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Improvement of the dielectric properties of rutile-doped Al_2O_3 ceramics by annealing treatment

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Abstract

The microwave dielectric properties of alumina (Al_2O_3) ceramics were studied. The objectives were to improve the large negative temperature coefficient of the resonant frequency (τ_f) of Al_2O_3 ceramics and to obtain a relatively large quality factor (*Qf*) through the addition of rutile (TiO_2), which has a large positive τ_f, and an annealing treatment. A near-zero τ_f (+1.5 ppm/°C), excellent *Qf* (148,000 GHz) and ε_r (12.4) were obtained in 0.9 Al_2O_3–0.1 TiO_2 ceramics sintered at 1350 °C for 2 h, followed by annealing at 1100 °C for 12 h in air.
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1. Introduction

Dielectric materials for microwave applications have been used in mobile phones, wireless local area networks (LAN), and intelligent transport systems (ITS). Recently, they are planed to be applied in ultrahigh speed wireless LAN in millimeter wave, because they can reduce the resource of electromagnetic wave. Dielectric ceramics for millimeter-wave applications are also planned for use in ITS, including a car anti-collision system.[1] In order to meet this application, they must have a high quality factor (*Q*), to significantly reduce dielectric loss ($Q = 1/\tan\delta$), and a low dielectric constant (ε_r), to shorten the time for electronic signal transition. Moreover, zero τ_f is required to provide stability at various service temperatures. *Q* is generally evaluated as *Qf* (*f*: frequency) because *Qf* is almost constant even with increasing frequency.[2] Al_2O_3, $MgTiO_3$ and Mg_2SiO_4 ceramics, which are high-*Qf* and low-ε_r materials, are both candidates for millimeter-wave applications.[1,3] However, with large negative τ_f values, significant improvement is still needed.[4] This obstacle might be overcome by two phases with different τ_f values.[5] For example, the combination of $MgTiO_3$ ceramics, which have a negative τ_f, and $CaTiO_3$ ceramics, which have a positive τ_f, could be selected to control τ_f toward zero.[3]

Al_2O_3 ceramics have an ultrahigh *Qf* of 360,000 GHz, low ε_r of 9.8, and a negative large τ_f of −60 ppm/°C,[6,7] while TiO_2 ceramics have a high *Qf* of 48,000 GHz, ε_r of 100, and a positive large τ_f of +450 ppm/°C.[8] Tzou et al. Reported that Al_2O_3–TiO_2 ceramics containing glass additives achieved a $\tau_f \sim 0$ ppm/°C by adjusting both sintering temperature and TiO_2 content.[9] However, dense ceramics were not obtained at a low sintering temperature (1300 °C). They also found that the formation of Al_2TiO_5 caused a decrease in *Qf* and τ_f when the sample was sintered at high temperature. Fig. 1 shows the diagram for Al_2O_3–TiO_2; this diagram indicates the appearance of Al_2TiO_5 at above 1200 °C.

In the previous letter, it was simply described that Al_2TiO_5 could be decomposed by using a post-annealing treatment, creating a ceramic with a near-zero τ_f (τ_f = +1.5 ppm/°C) and microwave dielectric properties (*Qf* = 117,000 GHz, ε_r = 12.4). These characteristics were obtained using a 0.9 Al_2O_3–0.1 TiO_2 ceramic which had been sintered at 1350 °C for 2 h, followed by an anneal at 1000 °C for 2 h in air.[10] In this paper, the previous letter is revised with additional data, and the effects of annealing hold time are studied in more detail.

2. Experimental procedures

Al_2O_3 (TM-DAR, 99.99% purity, Taimei Chemical Co. Ltd., Japan) and TiO_2 (99.9% purity, Ishihara Sangyo Ltd., Japan) powders were used as raw materials for synthesis of Al_2O_3–TiO_2 ceramics. Utilizing the MICROTRAC the average particle size of Al_2O_3 was 0.17 μm, and TiO_2 was 0.24 μm. The starting materials were mixed, according to the composition 0.9 Al_2O_3–0.1 TiO_2. The mixed powders were ball-milled in a

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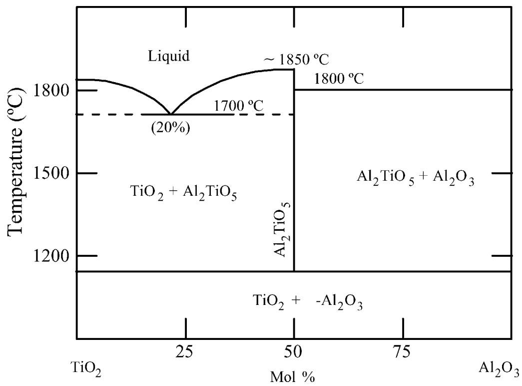

Fig. 1. Phase diagram of Al_2O_3–TiO_2 (after Ref. [12]).

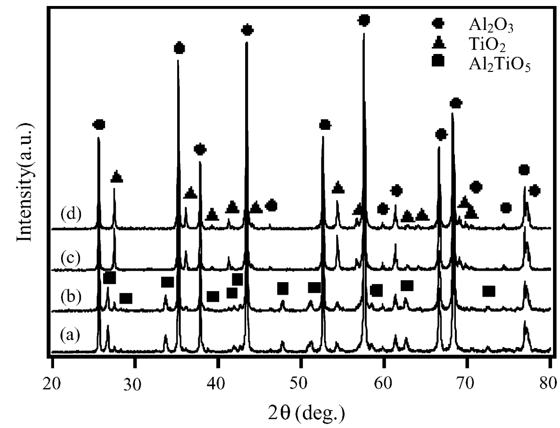

Fig. 2. XRPD patterns of 0.9 Al_2O_3–0.1 TiO_2 ceramics sintered at (a) 1350 °C for 2 h and post annealed at (b) 900 °C; (c) 1000 °C and (d) 1100 °C for 2 h.

polyethylene bottle with Al_2O_3 balls and ethanol for 24 h. Pellets with a diameter of 12 mm were formed by uni-axial pressure of 98 MPa after the powders were dried and granulated. The pellets were sintered at temperatures from 1300 to 1550 °C for 2 h, followed by annealing at 900, 1000 and 1100 °C in air.

The crystalline phase of sintered pellets was investigated by X-ray powder diffraction (XRPD). The apparent density (ρ) was measured by the Archimedes' method. The microstructure was analyzed by transmission electron microscopy (TEM) equipped with energy dispersive X-ray spectroscopy (EDS). The microwave dielectric properties (*Qf*, ε_r, and τ_f) were measured by a network analyzer (Agilent 8720ES and HP 8757C) using a pair of parallel conducting Ag and Cu plates in the TE_{011} mode of modified Hakki and Coleman's resonator method. τ_f was estimated by a comparison of the resonant frequencies measured at 20 and 80 °C.

3. Results and discussion

0.9 Al_2O_3–0.1 TiO_2 compositions were designed to be τ_f nearly 0 ppm/°C based on the volume ratio of Al_2O_3 and TiO_2, considering the τ_f of Al_2O_3 and TiO_2.

Fig. 2 shows XRPD patterns of the samples sintered at 1350 °C for 2 h and post-annealed at 900, 1000 and 1100 °C for 2 h. Al_2TiO_5 phase in the specimen sintered at 1350 °C was confirmed as a secondary phase in main Al_2O_3 phase. The Al_2TiO_5 phase disappeared by annealing treatment at 1000 and 1100 °C due to the phase relation as shown previously in Fig. 1. At 900 °C of annealing temperature, the Al_2TiO_5 phase does not decompose due to too lower temperature for the decomposition. Fig. 3 shows the TEM images of the samples sintered and post annealed at 1000 °C for 2 h. In the as sintered sample, Al_2TiO_5 grains with 0.2–0.5 μm in particle size were deposited in the grain boundary of Al_2O_3, and the particle size of Al_2O_3 increased to 1–3 μm. It is considered that Al_2TiO_5 were formed by Al diffused into TiO_2, because the particle size of Al_2O_3 (0.17 μm) as raw materials, is smaller than that of TiO_2 (0.24 μm). In the post annealed sample, Al_2TiO_5 decomposed to TiO_2 and Al_2O_3 with 0.1–0.4 μm in particle sizes by the annealing treatment. They are embedded among large size Al_2O_3 grains with 1–3 μm.

Table 1 shows the τ_f, *Qf* and ε_r of the specimens sintered at 1350 °C for 2 h and post annealed at 900, 1000 and 1100 °C for 2 h. The τ_f values were improved from −36.2 to +1–2 ppm/°C

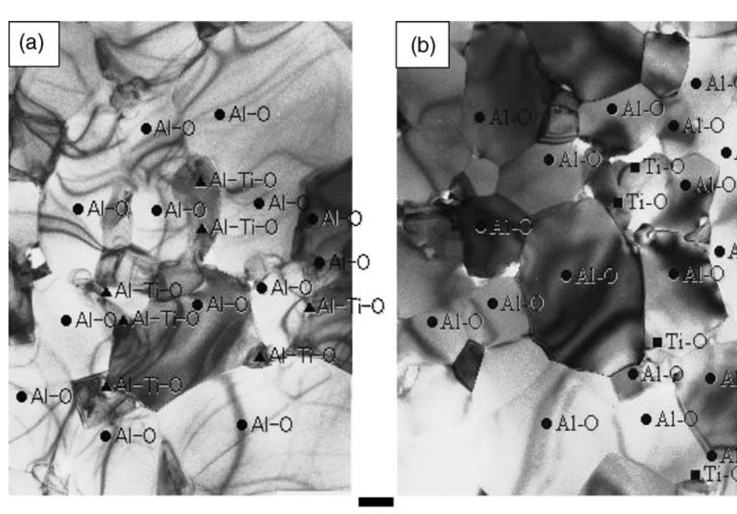

Fig. 3. TEM images of 0.9 Al_2O_3–0.1 TiO_2 ceramics sintered at 1350 °C for 2 h (a) as-sintered and (b) post-annealed at 1000 °C for 2 h.

Table 1
Microwave dielectric properties of as-sintered and post-annealed specimens

Annealing temperature (°C)	τ_f (ppm/°C)	*Qf* (GHz)	ε_r
As sintered (non-annealing)	−36.2	142,000	11.6
900	−39.5	125,000	11.7
1000	+1.5	117,000	12.4
1100	+1.4	114,000	12.6

by annealing at 1000 and 1100 °C. This improvement of τ_f is depend on the decomposition of Al_2TiO_5 with 79 ppm/°C[11] to Al_2O_3 and TiO_2 with 450 ppm/°C by the annealing treatment. This improvement was brought by the difference of τ_f between Al_2TiO_5 and TiO_2. At 900 °C of annealing temperature, the τ_f has not changed because of less decomposition of Al_2TiO_5 due to the lower temperature. The *Qf* decreased from 142,000 GHz to 114,000–117,000 GHz by the annealing treatment of 1000–1100 °C. This decreasing of *Qf* is recovered by the annealing hold time described later. Additionally, the ε_r of the sintered sample was 11.6, and those post annealed at 1000 and 1100 °C were 12.4–12.6, in regard of whether Al_2TiO_5 phase appeared or not.

Fig. 4 shows the τ_f and *Qf* of the specimens sintered at 1300, 1350, 1450 and 1550 °C and post annealed at 1000 °C for 2 h. Fig. 5 shows XRPD patterns of the as sintered samples. At 1300 °C of the sintering temperature there was no observed difference in the properties between the as sintered and post-annealed samples. It should be noted that the Al_2TiO_5 phase was not confirmed in the as sintered specimen, and therefore the effect of the annealing treatment cannot be commented on. Additionally, the τ_f tended to become increasingly negative by increasing the sintering temperature from 1350 to 1500 °C. In fact, there was an increase in the Al_2TiO_5 phase present as the temperature was increased. However, by the annealing treatment the τ_fs were greatly improved to −7 to +1.5 ppm/°C; close to 0 ppm/°C. Finally, the *Qf* value decreased as the sintering temperature increased, which is thought to be attributed to the formation of the Al_2TiO_5 phase. Moreover, the *Qf* showed a decrease by the annealing treatment.

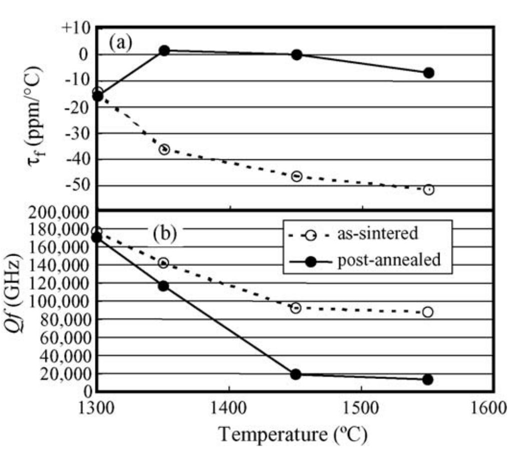

Fig. 4. (a) τ_f and (b) *Qf* of 0.9 Al_2O_3–0.1 TiO_2 ceramics sintered and post annealed at 1000 °C for 2 h as a function of sintering temperature.

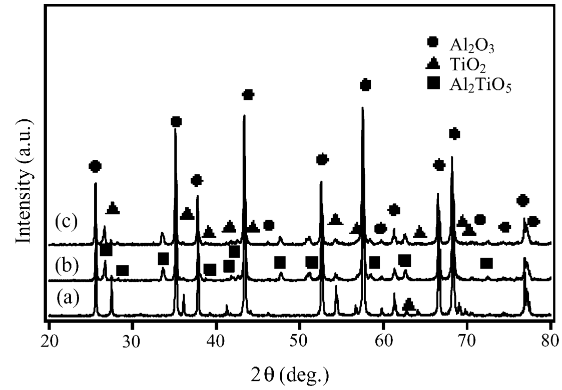

Fig. 5. XRPD patterns of 0.9 Al_2O_3–0.1 TiO_2 ceramics sintered at (a) 1300; (b) 1350 and (c) 1550 °C for 2 h.

The annealing hold time at 1100 °C was investigated. Fig. 6 shows the *Qf*, ε_r and τ_f as a function of annealing time. The *Qf* decreased from 142,000 to 114,000 GHz with a post annealing treatment of 2 h; it is thought that the Al_2TiO_5 to Al_2O_3 and TiO_2 decomposition reaction also occurs during this time and may serve to decrease the *Qf* while the reaction is taking place. However, when the sample was post annealed for longer than 6 h, the *Qf*s of as sintered and post annealed were the same. The effects of strain on this phenomenon were investigated using XRPD. The strain of Al_2O_3 phase in the post annealed sample for 2 h was 0.503×10^{-3}, while the sample post annealed for 12 h had a strain of 0.332×10^{-3}, showing a decrease in strain as the post annealing time was increased. The improvement in the *Qf* can therefore be attributed to a decrease in strain within the sample. The ε_r of the 2 h annealing sample as shown Fig. 6(b) was increased from 11.6 on the 0 h sample to 12.5, in regard

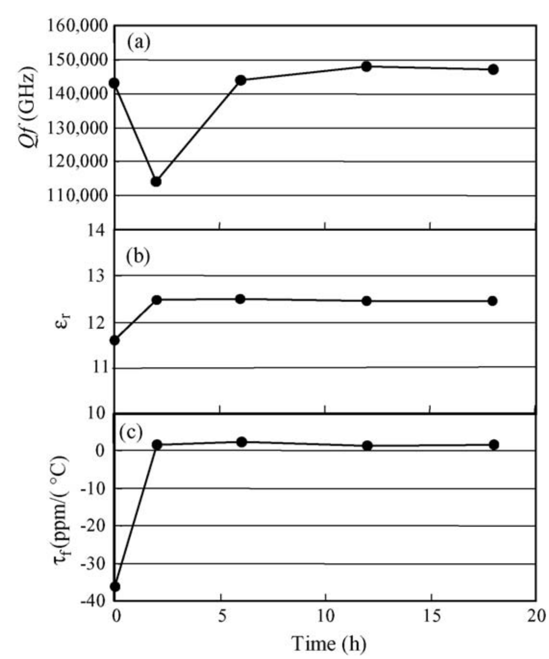

Fig. 6. (a) *Qf*; (b) ε_r and (c) τ_f of 0.9 Al_2O_3–0.1 TiO_2 ceramics sintered at 1350 °C and post annealed at 1100 °C as a function of annealing hold temperature.

of whether Al_2TiO_5 phase appeared or not. Further, the ε_r is relatively constant, above 2 h, a dependence of ε_r on the hold time was not established. Also, the τ_f was improved to nearly zero by annealing. These phenomena can be explained by the absence of the Al_2TiO_5 phase as described before.

4. Conclusions

Rutile (TiO_2) added alumina (Al_2O_3) ceramics have been studied for the improvement of τ_f, the following conclusions are established:

(1) Al_2TiO_5 phase generated by sintering at 1350 °C or more in the Al_2O_3–TiO_2 system is eliminated by the addition of an annealing treatment. By tailing the post annealing treatment, the τ_f can be easily adjusted to 0 ppm/°C.
(2) The *Qf* is improved by optimizing the hold time of the annealing treatment.

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