

# Sintering and dielectric properties of $(\text{Ta}_2\text{O}_5)_{1-x}(\text{TiO}_2)_x$ polycrystalline ceramics

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**Abstract**  $(\text{Ta}_2\text{O}_5)_{1-x}(\text{TiO}_2)_x$  system ceramics has been studied intensively as a promising dielectric material for next generation of high density dynamic random access memories instead of  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$ . It is found that the dielectric permittivity of  $(\text{Ta}_2\text{O}_5)_{1-x}(\text{TiO}_2)_x$  ceramics was dependent of fabrication process. But in the previous work, their calcining and sintering time were too long, generally for 24 h or even more. A relatively quick sintering process was provided which calcining and sintering time can be decreased to 12 h at 1200°C and 1 h at 1550°C, respectively. This kind of sintering process can save a lot of energy and time that is in favor of the industrial production. Under this sintering process, the composition dependent dielectric properties of  $(\text{Ta}_2\text{O}_5)_{1-x}(\text{TiO}_2)_x$  ceramics have been studied in a wide range of composition ( $0.01 \leq x \leq 0.20$ ), and the dielectric constants of most compositions can be drastically enhanced. The maximum dielectric value can reach 216 at composition  $x=0.04$ . In the meantime, the mechanism of improvement of ceramic dielectric constants sintered at 1550°C was also discussed.

**Keywords**  $(\text{Ta}_2\text{O}_5)_{1-x}(\text{TiO}_2)_x$  · Dielectric properties · Sintering temperature

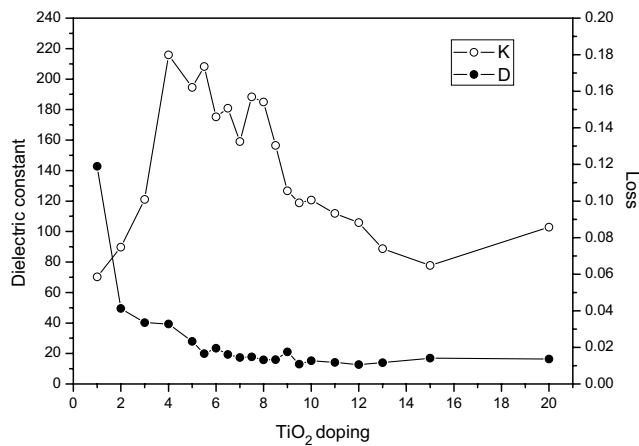
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## 1 Introduction

$\text{Ta}_2\text{O}_5$  has been studied intensively as capacitor materials due to its high dielectric constant and a high degree of compatibility with microelectronics manufacturing. It is considered as a promising dielectric material for next generation of high density dynamic random access memories instead of  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$  [1–4]. Recently, Cava et al. [2] have reported that the dielectric constant of  $\text{Ta}_2\text{O}_5$  can further be enhanced by nearly a factor of four – from 35 to 126 – through addition of 8 mol% titanium oxide,  $\text{TiO}_2$ . It is indicated that the pure  $\text{Ta}_2\text{O}_5$  would be substituted by the chemical system of  $(\text{Ta}_2\text{O}_5)_{1-x}(\text{TiO}_2)_x$  in future applications. Their sintering condition was that  $(\text{Ta}_2\text{O}_5)_{1-x}(\text{TiO}_2)_x$  system ceramics was first calcined at 1350–1400°C for several nights, then sintered at 1400°C for 16–20 h. Gou et al. have studied the dielectric properties of  $(\text{Ta}_2\text{O}_5)_{0.92}(\text{TiO}_2)_{0.08}$  polycrystalline ceramics prepared under different processing and annealing conditions [5]. They found that the permittivity can be significantly enhanced by increasing calcination time (24–28 h at 1350°C) and sintering temperature (at 1400–1600°C for 28–6 h). It is indicated that the dielectric properties of  $(\text{Ta}_2\text{O}_5)_{1-x}(\text{TiO}_2)_x$  system ceramics were highly dependent upon the processing condition. But by overlong time of calcining and sintering to achieve higher dielectric permittivity was not in favor of future industrial production. In the present work, a relatively quick processing condition of  $(\text{Ta}_2\text{O}_5)_{1-x}(\text{TiO}_2)_x$  system ceramics were developed. Under this processing condition, the dielectric properties of  $(\text{Ta}_2\text{O}_5)_{1-x}(\text{TiO}_2)_x$  were investigated in detail in a wide range of composition from  $x=0.01$  to 0.20. And the reason why the dielectric permittivity can be improved a lot was also discussed.



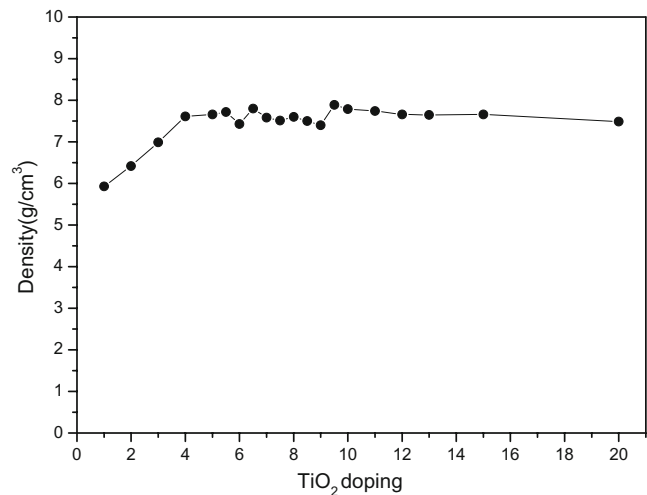
**Fig. 1** Permittivity  $\kappa$  and dielectric loss  $\tan\delta$  at 1 MHz for  $(\text{Ta}_2\text{O}_5)_{1-x}(\text{TiO}_2)_x$  polycrystalline ceramics at 20°C as a function of composition

## 2 Experiment

The  $(\text{Ta}_2\text{O}_5)_{1-x}(\text{TiO}_2)_x$  powders were prepared by the conventional solid-state reaction technique. High-purity reagents,  $\text{Ta}_2\text{O}_5$  and  $\text{TiO}_2$  were mixed in appropriate molar ratios. The mixed powders were mechanically ground in ethanol for 9 h. After sieving and drying, they were calcined at 1200°C for 12 h in air. The calcined powders were reground in ethanol for 9 h. After drying, the powders were mixed with organic binder of 6 wt.% polyvinyl

**Table 1** Dielectric properties (at 1 MHz) of  $(\text{Ta}_2\text{O}_5)_{1-x}(\text{TiO}_2)_x$  polycrystalline ceramics.

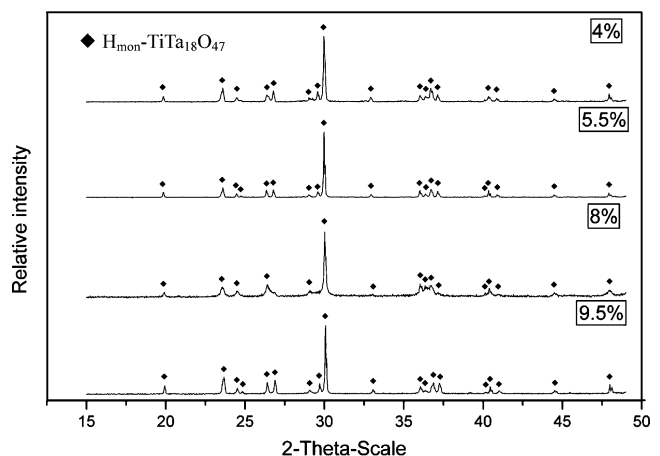
$x$ (mol%)	Present work		Cava et al. [2]	
	$\kappa$	$\tan\delta$	$\kappa$	$\tan\delta$
0.01	70.3	0.12	\	\
0.02	89.8	0.041	20.3	0.016
0.03	121.1	0.033	\	\
0.04	215.9	0.033	46.6	0.038
0.05	194.5	0.023	\	\
0.055	208.3	0.017	\	\
0.06	175.3	0.019	94.0	0.016
0.065	180.8	0.016	\	\
0.07	159.0	0.014	\	\
0.075	188.4	0.015	\	\
0.08	185.0	0.013	126.2	0.010
0.085	156.5	0.013	\	\
0.09	126.8	0.017	\	\
0.095	118.8	0.011	\	\
0.10	120.6	0.013	97.8	0.026
0.11	111.9	0.012	\	\
0.12	105.8	0.011	\	\
0.125	\	\	88.6	0.008
0.13	88.7	0.012	\	\
0.15	77.8	0.014	\	\
0.20	102.8	0.014	\	\



**Fig. 2** Density of  $(\text{Ta}_2\text{O}_5)_{1-x}(\text{TiO}_2)_x$  polycrystalline ceramics at 20°C as a function of composition

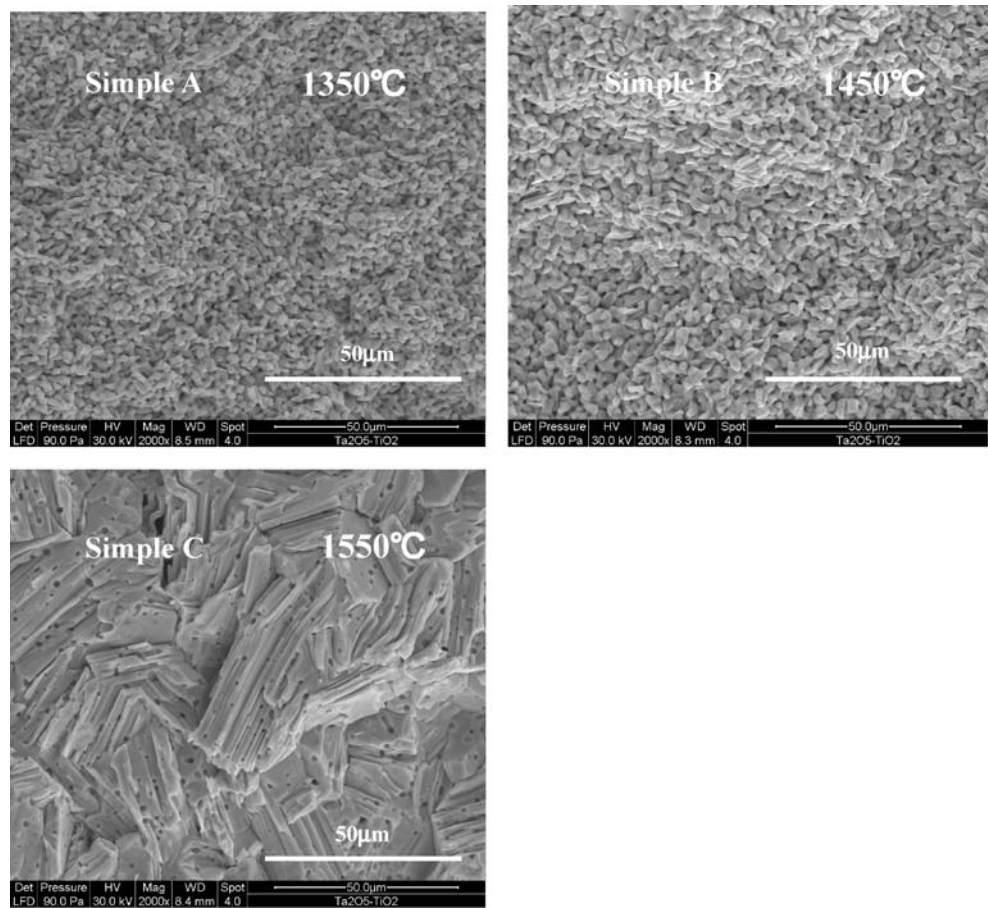
alcohol and pressed uniaxially at 200 MPa into cylindrical discs/pellets of half-inch diameter. The pellets were sintered in air at 1550°C for 1 h, with a heating and cooling rate of 10°C/min.

Densities of the sintered samples were determined by a liquid immersion method. All samples were polished on both sides and gold electrodes were deposited on via sputtering. Measurements of the dielectric constants (at an applied voltage signal 1.0 V) and dissipation factors (loss tangents) were measured at 1 MHz by using an Agilent 4284A precision LCR impedance analyzer. Crystalline phase were identified by x-ray diffraction (XRD; BRUKER/AXS D8 Advance). The microstructure was characterized by scanning electron microscopy (SEM; FEI Quanta 200).



**Fig. 3** X-ray diffraction patterns of  $(\text{Ta}_2\text{O}_5)_{1-x}(\text{TiO}_2)_x$  polycrystalline ceramics at 20°C. Top to bottom: 4, 5.5, 8, and 9.5 mol%

**Fig. 4** SEM micrograph of  $(\text{Ta}_2\text{O}_5)_{0.92}(\text{TiO}_2)_{0.08}$  polycrystalline ceramics sintered at different temperature. *Sample A* at 1350°C, *sample B* at 1450°C, *sample C* at 1550°C



**3 Results and discussion**

Figure 1 shows variation of dielectric constants ( $\kappa$ ) and dissipation factor ( $\tan\delta$ ) at 1 MHz with composition at room temperature.

Compared with Cava et al. [2], the composition dependence of the dielectric properties of  $(\text{Ta}_2\text{O}_5)_{1-x}(\text{TiO}_2)_x$  system is summarized in Table 1.

From Fig. 1, it can be seen that the dielectric constants increased with increasing the amount of  $\text{TiO}_2$  in the range between  $x=0.01$  and 0.04. The values of  $\kappa$  were more than 100 in a wide range from  $x=0.04$  to 0.012. The dielectric constants of compositions  $x=0.04, 0.05, 0.055, 0.065, 0.075,$  and 0.08 can reach more than 180. The maximum value of  $\kappa$  can reach 216 at the composition  $x=0.04$ .

**Table 2** Dielectric properties and density of  $(\text{Ta}_2\text{O}_5)_{0.92}(\text{TiO}_2)_{0.08}$  ceramics sintered at various temperature for 1 h.

$(\text{Ta}_2\text{O}_5)_{0.92}(\text{TiO}_2)_{0.08}$	1350°C	1450°C	1550°C
$\kappa$	111.1	145.1	185.0
$\tan\delta$	0.019	0.016	0.013
$\rho(\text{g}/\text{cm}^3)$	6.05	6.73	7.60

Considering the dielectric loss, the optimum point was considered at  $x=0.08$  which  $\kappa$  and  $\tan\delta$  were equal to 185.0 and 0.013, respectively.

The density of  $(\text{Ta}_2\text{O}_5)_{1-x}(\text{TiO}_2)_x$  system is shown in Fig. 2. The density rose, with increasing the amount of  $\text{TiO}_2$  in the range between  $x=0.01$  and 0.04. As can be seen that the values of density were stable in the vicinity of  $7.5 \text{ g}/\text{cm}^3$  in a wide rang of compositions.

Figure 3 shows the x-ray diffraction patterns obtained from four  $\text{TiO}_2$  substituted  $\text{Ta}_2\text{O}_5$  samples. The XRD patterns of these samples are identified as high temperature monoclinic  $(\text{Ta}_2\text{O}_5)_{0.9}(\text{TiO}_2)_{0.1}$  solid-solution ( $H'_{\text{mon}}\text{-Ta}_2\text{O}_{5\text{ss}}$ ) published by Waring and Roth [6]. And no other phase was observed. It is indicated that  $(\text{Ta}_2\text{O}_5)_{1-x}(\text{TiO}_2)_x$  ceramics sintered at 1550°C can easily obtain the complete  $H'_{\text{mon}}\text{-Ta}_2\text{O}_{5\text{ss}}$  phase which possibly lead to the enhancement of dielectric permittivity based upon the previous research [2, 5].

In order to investigate the reason why the larger dielectric constants could be achieved at sintering temperature of 1550°C, the SEM photographs of fractured surfaces of  $(\text{Ta}_2\text{O}_5)_{0.92}(\text{TiO}_2)_{0.08}$  ceramics sintered under various temperature were shown as Fig. 4. The microstructures were characterized by grains of various sizes and

morphologies, containing amount of intergranular porosity which was formed by removal of the binder and much sensitive to the sintering temperature. With increasing of sintering temperature, the tend of crystallization and grain sizes increased and the porosity relatively reduced. The columnar shaped grains as sintered were packed together along preferred direction. The dielectric properties of  $(\text{Ta}_2\text{O}_5)_{0.92}(\text{TiO}_2)_{0.08}$  ceramics sintered under various temperature were listed in Table 2. With increasing of sintering temperature, the dielectric constant increased and the dielectric loss reduced. It is suggested that higher dielectric constants were involved in the larger and oriented grains and lower dielectric loss involved in the reduction of porosity. It is anticipated that  $(\text{Ta}_2\text{O}_5)_{1-x}(\text{TiO}_2)_x$  system ceramics sintered at  $1550^\circ\text{C}$  for 1 h, the oriented grains can grow up sufficiently and porosity can be reduced effectively. It is why the dielectric properties of  $(\text{Ta}_2\text{O}_5)_{1-x}(\text{TiO}_2)_x$  ceramics can be enhanced.

#### 4 Conclusions

A quick sintering condition of  $(\text{Ta}_2\text{O}_5)_{1-x}(\text{TiO}_2)_x$  system ceramics was provided. At sintering temperature of  $1550^\circ\text{C}$ , reducing the time of calcining and sintering can save a lot of energy and time which is in favor of future industrial production. Under this condition, the dielectric permittivity

of  $(\text{Ta}_2\text{O}_5)_{1-x}(\text{TiO}_2)_x$  ceramics can be dramatically enhanced not only at composition  $x=0.08$ , but also at many other compositions. The maximum value of  $\kappa$  can reach 216 at the composition  $x=0.04$ . But considering dissipation factor, the optimal point of dielectric properties was also at  $x=0.08$ . It is also suggested that the dielectric permittivity of  $(\text{Ta}_2\text{O}_5)_{1-x}(\text{TiO}_2)_x$  ceramics was sensitive not only to  $\text{TiO}_2$  addition but also to sintering temperature. Through the investigation of x-ray diffraction and the SEM, the mechanism of enhancement of dielectric constants is related to the appearance of  $\text{H}'_{\text{mon}}\text{-Ta}_2\text{O}_5$  solid-solution phase and the large and oriented grains in  $(\text{Ta}_2\text{O}_5)_{1-x}(\text{TiO}_2)_x$  ceramics sintered at  $1550^\circ\text{C}$ .

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#### Reference

1. K.W. Kwon, I.S. Park, D.H. Han, E.S. Kim, S.T. Ahn, M.Y. Lee, in *International Electronic Devices Meeting, Technical* (IEEE, Piscataway, 1994), pp. 835–838
2. R.F. Cava, W.F. Peck, Jr., J.J. Krajewski, *Nature* **377**, 215 (1995)
3. J.Y. Gan, Y.C. Cheng, T.B. Wu, *Appl. Phys. Lett.* **72**(3), 332 (1998)
4. K.M.A. Salam, H. Konish, M. Mizuno, H. Fukuda, S. Nomura, *Jpn. J. Appl. Phys.* **40**, 1431 (2001)
5. R. Guo, Y. Jiang, A.S. Bhalla, *Mater. Lett.* **57**, 270 (2002)
6. J.L. Waring, R.S. Roth, *J. Res. Natl. Bur. Stand.* **72A**, 175 (1968)