^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}) family would follow the similar phenomenon as $ATiNb_2O_8$ family, which deserves further research. Like $ZnTiTa_2O_8$, the $MgTiTa_2O_8$ ceramic also exhibited the trirutile-type structure, with metal cations Mg^{2+}/Ti^{4+}/Ta^{5+} in order arrangement, reported by Nobuhiro Kumada [20], however, to our best knowledge, its microwave dielectric properties have not been reported yet.

In this work, the $MgTiTa_2O_8$ ceramics were prepared, and their sinterability, phase structure, microstructure and microwave dielectric properties were investigated.

2 Experiments

The $MgTiTa_2O_8$ ceramics were prepared by the solid-state method [21]. Firstly, the raw materials MgO (99.99%), TiO_2 (99.99%) and Ta_2O_5 (99.99%) with molar ratio of 1: 1: 1 were mixed by ball milling for 12 h with anhydrous alcohol as medium. Secondly, the obtained precursor mixtures were pre-calcined at 950 °C for 3 h. Then, the as-calcined powders were ball milled again for 12 h. After being dried at 60 °C overnight, the powders were granulated, screened by a 120-mesh sieve, and then

pressed into cylindrical pellets with diameter and thickness of about 10 mm and 5 mm. Finally, the compacted green pellets were sintered in air from 1150 °C to 1300 °C for 4 h at the heating rate of 2 °C/min.

The phase structural analysis of sintered specimens was conducted by the X-ray diffraction (XRD, Rigaku D/MAX2550, Tokyo, Japan) using Cu-Kα radiation. The microstructure was collected with the scanning electron microscope (FEI Company, Eindhoven) equipped with energy dispersive X-ray spectroscopy (EDS) . Microwave dielectric properties of sintered samples were acquired by the Hakki-Coleman method [22-23] using a network analyzer (ZVB20, Rohde & Schwarz, Munich, Germany). The temperature coefficients of resonant frequency (τ_f) were determined using the formula, $\tau_f = (f_2-f_1) \times 10^6/[f_1 \times (T_2-T_1)]$, where f_1 and f_2 are the $TE_{01\sigma}$ resonant frequency of samples at 25 °C and 80 °C, respectively.

3 Result and Discussions

The phase structure of as-sintered ceramics was identified by XRD. As displayed in Fig. 1(a), the patterns of all samples sintered at temperatures from 1150 °C to 1300 °C exhibit the consistent reflections, indicating the same phase composition. It was found that no PDF card could be found to match the diffraction peaks in the latest Inorganic Crystal Structure Database. In the reference [20], $MgTiTa_2O_8$ was revealed to possess trirutile-type structure with space group of $P4_2/mnm$ (136), based on which the simulated XRD pattern was calculated (Fig. 1(a)). It is clear that all reflections for every sample could be completely indexed without any additional phase. Rietveld

XRD refinement was carried out on the ceramic sintered at 1300 °C by the Fullprof software, in which the trirutile-type $MgTiTa_2O_8$ was chosen as the simulation model, as seen in Fig. 1(b). Results show that the calculated pattern could fit well to the experimental data with acceptable R_p = 5.13%, R_{wp} = 7.79%, R_{exp} = 2.92% and χ^2 = 7.13%, which further revealed that the specimen crystallized in a tetragonal trirutile structure with a = 4.6894 Å, b = 4.6894 Å, c = 9.1385 Å, $\alpha = \beta = \gamma = 90°$. The inset of Fig. 1(b) displays the trirutile structure for $MgTiTa_2O_8$, where the metal cations $Mg^{2+}/Ti^{4+}/Ta^{5+}$ are arranged in order with M1 and M2 sites occupied by ($Mg_{0.39}Ti_{0.39}Ta_{0.22}$) and ($Mg_{0.18}Ti_{0.18}Ta_{0.64}$) [20].

Fig. 2 shows the SEM images of the $MgTiTa_2O_8$ ceramics sintered from 1150 °C to 1300 °C for 4 h. As observed in Fig. 2(a), the microstructure ceramic sintered at 1150 °C exhibits more pores and smaller grain size, about 2.7 μm in average size. When the temperature increased to 1200 °C, the grain size increased to around 5.8 μm and the pores were almost eliminated. For the sample sintered at 1225 °C, the dense and uniform microstructure were achieved, which would, in general, benefit for excellent microwave dielectric properties [24]. However, the grain size grew rapidly when the temperature was above 1225 °C due to the over-sintering of the specimens [25]. The temperature-dependence of average grain size shown in Fig.2(f) indicates the linear growth trend as the sintering temperature increases. And there is only one kind of grains in terms of microstructure in all samples, agreeing with the nature of pure phase. In order to identify the composition of the phase, the EDS analysis was conducted on the grain marked as A, seen in the inset of Fig.2(c). Results show that

the atomic ratio of Mg/Ti/Ta/O ions were approximately to be 1:0.98:2.1:7.0, which further confirmed the $MgTiTa_2O_8$ phase.

Fig. 3 presents the variations of apparent density, ε_r, Q×f, and τ_f value of $MgTiTa_2O_8$ ceramics as a function of the sintering temperature. As observed in Fig. 3(a), the apparent densities initially increased with increasing temperature, reached the maximum value (6.59 g/cm^3) at 1225 °C, and then decreased slightly, which is in agreement with the change of microstructures in Fig. 2. The over-sintering behavior of specimens at high temperatures may account for the slight decrease in bulk density [25]. It is noted that the permittivity ε_r and Q×f values show the same variation tendency, that is, firstly increasing up to the optimized values (ε_r ~ 41.6, Q×f ~ 30,000 GHz, Resonant frequency = 7.6 GHz) at 1225 °C and then slightly decreasing with the sintering temperature. This phenomenon indicates the main influence of remaining pores for microwave dielectric properties in a fixed material system [26]. The corrected permittivity values ε_{corr} with pores effects excluded were achieved, shown in Fig.3(a), according to the correction formula $\varepsilon_{corr} = \varepsilon_{meas}(1+1.5P)$ [27], where ε_{meas} and P represented the measured permittivity and porosity values, respectively. The results exhibit that the ε_{corr} kept almost constant (around 42.4) as the temperature increases, larger than the measured permittivity ε_r, quite agreeing with the theoretical value (around 42.2) calculated by the Clausius-Mossotti relationship [28]. As for the τ_f , the value lied in +102~ +112 ppm/°C. Compared with the microwave dielectric properties of some ixiolite or rutile-structured ceramics (list in Table 1), one can find that $MgTiTa_2O_8$ ceramics reported here exhibited a quite high positive τ_f value (~ +104

ppm/°C), which would impede its practical application. To adjust the τ_f to near zero will be conducted in the subsequent work.

Table 1 Summarized microwave dielectric properties of $ATiB_2O_8$ (A: Mg^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}; B: Nb^{5+}, Ta^{5+}) ceramics

Materials	S.T. (°C)	ε_r	τ_f (ppm/°C)	$Q\times f$ (GHz)	Crystal Structure	Ref
$ZnTiNb_2O_8$	1100	37.4	-58	194000	ixiolite	[8]
$ZnTiNb_2O_8$	1100	34.3	-52	42500	ixiolite	[29]
$ZnTiNb_2O_8$	1100	34.4	-47.94	56900	ixiolite	[9]
$MgTiNb_2O_8$	1300	44.36	-41.7	13600	ixiolite	[6]
$CuTiNb_2O_8$	960	71.2	+49.2	11000	rutile	[11]
$CoTiNb_2O_8$	1080	64.7	+202	12141	rutile	[12]
$CoTiNb_2O_8$	1200	64	+223.2	65300	rutile	[8]
$NiTiNb_2O_8$	1140	60.6	+76.6	70100	rutile	[14]
$NiTiNb_2O_8$	1160	56.8	+79.1	21100	rutile	[13]
$ZnTiTa_2O_8$	1250	46.2	+74	36700	trirutile	[19]
$MgTiTa_2O_8$	1225	41.6	+103.9	30000	trirutile	This work

4 Conclusions

In this work, novel microwave dielectric ceramics $MgTiTa_2O_8$ were prepared by the

solid-state reaction method. The crystal structure, sintered behavior and microwave dielectric properties of $MgTiTa_2O_8$ ceramics have been studied. The $MgTiTa_2O_8$ ceramics showed a trirutile-type structure at sintering temperatures (1150-1300 °C), in which the cations were orderly arranged as ($Mg_{0.39}Ti_{0.39}Ta_{0.22}$) and ($Mg_{0.18}Ti_{0.18}Ta_{0.64}$) at two crystallographic sites 2a and 4f. At 1225 °C, the ceramics possessed the highest density and exhibited excellent microwave dielectric properties with a ε_r value of 41.6, $Q\times f$ value of 30,000 GHz and τ_f value of +103.9 ppm/°C, which would make these ceramics promising for application in microwave components.

Acknowledge

This study was financially supported by National Natural Science Foundation of China (Grant No. 51572162).

References

[1] R. Freer, F. Azough, Microstructural engineering of microwave dielectric ceramics, J. Eur. Ceram. Soc. 28 (2008) 1433-1441.

[2] S. G. Mhaisalkar, W. E. Lee, D. W. Readey, Processing and Characterization of $BaTi_4O_9$, J. Am. Ceram. Soc. 72 (1989) 2154-2158.

[3] G. H. JONKER, The Ternary Systems BaO-TiO_2-SnO_2 and BaO-TiO_2-ZrO_2, J. Am. Ceram. Soc. 14 (1958) 390-394.

[4] Shin-ichi Hirano, Takashi Hayashit, Akiyoshi Hattori, Chemical Processing and Microwave Characteristics of (Zr,Sn)TiO_4 Microwave Dielectrics, J. Am. Ceram.

Soc. 74 (1991) 1320-1324.

[5] Ian M. Reaney, Microwave Dielectric Ceramics for Resonators and Filters in Mobile Phone Networks, J. Am. Ceram. Soc. 89 (2006) 2063-2072.

[6] Jinxin Bi, Changhong Yang, Haitao Wu, Synthesis, Characterization, and Microwave Dielectric Properties of $MgTiNb_2O_8$ Ceramics Produced Through the Solid State Reaction Method, 2016 3rd International Conference on Smart Materials and Nanotechnology in Engineering, 2016, pp. 76-79.

[7] H. Barzegar Bafrooei, E. Taheri Nassaj, T. Ebadzadeh, C. F. Hu, A. Sayyadi-Shahraki, T. Kolodiazhnyi, Sintering behavior and microwave dielectric characteristics of $ZnTiNb_2O_8$ ceramics achieved by reaction sintering of ZnO–TiO_2–Nb_2O_5 nanosized powders, Ceram. Int. 42 (2016) 3296-3303.

[8] Ching-Fang Tseng, Microwave dielectric properties of low loss microwave dielectric ceramics: $A_{0.5}Ti_{0.5}NbO_4$ (A=Zn, Co), J. Eur. Ceram. Soc. 34 (2014) 3641-3648.

[9] Q. W. Liao, L. X. Li, Structural dependence of microwave dielectric properties of ixiolite structured $ZnTiNb_2O_8$ materials: crystal structure refinement and Raman spectra study, Dalton T. 41 (2012) 6963-6969.

[10] H. T. Wu, Z. B. Feng, Q. J. Mei, J. D. Guo, J. X. Bi, Correlations of crystal structure, bond energy and microwave dielectric properties of $AZrNb_2O_8$ (A = Zn, Co, Mg, Mn) ceramics, J. Alloy. Compd. 648 (2015) 368-373.

[11] Ching-Fang Tseng, Microwave dielectric properties of a new $Cu_{0.5}Ti_{0.5}NbO_4$ ceramics, J. Eur. Ceram. Soc. 35 (2015) 383-387.

[12] Yaoyao Li, Haikui Zhu, Yan Zhang, Xiaochi Lu, Zhenxiao Fu, Yanyan Zou, Qitu Zhang, Lixi Wang, Synthesis mechanism and microwave dielectric properties of $Co_{0.5}Ti_{0.5}NbO_4$ ceramics, J. Mater. Sci.: Mater. Electron. 28 (2017) 3380–3385.

[13] Qingwei Liao, Lingxia Lin, Xiang Ren, Xiaoxu Yu, Qinglei Meng, Wangsuo Xia, A new microwave dielectric material $Ni_{0.5}Ti_{0.5}NbO_4$, Mater. Lett. 89 (2012) 351-353.

[14] Kai-Yuan HSIAO, Ching-Fang TSENG, Cheng-Hsing HSU, Hsin-Han TUNG, Effect of Sintering Conditions on Microwave Dielectric Properties of $Ni_{0.5}Ti_{0.5}NbO_4$ Ceramics, Proceedings of the 12th Asia Pacific Physics Conference, 2014, pp. 012078.

[15] Liang-Ying Zhang, Xi Yao, Dielectric physics, Xi'an Jiaotong University Press, Xi'an, 1991.

[16] Eung Soo Kim, Woong Choi, Effect of phase transition on the microwave dielectric properties of $BiNbO_4$, J. Eur. Ceram. Soc. 26 (2006) 1761-1766.

[17] Dong Ho Kang, Eung Soo Kim, Microwave dielectric properties of rutile $(Zn_{1/3}Nb_{2/3})_{0.40}(Ti_{1-x}Sn_x)_{0.60}O_2$ ($0.15 \leq x \leq 0.30$) ceramics, Ceram. Int. 34 (2008) 889-892.

[18] Eung Soo Kim, Dong Ho Kang, Relationships between crystal structure and microwave dielectric properties of $(Zn_{1/3}B_{2/3}{}^{5+})_xTi_{1-x}O_2$ (B^{5+}=Nb, Ta) ceramics, Ceram. Int. 34 (2008) 883-888.

[19] Jeong-Hyun Park, Sahn Nahm, Jae-Gwan Park, Crystal structure and microwave dielectric properties of $(1- x)ZnTa_2O_6 – xTiO_2$ ceramics, J. Alloy. Compd. 537

(2012) 221-226.

[20] Nobuhiro Kumada, Kohsuke Nakanome, Sayaka Yanagida, Takahiro Takei, Ichiro Fujii, Satoshi Wada, Chikako Moriyoshi, Yoshihiro Kuroiwa, Crystal structure photocatalytic and dielectric property of $ATiM_2O_8$ (A: Mg, Zn; M: Nb, Ta), J. Asian. Ceram. Soc. 6 (2018) 247-253.

[21] Zhifen Fu, Peng Liu, Jianli Ma, Xiaogang Zhao, Huaiwu Zhang, Novel series of ultra-low loss microwave dielectric ceramics: $Li_2Mg_3BO_6$ (B= Ti, Sn, Zr), J. Eur. Ceram. Soc. 36 (2016) 625-629.

[22] B. W. Hakki, P. D. Coleman, A Dielectric Resonator Method of Measuring Inductive Capacitance in the Millimeter Range, IEEE T. Microw. Theory, 8(1960) 402-410.

[23] W.E. Courtney, Analysis and Evaluation of a Method of Measuring the Complex Permittivity and Permeability of Microwave Insulators, IEEE T. Microw. Theory, 18 (1970) 476-485.

[24] Stuart J. Penn, Neil McN. Alford, Alan Templeton, Xiaoru Wang, Meishing Xu, Michael Reece, Kevin Schrapel, Effect of Porosity and Grain Size on the Microwave Dielectric Properties of Sintered Alumina, J. Am. Ceram. Soc. 80 (1997) 1885-1888.

[25] P. R. RIOS, Abnormal grain growth development from uniform grain size distributions, Acta Mater. 45 (1997) 1785-1789.

[26] Eung Soo Kim, Chang Jun Jeon, Paul G. Clem, Effects of Crystal Structure on the Microwave Dielectric Properties of ABO_4 (A = Ni, Mg, Zn and B = Mo, W)

Ceramics, J. Am. Ceram. Soc. 95 (2012) 2934-2938.

[27] A. J. Bosman, E. E. Havinga, Temperature Dependence of Dielectric Constants of Cubic Ionic Compounds, Phys. Rev. 129 (1963) 1593-1600.

[28] William T. Doyle, The Clausius‐Mossotti problem for cubic arrays of spheres, J. Appl. Phys. 49 (1978) 795-797.

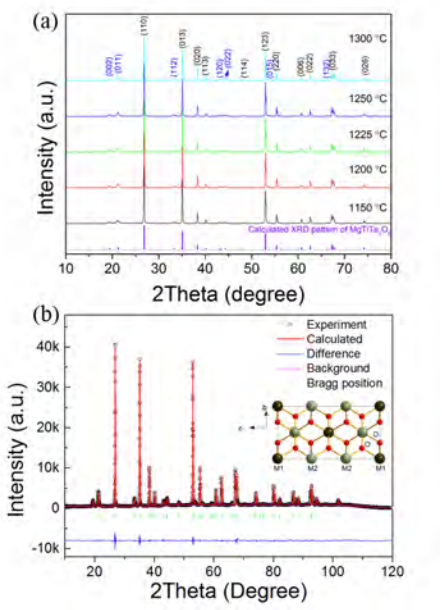
[29] Dong-Wan Kim, Deok-Yang Kim, Kug Sun Honga, Phase relations and microwave dielectric properties of $ZnNb_2O_6$ –TiO_2, J. Mater. Res. 15 (2000) 1331-1335.

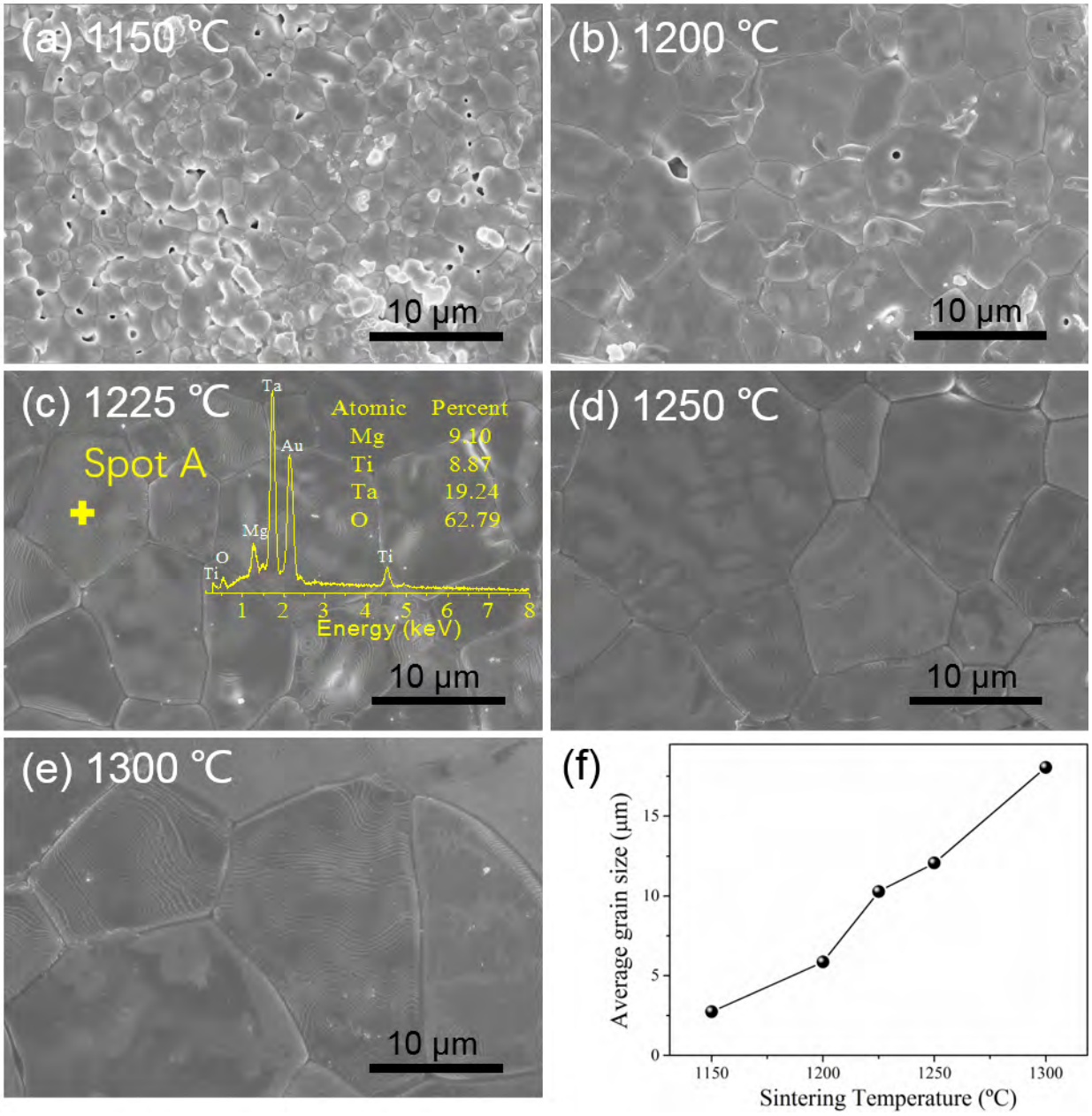
Fig. 1 (a) XRD patterns of $MgTiTa_2O_8$ ceramics sintered from 1150 °C to 1300 °C for 4 h. (b) Rietveld refinement pattern of XRD for the $MgTiTa_2O_8$ ceramic sintered at 1300 °C for 4 h.

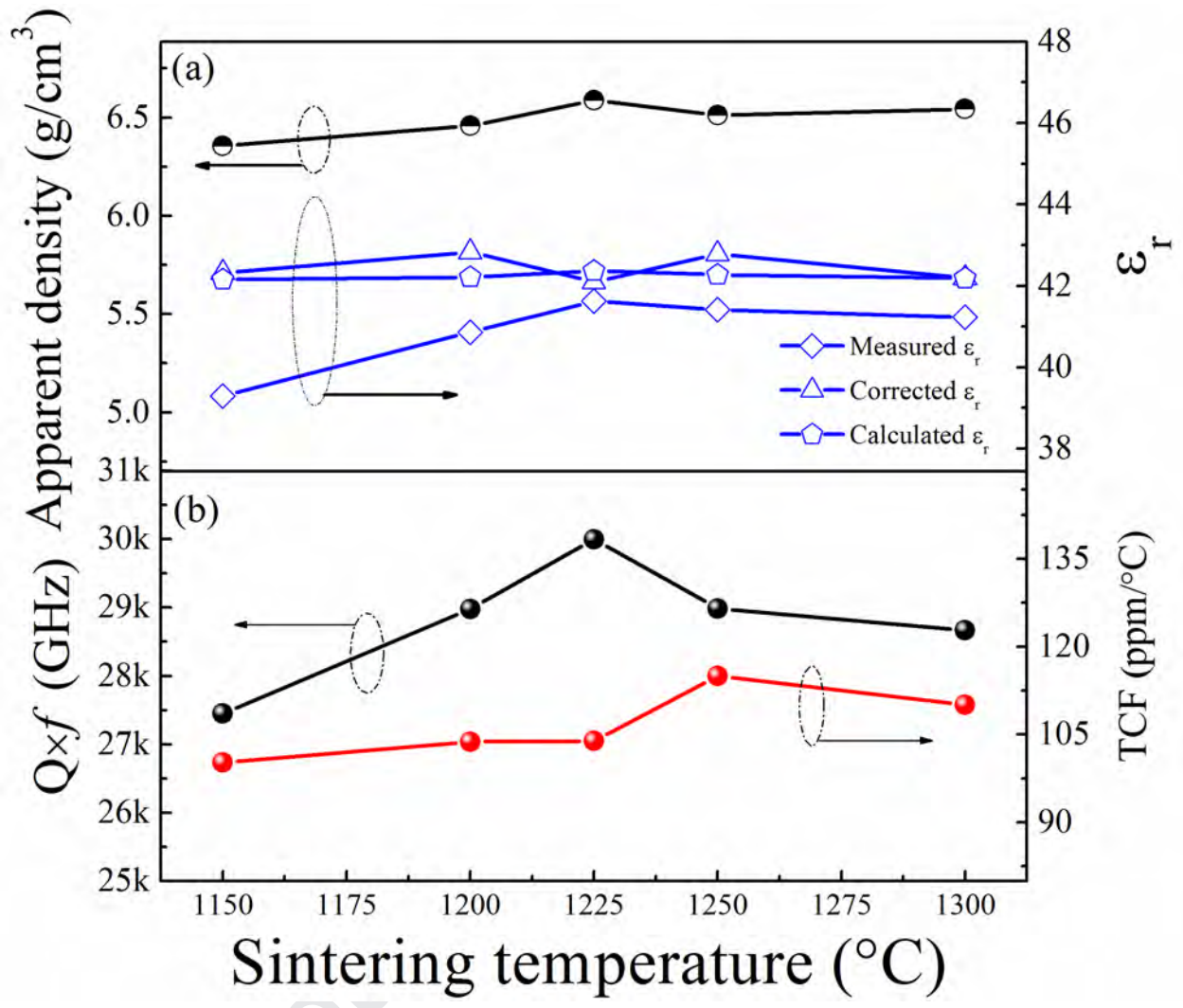
Fig. 2 SEM images of $MgTiTa_2O_8$ ceramics sintered at: (a) 1150 °C, (b) 1200 °C, (c) 1225 °C, (d) 1250 °C, and (e) 1300 °C. (f) The temperature dependence of average size of ceramic grains. The inset of Fig. 2(c) is the EDS spectrum of grain A.

Fig. 3 Apparent density and microwave dielectric properties of the $MgTiTa_2O_8$ ceramics sintered at different temperatures.

Table 1 Summarized microwave dielectric properties of $ATiB_2O_8$ (A: Mg^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}; B: Nb^{5+}, Ta^{5+}) ceramics




(a) 1150 ℃
10 μm
(b) 1200 ℃
10 μm
(c) 1225 ℃
Spot A
Ta
Au
Mg
O
Ti
Ti
Atomic Percent
Mg 9.10
Ti 8.87
Ta 19.24
O 62.79
1 2 3 4 5 6 7 8
Energy (keV)
10 μm
(d) 1250 ℃
10 μm
(e) 1300 ℃
10 μm
(f)
Average grain size (μm)
0 5 10 15
1150 1200 1250 1300
Sintering Temperature (ºC)


(a)
(b)
Apparent density (g/cm3)
Qxf (GHz)
εr
TCF (ppm/°C)
Measured εr
Corrected εr
Calculated εr
Sintering temperature (°C)
6.5
6.0
5.5
5.0
31k
30k
29k
28k
27k
26k
25k
48
46
44
42
40
38
135
120
105
90
1150
1175
1200
1225
1250
1275
1300