MR. HUIXING LIN (Orcid ID : 0000-0002-6413-2112)

Article type : Article

Investigation of phase composition and microwave dielectric properties of $MgO-Ta_2O_5$ ceramics with ultra-high Qf value

Mingzhao Dang [a, b], Haishen Ren [a, b], Xiaogang Yao [a], Haiyi Peng [a, b], Tianyi Xie [a, c], Huixing Lin [a*], Lan Luo [a]

[a] *Key Laboratory of Inorganic Functional Material and Device, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China.*

[b] *University of Chinese Academy of Sciences, Beijing 100049, China*

[c] *Department of materials, Chongqing University of Technology, Chongqing, 400050, China*

Abstract: Four $MgO-Ta_2O_5$ ceramics with the MgO/Ta_2O_5 mole ratio x=1, 2, 3 and 4 were prepared by traditional solid state reaction method, and the influence of x on

* Corresponding author. Tel: +86 21 6990 3555; Fax: +86 21 6990 6330.

E-mail address: huixinglin@mail.sic.ac.cn

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record. Please cite this article as doi: 10.1111/jace.15434

the phase composition, microstructure and dielectric properties (the dielectric constant ε_r, the temperature coefficient of resonant frequency τ_f and the quality factor Qf) of the materials was investigated by using XRD, SEM, etc. The results indicated that the ceramics were composed of two crystalline phases $MgTa_2O_6$ and $Mg_4Ta_2O_9$ in the composition range studied, and that the dielectric properties ln ε, 1/Qf and τ_f changed proportionally to the fraction of main crystal phases, which meet perfectly with the mixing model proposed in this study. It is obvious that the proportion of the two crystal phases could be precisely controlled by x, and thereby, the dielectric properties can be conveniently and precisely tailored. Our research provided a new microwave dielectric ceramic with the composition of $2MgO\text{-}Ta_2O_5$, which has an ultra-high Qf value (211 000 GHz), low dielectric constant ε_r (19.9) and near zero temperature coefficient of resonant frequency τ_f (8 ppm/°C).

Keywords: $MgO\text{-}Ta_2O_5$ ceramics; microwave dielectric properties; ultra-high quality factor

1. Introduction

Nowadays, low permittivity (ε_r=6-20) and high quality factor (Qf>75 000 GHz) microwave dielectric ceramics which are mainly used in the areas of millimeter-wave communications have generated considerable research interest because of the fast

development of mobile communications, satellite communications and intelligent transportation systems etc.[1, 2]. It was expected that $ZnAl_2O_4$-TiO_2-, $Mg_4Ta_2O_9$-, Mg_2SiO_4- and Al_2O_3-based materials were some examples for possible applications in millimeter-wave communications[3]. However, these materials did not have the near zero temperature coefficient of resonant frequency ($\tau_f \approx 0$ ppm/°C) which was demanded in that application field. Unfortunately, satisfying the three properties simultaneously was very difficult.

It has been reported that some Ta-containing microwave dielectric ceramics have high Qf values due to the high covalencies of Ta-O bonds, such as $Ba(Mg_{1/3}Ta_{2/3})O_3$[4], $Ba(Zn_{1/3}Ta_{2/3})O_3$[5], $MgZrTa_2O_8$[6], $Mg_4Ta_2O_9$[7], et al. Because of the low permittivity of $Mg_4Ta_2O_9$, numerous investigations have established to make the $Mg_4Ta_2O_9$-based ceramics satisfy the performance mentioned above. In 2007, Kan et al.[7] first reported the $Mg_4Ta_2O_9$ ceramics with corundum's structure and excellent microwave dielectric properties: ε_r=10, Qf=345 000 GHz, τ_f=-70 ppm/°C. But its τ_f is so negative that it cannot be applied. Kim[8, 9] provided a method to obtain the near zero τ_f ceramics (ε_r=14.8, Qf=102 100 GHz, τ_f=3.86 ppm/°C) by mixing the positive τ_f ceramic phase TiO_2 and negative phase $Mg_4Ta_2O_9$ with the ratio of 1:1. However they pointed out that TiO_2 would interact with $Mg_4Ta_2O_9$ to form $MgTi_2O_5$ etc. which hindered the enhancement of Qf values of the composite ceramics. Similar results also occurred in $Mg_4Nb_2O_9$ ceramics[10, 11]. Thus it is very important to choose the proper positive τ_f material to prevent new phases with low Qf values synthesized during tailoring the τ_f. The binary phase diagram of MgO-Ta_2O_5[12] indicates that

$MgTa_2O_6$ with trirutile-type structure is another stable phase which can co-exist with $Mg_4Ta_2O_9$. Moreover, it possesses high Qf values (Qf=59 600 GHz)[13, 14] and positive τ_f (τ_f=30 ppm/°C). These properties are very beneficial for adjusting the τ_f to near zero and guaranteeing the Qf values of ceramics. Some attentions have been paid to the selection of $MgTa_2O_6$ as a τ_f controlling material[10, 14].

In this paper, the phase composition and microstructures of ceramics which were obtained from $xMgO\text{-}Ta_2O_5$ (x=1, 2, 3, 4) system were studied, and then the relationships between the phase composition and microwave dielectric properties were carefully analyzed and discussed.

2. Experimental Procedure

High purity (≥99.9%) MgO (calcined at 800 °C for 4 h) and Ta_2O_5 powders were weighed according to the stoichiometric ratio of $xMgO\text{-}Ta_2O_5$ and noted as xMT (x=1, 2, 3, 4), adding with 0.5 wt% B_2O_3 and then mixed in deionized water for 1 h with zirconia balls as milling media. The mixtures were dried and then calcined at 800~1200 °C for 8 h in air. The calcined powders were re-milled and ground with polyvinyl alcohol. The granules were pressed into pellets (Φ10 mm×5 mm) under a pressure of 100 MPa and then the pellets were sintered to get the ceramic samples at 1275 °C~1600 °C for 4 h in air.

The bulk densities of the xMT ceramic samples were measured by the Archimedes method. The crystalline phase of the powders and the ceramics were identified by XRD (BRUKER AXS GMBH, Germany) using Cu Kα radiation operated at 40 kV and 40 mA. The scanning electron microscopy (SEM; Magellan 400, FEI, American) with an energy dispersive spectrometer (EDS, Bruker) and an electron back scattered diffraction (EBSD, Oxford) were employed to exame the morphology of ceramics. The dielectric properties of samples were tested by Agilent E8362B network analyzer by the $TE_{01\delta}$ mode dielectric resonator method[15], and the τ_f was obtained from the resonant frequencies which were measured at 25 °C and 85 °C.

3. Results and discussion

In order to study the solid reaction and phase transformation processes of the xMT (x=1, 2, 3, 4) powders, all the four powders were calcined at the temperature from 800~1200 °C for 8 h, and X-ray diffraction analysis of all samples was taken. As an example, Fig. 1 shows the XRD patterns of 4MT powder calcined at different temperatures. It can be found from the figure that the reaction process of MgO with Ta_2O_5 could be divided into two phases. First one, when T<1000 °C, MgO reacted with Ta_2O_5 to form $MgTa_2O_6$, and then the second, with the increase of temperature (T≥1000 °C), the formed $MgTa_2O_6$ further reacted with the surplus MgO to form a new phase of $Mg_4Ta_2O_9$. The whole process can be expressed by the following equations:

$$MgO+Ta_2O_5 \xrightarrow{800\sim900℃} MgTa_2O_6 \quad (1)$$

$$3MgO+MgTa_2O_6 \xrightarrow{\geq1000℃} Mg_4Ta_2O_9 \quad (2)$$

Besides, there were still some remaining $MgTa_2O_6$ which has not been reacted with MgO in the synthesis process, which is in general agreement with Reference[16]. Therefore, all sintered ceramic samples were obtained from the powders calcined at 1100 °C for 8 h in this study.

Fig. 2 shows the relative density of xMT (x=1, 2, 3, 4) ceramics as a function of sintering temperature. It can be seen that the maximum density was acquired at 1550 °C for the sample MT (x=1) and the ones for the samples 2MT, 3MT and 4MT (x=2, 3, 4) were obtained at around 1325 °C (more details are listed in Table 1). Then, XRD patterns of xMT ceramics sintered at optimum temperature are illustrated in Fig. 3. It was found that there were three crystalline phases, the two main phases $MgTa_2O_6$, $Mg_4Ta_2O_9$, and the slight $Mg_5TaO_3(BO_3)_3$, besides, the content of $Mg_4Ta_2O_9$ increased with the increasing of x. In order to quantitatively analyze the relative percentage of $MgTa_2O_6$ and $Mg_4Ta_2O_9$, the Rietveld Analysis method in GSAS 2.0 was employed using the ICSD No.79-0380 and No.84-1679 as standard references. The results are given in Table 2. Meanwhile, from reaction (1) and (2), it can be concluded that the reaction of MgO with Ta_2O_5 when samples are with different MgO/Ta_2O_5 mole ratio x could be written as equation (3). Then, the theoretical quantitative percentage of $Mg_4Ta_2O_9$ was calculated and the results are also listed in Table 2. It can be seen that the theoretical values were very close to that calculated

from Jade. Hence, it is apparent that the phase content of $Mg_4Ta_2O_9$ can be controlled by the MgO/Ta_2O_5 mole ratio x.

$$x\mathrm{MgO}+\mathrm{Ta_2O_5} \longrightarrow \frac{x-1}{3}\mathrm{Mg_4Ta_2O_9}+\frac{4-x}{3}\mathrm{MgTa_2O_6} \quad (3)$$

The SEM images of ceramic samples with different x and sintered at the optimum temperatures were displayed in Fig. 4. Two phases $MgTa_2O_6$ (grey) and $Mg_4Ta_2O_9$ (black) had been clearly seen in the figure, which were identified by EDS spectrum and XRD diffraction. Interestingly, although both MT and 4MT were highly densified (>95%), their grain size was not uniform which could distribute from 7 μm to 37 μm and 4MT even contented some closed pores. Furthermore, as evident in Fig. 4b and Fig. 4c, when two phases co-existed in the samples, the grain size of each phase was less than 8 μm. It might be reasonable to assume that two phases had the similar grain growth rate at the same temperature and thermodynamic stability. So the grain size was decreased by their contest. When their content was close to each other, the inhibitory effect is more obvious. The EBSD phase map of 2MT ceramic (Fig. 5) was also collected to confirm distribution and fraction of different phases. It was evident that there were two main phases $Mg_4Ta_2O_9$ and $MgTa_2O_6$ which were randomly distributed in 2MT ceramic and the fraction of $Mg_4Ta_2O_9$ was 35% which was very close to the theoretical values 38.5%.

The optimum microwave dielectric properties of samples were given in Table 1. It can be found that the 2MT sample has very excellent dielectric properties, which

could be applied in millimeter-wave communications, through the microwave dielectric properties comparison of the materials with similar permittivity in Table 3.

It is also known from the literature[17] that the dielectric properties of mixture phases of two compounds can be predicted by some empirical models. The models are given below:

$$\ln \varepsilon = V_1 \ln \varepsilon_1 + V_2 \ln \varepsilon_2 \quad (4)$$

$$\tau_f = V_1 \tau_{f1} + V_2 \tau_{f2} \quad (5)$$

$$\frac{1}{Q} = \frac{V_1}{Q_1} + \frac{V_2}{Q_2} \quad (6)$$

where V_1, V_2, ε_1, ε_2, τ_{f1}, τ_{f2}, Q_1 and Q_2 are the volume fractions, permittivity, temperature coefficient of resonant frequency and quality factors of the two components, while ε, τ_f and Q are the resultant of the mixture. As we all know, it is predicted from the classical dispersion theory that the dielectric loss increases proportionately with frequency at microwave frequency[5, 18]. Therefore the Qf value which is inherent in each material is a constant, so the equality (6) can be rewritten as:

$$\frac{1}{Qf} = \frac{V_1}{Q_1 f_1} + \frac{V_2}{Q_2 f_2} \quad \text{or} \quad \frac{1}{Qf} = \frac{V_1}{C_1} + \frac{V_2}{C_2} \quad (7)$$

where the C_1 and C_2 are a constant value of phase 1 and phase 2. It should be noted that the measured ε_r should be corrected for porosity to get the actual permittivity of the material. The following equation was used in this work[19]:

$$\varepsilon_r = \varepsilon\left(1-\frac{3P(\varepsilon-1)}{2\varepsilon+1}\right) \quad (8)$$

where P is the fractional porosity and others symbol have been mentioned above. In order to further verify the empirical models, variations of ln ε, 1/Qf, τ_f as a function of the volume fraction of $Mg_4Ta_2O_9$ in the xMT ceramics were shown in Fig. 6. It can be seen that the values located near a straight line, which indicates that this mixture perfectly meet the mixing models. So, it is obvious that the dielectric properties can be conveniently and precisely tailored by this method.

4. Conclusions

In summary, the influence of x on the phase composition, microstructure and dielectric properties in xMgO-Ta_2O_5 (xMT, x=1, 2, 3, 4) ceramics was investigated. The results indicated that the ceramics were composed of two crystalline phases $MgTa_2O_6$ and $Mg_4Ta_2O_9$ in the composition range studied, and that the dielectric properties ln ε, 1/Qf and τ_f changed proportionally to the fraction of main crystal phases. This result provided compelling evidence that the proportion of the two crystal phases could be precisely controlled by x, and thereby, the dielectric properties can be conveniently and precisely tailored. Our study also provided an ultra-high Qf value (Qf=211 000 GHz, ε_r=19.9, τ_f=8 ppm/°C) materials 2MgO-Ta_2O_5 ceramic.

Reference

1. Tummala RR. Ceramic and glass-ceramic packaging in the 1990s. *J Am Ceram Soc*. 1991;74:895-908.

2. Ohsato H. Research and development of microwave dielectric ceramics for wireless communications. *J Ceram Soc Jpn*. 2005;113:703-711.

3. Sebastian MT, Ubic R,Jantunen H. Low-loss dielectric ceramic materials and their properties. *Int Mater Rev*. 2015;60:392-412.

4. Nomura S, Toyama K,Kaneta K. $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics with temperature-stable high dielectric-constant and low microwave loss. *Jpn J Appl Phys Part 2 - Lett*. 1982;21:L624-L626.

5. Wakino K, Murata M,Tamura H. Far infrared reflection spectra of $Ba(Zn,Ta)O_3$-$BaZrO_3$ dielectric resonator material. *J Am Ceram Soc*. 1986;69:34-37.

6. Lyu XS, Li LX, Sun H, et al. High-Q microwave dielectrics in wolframite magnesium zirconium tantalate ceramics. *Ceram Int*. 2016;42:2036-2040.

7. Kan A, Ogawa H, Yokoi A, et al. Crystal structural refinement of corundum-structured $A_4M_2O_9$ (A=Co and Mg, M=Nb and Ta) microwave dielectric ceramics by high-temperature x-ray powder diffraction. *J Eur Ceram Soc*. 2007;27:2977-2981.

8. Kim JS, Choi ES, Lee YH, et al. A study on MgO-Ta_2O_5 system ceramics for microwave component application. *IEICE Trans Electron*. 2008;E91c:772-775.

9. Kim JS, Choi ES, Ryu KW, et al. Microwave dielectric properties of $Mg_4Ta_2O_9$ ceramics with TiO_2 additions for dielectric resonator oscillator. *Mater Sci Eng B-Adv Funct Solid-State Mater*. 2009;162:87-91.

10. Khalam LA, Thomas S, Sebastian MT. Tailoring the microwave dielectric properties of $MgNb_2O_6$ and $Mg_4Nb_2O_9$ ceramics. *Int J Appl Ceram Technol*. 2007;4:359-366.

11. Lim SW, Bang J. Microwave dielectric properties of $Mg_4Nb_2O_9$ ceramics produced by hydrothermal synthesis. *J Electroceram*. 2009;23:116-120.

12. Baskin Y, Schell DC. Phase studies in the binary system MgO-Ta_2O_5. *J Am Ceram Soc*. 1963;46:174-178.

13. Lee HJ, Kim IT, Hong KS. Dielectric properties of AB_2O_6 compounds at microwave frequencies (A=Ca, Mg, Mn, Co, Ni, Zn, and B=Nb, Ta). *Jpn J Appl Phys Part 2 - Lett*. 1997;36:L1318-L1320.

14. Tzou WC, Chen YC, Yang CF, et al. Microwave dielectric characteristics of $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics. *Mater Res Bull*. 2006;41:1357-1363.

15. Krupka J, Derzakowski K, Riddle B, et al. A dielectric resonator for measurements of complex permittivity of low loss dielectric materials as a function of temperature. *Meas Sci Technol*. 1998;9:1751-1756.

16. Wu HT, Yang CH, Wu WB, et al. Study on synthesis and evolution of nanocrystalline Mg_4Ta2O_9 by aqueous sol-gel process. *Surf Rev Lett*. 2012;19:1-6.

17. Fukuda K, Kitoh R, Awai I. Microwave characteristics of TiO_2-Bi_2O_3 dielectric resonator. *Jpn J Appl Phys Part 1 - Regul Pap Short Notes Rev Pap*. 1993;32:4584-4588.

18. Wakino K. Recent development of dielectric resonator materials and filters in Japan. *Ferroelectrics*. 1989;91:69-86.

19. Penn SJ, Alford NM, Templeton A, et al. Effect of porosity and grain size on the microwave dielectric properties of sintered alumina. *J Am Ceram Soc*. 1997;80:1885-1888.

20. Huang CL, Yang TJ, Huang CC. Low dielectric loss ceramics in the $ZnAl_2O_4$-TiO_2 system as a τ_f compensator. *J Am Ceram Soc*. 2009;92:119-124.

21. Belous A, Ovchar O, Durilin D, et al. High-Q microwave dielectric materials based on the spinel Mg_2TiO_4. *J Am Ceram Soc*. 2006;89:3441-3445.

22. Bian JJ, Yan K, Dong YF. Microwave dielectric properties of $A_{1-3x/2}La_x(Mg_{1/2}W_{1/2})O_3$ (A=Ba, Sr, Ca; $0.0 \le x \le 0.05$) double perovskites. *Materials Science and Engineering: B*. 2008;147:27-34.

Table 1. Microwave characteristics of xMT ceramics.

x values	Sintering temperature (°C)	Bulk density (g/cm^3)	Dielectric properties		
			ε_r	Qf (GHz)	τ_f (ppm/°C)
1	1550	7.56	28.0	188000	54
2	1325	6.83	19.9	211000	8
3	1325	6.39	15.2	230000	-31
4	1325	6.03	12.2	261000	-68

Table 2. Comparison of calculated and theoretical values of xMT ceramics.

x values	The Stoichiometric coefficients of $Mg_4Ta_2O_9$	The mass fraction of $Mg_4Ta_2O_9$		The volume fraction of $Mg_4Ta_2O_9$	Theoretical density (g/cm^3)
		Calculation from GSAS 2.0 (%)	Theoretical values (%)		
1	0	0.0	0.0	0.0	7.80
2	1/3	37.7	38.5	44.1	7.09
3	2/3	68.9	71.4	75.9	6.57
4	1	96.0	100.0	100.0	6.18

Table 3. Microwave dielectric properties comparison of the materials with similar permittivity.

No.	Composition	ε_r	Qf (GHz)	τ_f (ppm/°C)	Ref.
1	$0.23MgTiO_3$-0.77 ($0.5ZnAl_2O_4$–$0.5TiO_2$)	18.7	190000	-1.8	20
2	$Ba(Mg_{1/3}Ta_{2/3})O_3$	25	180000	2.7	4
3	$0.93(0.99Mg_2TiO_4$–$0.01Co_2TiO_4)$-0.07$CaTiO_3$	17	105000	-5	21
4	$Ba_{1.94}La_{0.04}(Mg_{1/2}W_{1/2})O_3$	20	87680	-1.2	22
5	2MgO-Ta_2O_5+0.5 wt% B_2O_3	19.9	211000	8	Presented

Fig. 1. XRD patterns of 4MT powders calcined at different temperatures.

Fig. 2. Relative density of xMT ceramics as a function of sintering temperature.

Fig. 3. XRD patterns of xMT ceramics sintered at optimum temperature.

Fig. 4. The typical microstructures of xMT ceramics at optimum sintering temperature.①$MgTa_2O_6$ and ②$Mg_4Ta_2O_9$.

Fig. 5. EBSD phase map of 2MT ceramic showing phase distribution and fraction.

Fig. 6. Variation of ln ε, 1/Qf, τ_f as a function of volume fraction of $Mg_4Ta_2O_9$ in the xMT ceramics.