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Low-temperature sintered Zn_2TiO_4:TiO_2 with near-zero temperature coefficient of resonant frequency at microwave frequency

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ABSTRACT

This work presents the microwave dielectric properties of TiO_2 incorporated Zn_2TiO_4 sintered at low-temperatures. The Zn_2TiO_4 was synthesized using ZnO and TiO_2 nanowires as starting materials. Within the interim studied ($TiO_2 = 0–12\%$), the bulk density, the dielectric constant, and the quality factor markedly increased with sintering temperature. When the TiO_2 content (x) was 8% (970 °C), the value of quality factor multiples its resonant frequency of the Zn_2TiO_4:8% TiO_2 achieved a maximum of ~35,000 GHz. From XRD patterns, the phase stability of TiO_2 added Zn_2TiO_4 changed when the TiO_2 content exceeded 10 wt%. Further addition of TiO_2 up to 12% approached zero, with high quality factor and k values of 30,000 GHz and 22, respectively. The high quality factor was attributed to the good cyrstallinity of Zn_2TiO_4. The fabricated Zn_2TiO_4:12% TiO_2 ceramic is suitable for microwave dielectric applications.

1. Introduction

ZnO–TiO_2 alloy system has been shown to have great potential for use in low-temperature co-fired ceramics (LTCCs), microwave dielectrics, phosphors, and catalysts [1–5]. Three compounds are known to exist in the ZnO–TiO_2 system. Cubic $Zn_2Ti_3O_8$ has been regarded as a low-temperature phase of hexagonal zinc metatitanate (h-$ZnTiO_3$), stabilizing in ~600–800 °C, transforming to h-$ZnTiO_3$ at ~820 °C [6]. The h-$ZnTiO_3$ decomposes into rutile and zinc orthotitanate (Zn_2TiO_4) when the temperature exceeds 945 °C. Particularly, the ilmentite $ZnTiO_3$ draw the most attention among this alloy system due to it potential applications to the LTCCs and microwave dielectrics. As a good microwave dielectric, however, single-phase $ZnTiO_3$ ceramic is rarely obtained solely from the conventional solid-state reaction method because it decomposes at high temperature and poor sinterability at low-temperature (<945 °C) [7]. Generally, the microwave dielectric properties of h-$ZnTiO_3$ sintered below 945 °C were: dielectric constant (ε_r) = 22, temperature coefficient of resonant frequency (τ_f) = −60 ppm/°C, and quality factor ($Q \times f$) = 40,000 GHz. Increasing the sintering temperature to exceed 945 °C always degraded the $Q \times f$ (<20,000 GHz) [1,2].

In the same alloy system, Zn_2TiO_4 ($\varepsilon_r = 21$, $\tau_f = -60$ ppm/°C, $Q \times f = 20{,}000$ GHz) [8] is also a good candidate for microwave dielectric applications. Compared with $ZnTiO_3$, Zn_2TiO_4 has several advantages. For instance, it can be easily formed via solid-state sintering of the 2ZnO:1TiO_2 at elevated temperature. However, the Zn_2TiO_4 shows similar dielectric constant but much poor quality factor at microwave frequencies than the $ZnTiO_3$. It is known that the quality factor is related not only to the crystal structure of the dielectrics, but also the material imperfections. Accordingly, the sintering temperature of Zn_2TiO_4-based microwave dielectrics should be high enough to overcome the low quality factor problem.

Recently, Kim reported the microwave dielectric properties of the titanium incorporated Zn_2TiO_4 [2]. Accordingly, the TiO_2 forms solid solution within the Zn_2TiO_4 matrix that improves the dielectric properties of Zn_2TiO_4. However, the required temperature (~1100 °C) is still high to obtain satisfying dielectric properties. More recently, we reported a method to synthesize the high quality Zn_2TiO_4 with promising microwave properties at low-temperature (<1000 °C) [9,10]. Taking advantages of the high specific surface area of the TiO_2 and ZnO nanowires, the Zn_2TiO_4 was sintered via a calcine and additives-free process. Further, we found that the Zn_2TiO_4 showed negative τ_f value in a wide temperature range (900–1000 °C). However, from the view point of practical application, the near-zeroτ_f is desired to prevent the disturbance from temperature variation.

In this paper, an attempt was made to achieve the near-zeroτ_f Zn_2TiO_4 by incorporating the TiO_2. Due to the high crystallinity of the Zn_2TiO_4 prepared by nano-scaled starting materials, the

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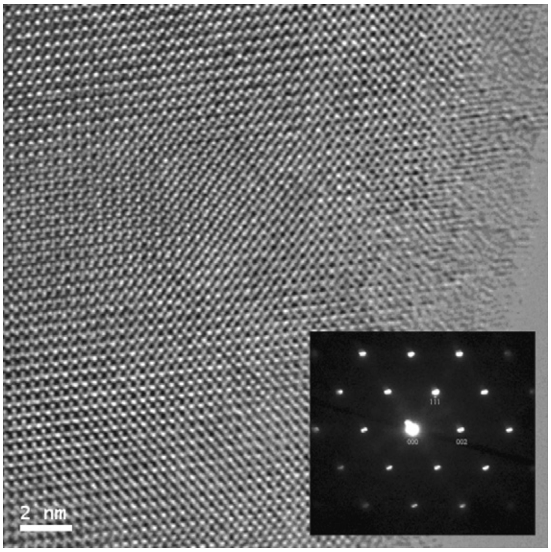

Fig. 1. HR-TEM image of Zn_2TiO_4 sintered at 970 °C for 4 h. Inset shows selection-area diffraction pattern of Zn_2TiO_4.

Zn_2TiO_4:$x$$TiO_2$ (x = 0.02–0.12) showed good dielectric properties even at low sintering temperatures. When x = 0.08 and 0.12, the $Q \times f$ value reached a maximum of ~35,000 GHz and the value of τ_f approached zero, respectively.

2. Experimental

ZnO and TiO_2 nanopowders were prepared separately by hydrothermal processes as reported previously [9,10]. TiO_2:ZnO (1:1 molar ratio) nanowires were mixed and ball-milled for 24 h with zirconia beads and distilled water. The milled mixture was dried at 80 °C, ground, and sieved through a 100 mesh screen. The powders were calcined at 850 °C for 2 h to form the spinel Zn_2TiO_4. After the calcination, powders were ground and sieved. 2 wt% polyvinyl alcohol (PVA) solution was added as a binder and the additional anatase TiO_2 nanowires (2–12 wt%) were added at this stage. A disk with a diameter of 11 mm and a thickness of 5 mm was formed using uniaxial pressing. The compacts were sintered for 4 h at elevated temperatures (900, 930, 970, and 1000 °C).

The structures of the ceramic compacts were examined by X-ray diffractometry (XRD; Siemens D500). Field-emission scanning electron microscope (FESEM; Philips XL-40FEG) was used to examine the morphology of the samples. High-resolution transmission electron microscopy (HR-TEM, JEOL 2100) was used to determine the presented phase. The apparent densities (d) of the sintered compacts were determined by the Archimedes method. The relative dielectric constant (ε_r) and quality factor at microwave frequencies were measured using the Hakki–Coleman dielectric resonator method [11]. τ_f at microwave frequencies was measured in the temperature range from 25 to 80 °C, and was defined as

$$\tau_f = \frac{\Delta f_0}{f_0\ \Delta T}\ (\text{ppm}/{}^\circ\text{C}), \tag{1}$$

where Δf_0 is the shift in the central frequency caused by a temperature change (ΔT) in the range 20–80 °C.

3. Results and discussion

Fig. 1 shows the HR-TEM image of the pure Zn_2TiO_4 sintered at 970 °C. The lattice image indicates a good lattice arrangement. Only few dislocations and defects were observed, revealing good inter-diffusion and sinterability between the ZnO and TiO_2 nanowires.

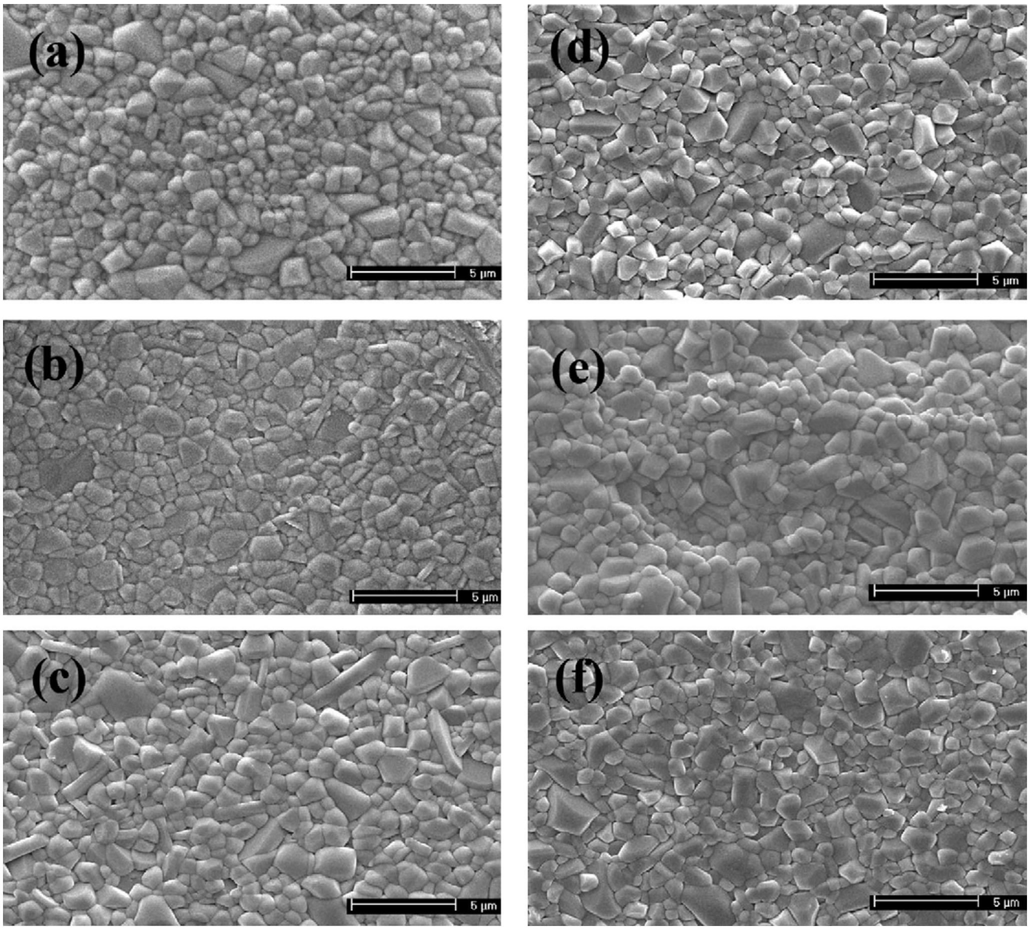

Fig. 2. SEM images of Zn_2TiO_4:$x$$TiO_2$ sintered at 970 °C, where x = (a) 0.02, (b) 0.04, (c) 0.06 (d) 0.08, (e) 0.1, and (f) 0.12.