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Journal of the European Ceramic Society 23 (2003) 2507–2510

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Microwave dielectric characteristics of $0.75(Al_{1/2}Ta_{1/2})O_2$–$0.25(Ti_{1-x}Sn_x)O_2$ ceramics

Ji-Won Choi[a,*], Jong-Yoon Ha[a], Seok-Jin Yoon[a], Hyun-Jai Kim[a], Ki Hyun Yoon[b]

[a] *Thin Film Technology Research Center, Korea Institute of Science and Technology, Seoul 130-650, South Korea*
[b] *Department of Ceramic Engineering, Yonsei University, Seoul 120-749, South Korea*

Abstract

The microwave dielectric characteristics of $0.75(Al_{1/2}Ta_{1/2})O_2$–$0.25(Ti_{1-x}Sn_x)O_2$ ceramics were investigated. The microwave dielectric properties of $0.75(Al_{1/2}Ta_{1/2})O_2$–$0.25TiO_2$ sintered at 1450 °C exhibited a dielectric constant (ϵ_r) of 31.2, a $Q{\cdot}f_0$ of 54,590 GHz, and the temperature coefficient of resonant frequency (τ_f) of +12.8 ppm/°C. To control of the τ_f and enhance the $Q{\cdot}f_0$ for $0.75(Al_{1/2}Ta_{1/2})O_2$–$0.25TiO_2$, Sn^{4+} was substituted for Ti^{4+}. With an increase of Sn content from 5 to 50 mol%, the ε_r slightly decreased, the $Q{\cdot}f_0$ increased and the τ_f shifted from positive to negative value. The τ_f within ±10 ppm/°C of zero was realized for the Sn content below 30 mol% and the microwave dielectric properties had the ε_r value of 31.2–26.3, the $Q{\cdot}f_0$ of 54,600–70,700 GHz, and τ_f of +12.8–−9.3 ppm/°C for this compositions. The relationship between microstructure and microwave dielectric characteristics was investigated.

Keywords: Dielectric constant; Microwave ceramics; Quality factor; $(Al,Ta)O_2$; $(Ti,Sn)O_2$

1. Introduction

The use of high frequency dielectric ceramics such things as resonators, band pass (stop) filters, duplexers, antennas has increased in mobile communications.[1,2] Therefore, the materials for microwave use have to exhibit three dielectric characteristics,[3–5] relatively low dielectric constant (ε_r), high quality factor (Q), and stable (≈0 ppm/°C) temperature coefficient of the resonant frequency (τ_f). It is known that microwave dielectric materials having $\varepsilon_r \approx 20$–40 can be used for duplexer filters and antennas in the frequency range 1.8–2.4 GHz. Candidate materials that have been developed with relatively low sintering temperature (⩽1450 °C) are $MgTiO_3$–$CaTiO_3$,[6] $Ba_2Ti_9O_{20}$,[7] $(Zr,Sn)TiO_4$,[8] $Ca[(Li_{1/3}Nb_{2/3})_{1-x}M_x]O_{3-\delta}$(M = Sn, Ti)[9] and others. However, these materials have relatively low quality factor (Q) values (≈26,000–50,000 GHz).

The purpose of present work is to find a new dielectric material having appropriate ε_r (about 20–30) for the applications described above, i.e. a material having $\tau_f = 0$ ppm/°C and a higher quality factor than developed candidate materials. $(Al_{1/2}Ta_{1/2})O_2$[10] having very low ϵ_r (8.7) and negative τ_f (−55 ppm/°C), and TiO_2[11] having very high ε_r (104) and positive τ_f (+450 ppm/°C) are good candidate materials. SnO_2 is a useful material to control the τ_f and enhance the Q factor. In this paper we report crystallographic data and relationship between the microwave dielectric properties and the microstructure of $0.75(Al_{1/2}Ta_{1/2})O_2$–$0.25(Ti_{1-x}Sn_x)O_2$ ($0 \leqslant x \leqslant 0.5$) ceramics.

2. Experimental procedure

$0.75(Al_{1/2}Ta_{1/2})O_2$–$0.25(Ti_{1-x}Sn_x)O_2$ powder compositions were synthesized using the conventional solid-state reaction method; the starting materials were Al_2O_3 (Aldrich, 99.7%), Ta_2O_5 (Aldrich, 99%), TiO_2 and SnO_2 (Aldrich, 99.9%). Stoichiometric compositions were mixed for 24 h with stabilized ZrO_2 ball media and distilled water, then dried and calcined. The calcined powders were re-milled and pressed into rods of 12 mm in diameter and 6 mm in thickness under a pressure of 150 MPa. The pellets were sintered at 1450C for 3 h in air, then ground and polished to precise dimensions to achieve the thickness to diameter ratio of 0.4–0.5.

X-ray diffractometry (XRD, CuK_α radiation, Model Rint/Dmax 2500, Rigaku, Japan) was conducted for

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* Corresponding author.

doi:10.1016/S0955-2219(03)00170-5

phase identification and lattice parameter measurements on powders obtained by crushing the sintered specimens. The bulk densities of the sintered pellets were determined by the Archimedes method. The polished surfaces of the ceramics were investigated by scanning electron microscopy (SEM, Model S-4200, Hitachi, Japan) after thermal etching. The ε_r, the unloaded Q and the τ_f values were measured at 8–10 GHz using the parallel-plate (Hakki and Coleman) method interfaced with a network analyzer (HP-8720C, Hewlett Packard, USA).[12] The τ_f was measured in the temperature range -20–$+80$ °C.

3. Results and discussion

Fig. 1 shows X-ray diffraction patterns for $0.75(Al_{1/2}Ta_{1/2})O_2$–$0.25(Ti_{1-x}Sn_x)O_2$ ceramics sintered at 1450 °C for 3 h. The diffraction peaks can be indexed based on tetragonal TiO_2 with four formula units per unit cell.[13] $0.75(Al_{1/2}Ta_{1/2})O_2$–$0.25(Ti_{1-x}Sn_x)O_2$ is tetragonal and single phased. Some of the crystallographic data for $0.75(Al_{1/2}Ta_{1/2})O_2$–$0.25(Ti_{1-x}Sn_x)O_2$ are listed in Table 1; the unit cell parameters are derived from a computerized least-squares refinement technique. The unit cell parameters increase with an increase in SnO_2 concentration because of the difference of average ionic radii of Ti^{+4} (0.061 nm) and Sn^{+4} (0.069 nm).[14]

Fig. 2 shows the densities for $0.75(Al_{1/2}Ta_{1/2})O_2$–$0.25(Ti_{1-x}Sn_x)O_2$ ceramics sintered at 1450 C for 3 h. X-ray density and apparent density increase with increasing SnO_2 concentration. The apparent density of the sintered specimens ranged between 92.0 and 94.6% of the theoretical density.

Fig. 3 shows SEM photographs for $0.75(Al_{1/2}Ta_{1/2})O_2$–$0.25(Ti_{1-x}Sn_x)O_2$ ceramics sintered at 1450 °C for 3 h. As the Sn concentration increases, the grain size increases. There were no significant differences in the number of pores and the pore size with an increase of Sn concentration.

Fig. 4 shows the ε_r of the $0.75(Al_{1/2}Ta_{1/2})O_2$–$0.25(Ti_{1-x}Sn_x)O_2$ ceramics sintered at 1450 °C for 3 h. The ε_r decreases from 31.2 to 23.9 with increase in x from 0 to 50 mol%. It is expected that the decrease of ε_r by substitution of Sn occurs because Sn^{4+} ion having ionic polarizability of 2.83 Å is incorporated to a Ti^{+4} site with polarizability of 2.93 Å.[15] It is also expected that the decrease of ε_r by substitution of Sn occurs because a slightly large Sn^{4+} ion (0.69 Å) is incorporated to a Ti^{+4} site with slightly smaller ionic radius (0.61 Å) hence, it is less easily displaced under an electrical field. This result is reasonable in agreement with

Table 1
Crystallographic data for $0.75(Al_{1/2}Ta_{1/2})O_2$–$0.25(Ti_{1-x}Sn_x)O_2$ ceramics sintered at 1450 °C for 3 h

x	Tetragonal		Vol per unit cell ($\times10^{-3}$ nm^3)	X-ray density (g/cm^3)
	a ($\times10^{-1}$ nm)	c ($\times10^{-1}$ nm)		
0	4.5819	2.9660	62.36	6.4925
0.05	4.5743	2.9666	62.07	6.5701
0.1	4.5815	2.9705	62.35	6.5877
0.2	4.5826	2.9753	62.48	6.6677
0.3	4.5862	2.9810	62.70	6.7384
0.4	4.5881	2.9855	62.85	6.8160
0.5	4.5948	2.9924	63.18	6.8732

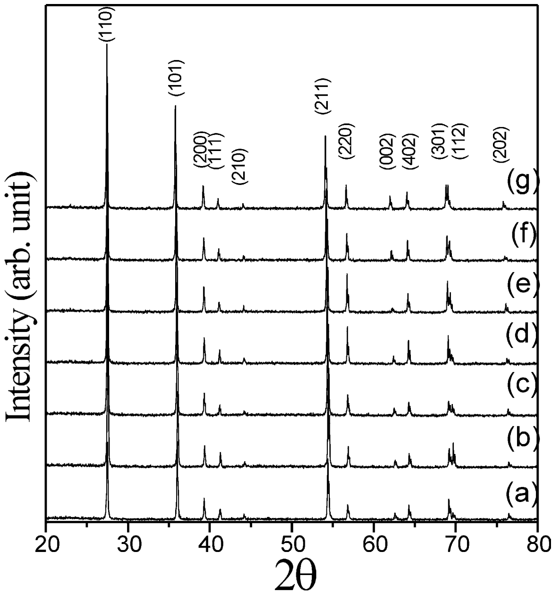


Fig. 1. X-ray diffraction pattern of $0.75(Al_{1/2}Ta_{1/2})O_2$–$0.25(Ti_{1-x}Sn_x)O_2$ ceramics sintered at 1450 °C for 3 h: (a) $x=0$, (b) $x=0.05$, (c) $x=0.1$, (d) $x=0.2$, (e) $x=0.3$, (f) $x=0.4$, (g) $x=0.5$.

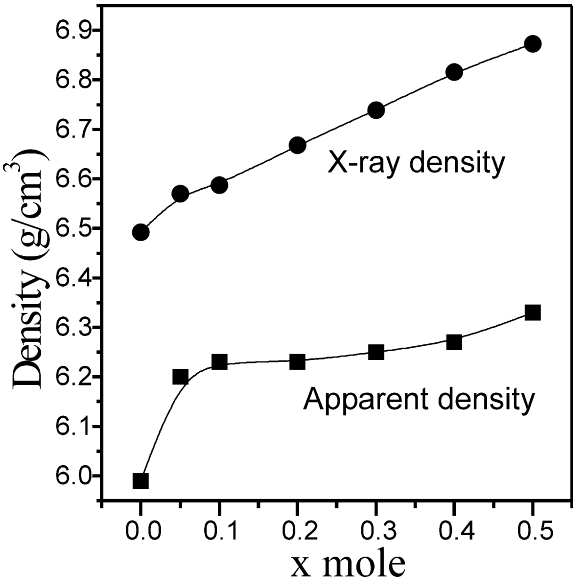
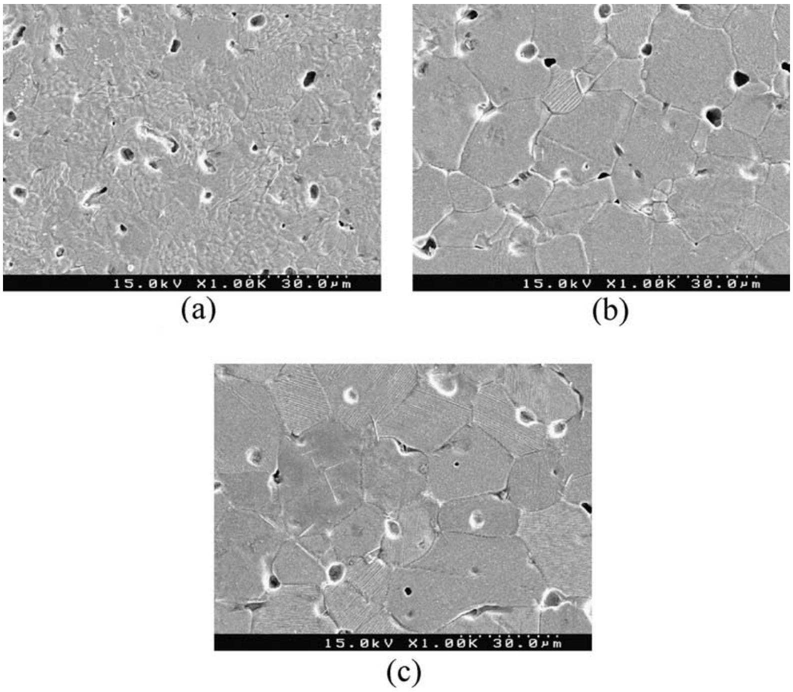


Fig. 2. Densities for $0.75(Al_{1/2}Ta_{1/2})O_2$–$0.25(Ti_{1-x}Sn_x)O_2$ ceramics sintered at 1450 °C for 3 h.



(a) (b)

(c)

Fig. 3. SEM photographs $0.75(Al_{1/2}Ta_{1/2})O_2$–$0.25(Ti_{1-x}Sn_x)O_2$ ceramics sintered at 1450 °C for 3 h: (a) $x = 0.05$, (b) $x = 0.2$, (c) $x = 0.5$.

Kucheiko et al.[16] that Sn addition decreases the dielectric constant in $(Pb,Ca)(Fe,Nb,Sn)O_3$.

Fig. 5 shows $Q{\cdot}f_o$ of the $0.75(Al_{1/2}Ta_{1/2})O_2$–$0.25(Ti_{1-x}Sn_x)O_2$ ceramics sintered at 1450 C for 3 h. The $Q{\cdot}f_o$ increases from 54,600 to 80,500 GHz with increase in x from 0 to 50 mol%. There are many reports that Sn substitution improves significantly the quality factor. In general, dielectric loss mechanisms can be divided into intrinsic loss by anharmonic interaction and extrinsic loss by pores and second phases in the microstructure. In this study, there was no difference in the number of pore, the pore size, nor any second phase with an increase of Sn concentration as shown in Figs. 1 and 3. Therefore, it can be considered that quality factor was improved by decreasing intrinsic loss as Sn concentration increased.

Fig. 6 shows the τ_f of the $0.75(Al_{1/2}Ta_{1/2})O_2$–$0.25(Ti_{1-x}Sn_x)O_2$ ceramics sintered at 1450 °C for 3 h.

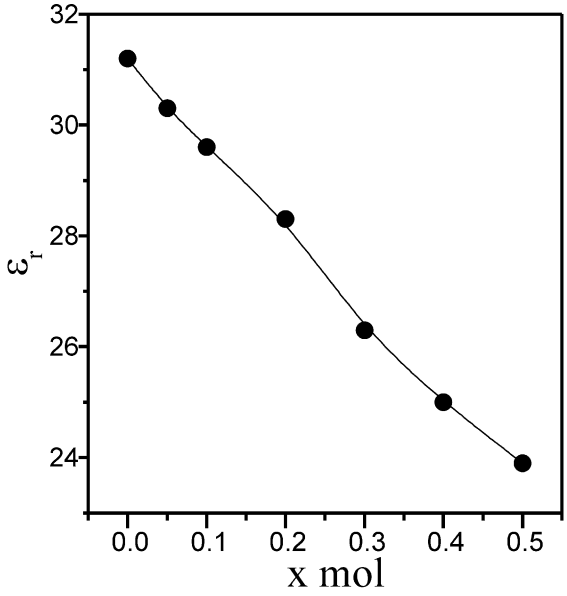


Fig. 4. ε_r of $0.75(Al_{1/2}Ta_{1/2})O_2$–$0.25(Ti_{1-x}Sn_x)O_2$ ceramics sintered at 1450 °C for 3 h.

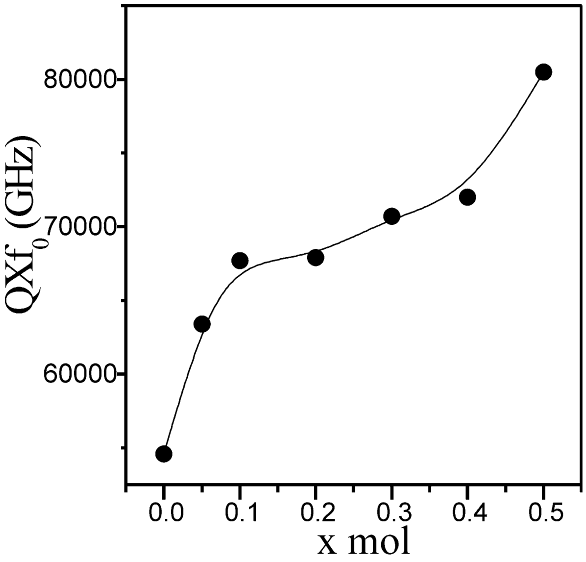


Fig. 5. $Q{\cdot}f_0$ of $0.75(Al_{1/2}Ta_{1/2})O_2$–$0.25(Ti_{1-x}Sn_x)O_2$ ceramics sintered at 1450 °C for 3 h.

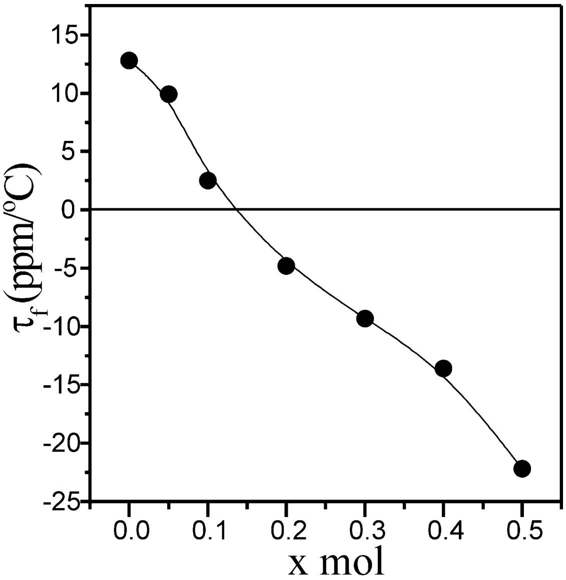


Fig. 6. τ_f of $0.75(Al_{1/2}Ta_{1/2})O_2$–$0.25(Ti_{1-x}Sn_x)O_2$ ceramics sintered at 1450 °C for 3 h.

The τ_f of the $0.75(Al_{1/2}Ta_{1/2})O_2$–$0.25(Ti_{1-x}Sn_x)O_2$ decreases from 12.8 to −22.2 ppm/°C with increasing Sn concentration from 0 to 50 mol%. Ceramics having τ_f of within ±10 ppm/°C was realized for Sn concentrations from 5 to 30 mol%. This composition range has ε_r of 26.3–30.0 and $Q{\cdot}f_o$ value of 63,400–70,700 GHz.

4. Conclusions

The microwave dielectric properties of $0.75(Al_{1/2}Ta_{1/2})O_2$–$0.25(Ti_{1-x}Sn_x)O_2$ $(0 \leqslant x \leqslant 0.5)$ ceramics have been investigated. A single phase ceramic with a tetragonal structure has been obtained $0 \leqslant x \leqslant 0.5$. An increase of Sn concentration in the system $0.75(Al_{1/2}Ta_{1/2})O_2$–$0.25(Ti_{1-x}Sn_x)O_2$ increases the Qf_o value and the dielectric constant slightly decreases, but the temperature coefficient of resonant frequency is controlled within ±10 ppm/°C. New high Q microwave dielectric compositions having $\varepsilon_r = 26.3$–30.0, $Q{\cdot}f_o = 63{,}400$–$70{,}700$ GHz and $\tau_f \leqslant |10|$ ppm/°C are obtained at the composition of $0.75(Al_{1/2}Ta_{1/2})O_2$–$0.25(Ti_{1-x}Sn_x)O_2$ $(0.05 \leqslant x \leqslant 0.3)$ for the application of microwave devices.

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