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Letter

Low-firable high-K dielectric in the $Zr_x(Zn_{1/3}Nb_{2/3})_{1-x}TiO_4$ ceramic system

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ABSTRACT

Composite ceramics in the solid solution of $Zr_x(Zn_{1/3}Nb_{2/3})_{1-x}TiO_4$ ($x = 0.1$–0.4) have been prepared by the mixed oxide route. Formation of solid solution was confirmed by the X-ray diffraction patterns. The microwave dielectric properties, such as dielectric constant (ε_r), $Q \times f$ value and temperature coefficient of resonant frequency (τ_f) have been investigated as a function of composition and sintering temperature. With x increasing from 0.1 to 0.4, the dielectric constant decreases from 70.9 to 43.2, and the τ_f decreases from 105 to 55 ppm/°C. The $Q \times f$ value, however, increases with increasing x value to a maximum 26,600 GHz (at 6 GHz) at $x = 0.3$, and then decreases thereafter. For low-loss microwave applications, a new microwave dielectric material $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$, possessing a fine combination of microwave dielectric properties with a high ε_r of 51, a high $Q \times f$ of 26,600 GHz (at 6 GHz) and a τ_f of 70 ppm/°C, is suggested.

1. Introduction

Miniaturization of patch antennas for volume efficiency in global positioning system (GPS) has become a primary issue in these few years. In particular, materials with dielectric constant in the 40 s and 50 s can reduce the antenna size from 25 mm × 25 mm to 18 mm × 18 mm or even to 15 mm × 15 mm [1]. A number of dielectric materials have been investigated to meet these requirements of the microwave applications [2–7]. In addition to the high dielectric constant, a high $Q \times f$ is also required [8,9] to simultaneously retain a small return loss and achieve a wide bandwidth of the GPS antennas for practical applications.

The $Zr_{1-x}(Zn_{1/3}Ta_{2/3})_xTiO_4$ [10] dielectrics, which partly replaced Zr^{4+} ions by one-third of Zn^{2+} ions and two-thirds Ta^{5+} ions in the $ZrTiO_4$ ceramics, have good combination of microwave dielectric properties with an ε_r of 42.5, a $Q \times f$ of 40,200 GHz and a temperature coefficient of resonant frequency (τ_f) of l.1 ppm/°C for specimen with $x = 0.3$ at 1300 °C. However, the use of such a compound for practical applications would be limited since the Ta_2O_5 is expensive.

In this study, Nb^{5+} (0.64 Å, CN = 6) ion was selected to replace Ta^{5+} (0.64 Å, CN = 6) ion to form the $Zr_x(Zn_{1/3}Nb_{2/3})_{1-x}TiO_4$ ($x = 0.1$–0.4) solid solutions. The resultant microwave dielectric properties were analyzed based upon the densification, the X-ray diffraction (XRD) patterns and the microstructures of the ceramics. The correlation between the microstructure and the $Q \times f$ value was also investigated.

2. Experimental procedures

Samples of $Zr_x(Zn_{1/3}Nb_{2/3})_{1-x}TiO_4$ ($x = 0.1$–0.4) ceramics were synthesized by conventional solid-state methods. High purity oxide powders (>99.9%): ZrO_2, ZnO, Nb_2O_5, and TiO_2 were weighted and mixed for 24 h with distilled water in a ball mill with zirconia balls. The mixtures were dried and calcined at 1000 °C for 3 h. Prepared powders were dried, ball-milled for 24 h with 5 wt% of a 10% solution of PVA as a binder, granulated by sieving through 200 mesh, and pressed into pellets with 11 mm in diameter and 5 mm in thickness. All samples were prepared by using an automatic uniaxial hydraulic press at 2000 kg/cm². These pellets were sintered at 1020–1290 °C for 3 h in air.

The crystalline phases of the sintered ceramics were identified by X-ray diffraction pattern analysis with Cu Kα radiation from 20° to 60° in 2θ. The

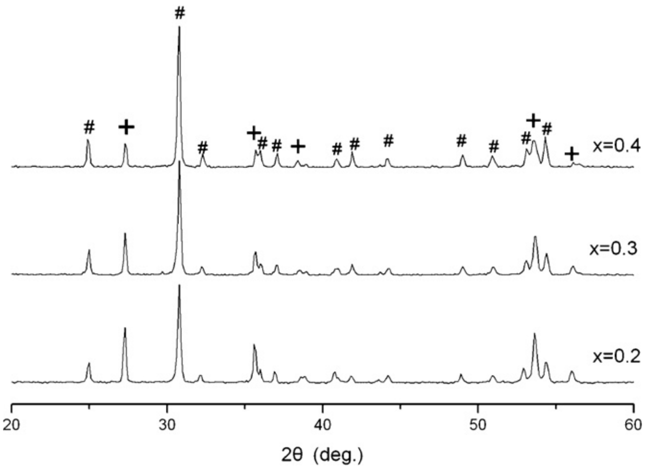

Fig. 1. X-ray diffraction patterns of $Zr_x(Zn_{1/3}Nb_{2/3})_{1-x}TiO_4$ ceramics for various values of x in the range 0.2–0.4 sintering at 1170 °C for 3 h.

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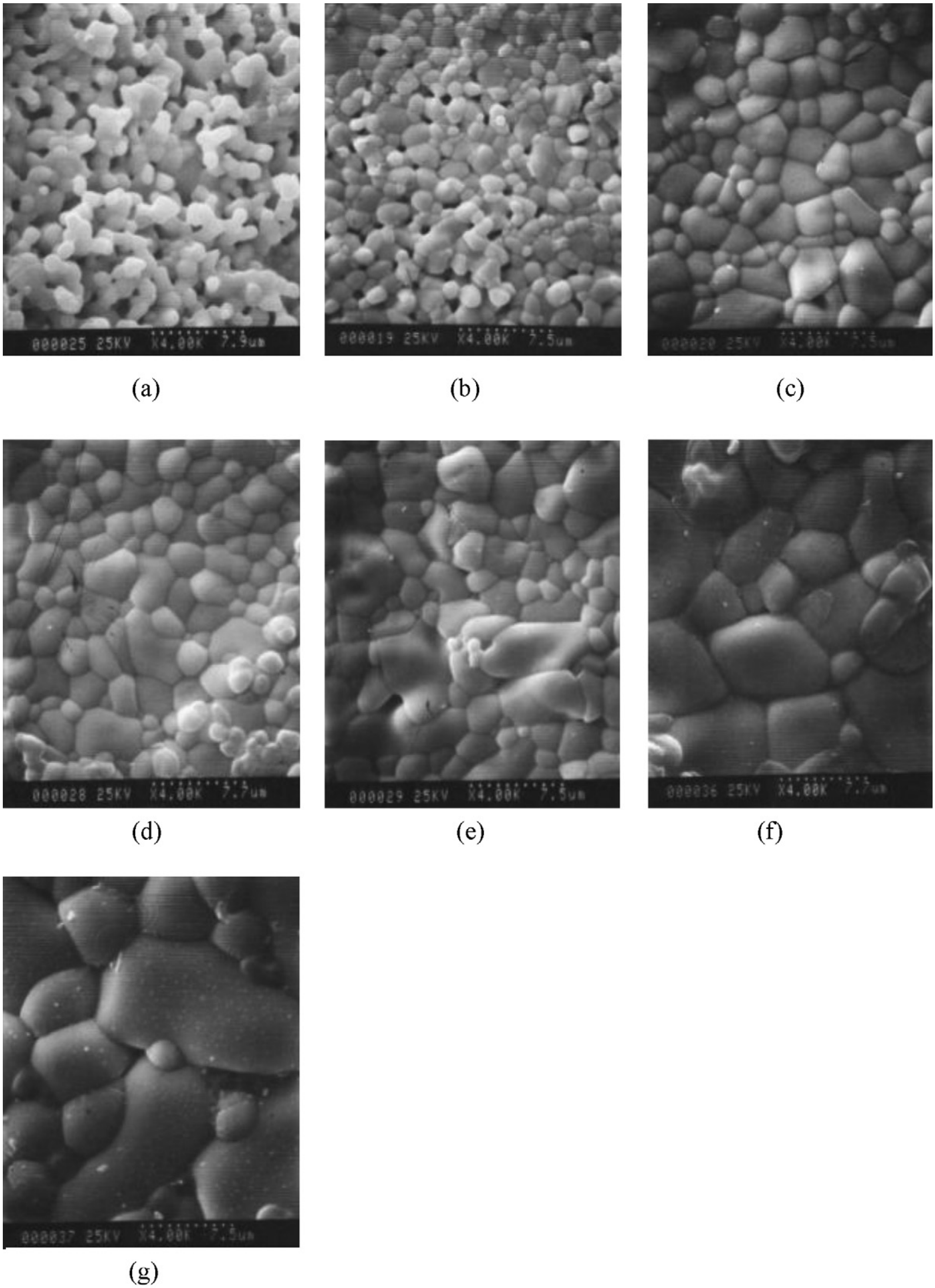

Fig. 2. SEM photographs of $Zr_x(Zn_{1/3}Nb_{2/3})_{1-x}TiO_4$ ceramics with $x = 0.3$ sintered at (a) 1110, (b) 1140, (c) 1170, (d) 1200, and (e) 1230 °C for 3 h and with $x = 0.4$ sintered at (f) 1230 and (g) 1260 °C for 3 h.

scanning rate was 4°/min. The microstructure was observed using a scanning electron microscope (SEM). The bulk densities of sintered samples were measured by the Archimedes method. The dielectric constants and the unloaded Q values were measured by employing the Hakki–Coleman dielectric resonator method as modified and improved by Courtney [11,12]. The apparatus consisted of parallel conducting brass plates and coaxial probes connected to an HP8757D network analyzer and an HP8350B sweep oscillator. The same technique was applied to measure the temperature coefficient of resonant frequency (τ_f). The test cavity was placed over a thermostat, with a temperature range of 20–80 °C.

3. Results and discussion

Fig. 1 illustrates the room temperature X-ray diffraction (XRD) patterns recorded from the $Zr_x(Zn_{1/3}Nb_{2/3})_{1-x}TiO_4$ ($x = 0.1–0.4$) ceramics sintered at 1170 °C for 3 h. The $Zr_x(Zn_{1/3}Nb_{2/3})_{1-x}TiO_4$ phase was identified as the main phase, along with a second phase $Zn_{1/3}Nb_{2/3}TiO_4$ which shows a decrease in its intensity as x increases. It confirms the formation of $Zr_x(Zn_{1/3}Nb_{2/3})_{1-x}TiO_4$ solid solutions. Moreover, it also indicated a high Zr content could effectively inhibit the formation of $Zn_{1/3}Nb_{2/3}TiO_4$.

Fig. 2 shows the scanning electron microscopy (SEM) micrographs of the specimens using $Zr_x(Zn_{1/3}Nb_{2/3})_{1-x}TiO_4$ ceramics at different sintering temperatures for 3 h. The result indicated that specimen using $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ sintered at 1110 °C, a porous microstructure was developed with numbers of pores and the grain size of the specimen was small, approximately 2 μm or less. The increase of sintering temperature helped to promote the grain growth and a relative increase in the grain size was achieved for specimen sintered at 1170 °C, which was also corresponding to a relatively uniform grain morphology. It was not until the temperature reached 1230 °C, that a rapid grain growth started to appear due to the over-sintering of the specimens and some of the grains are of relatively large size up to more than 7 μm. In comparison with that of $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ sintered at 1230 °C, the average grain size of the $Zr_{0.4}(Zn_{1/3}Nb_{2/3})_{0.6}TiO_4$ ceramics (Fig. 2f) is larger suggesting the Zr content would enhance the grain growth of the specimen; whereas the grain uniformity is lowered.

Fig. 3 shows the apparent densities and ε_r of the $Zr_x(Zn_{1/3}Nb_{2/3})_{1-x}TiO_4$ ceramics sintered at different temperatures for 3 h. The density for the specimen with $x = 0.1$ sintered at 1020 °C was low, but increased with increasing sintering temperature to a maximum value of 4.81 g/cm^3 at 1050 °C and then saturated. The saturated temperature is a function of x value and increases with increasing x implying high Zr content requires a high sintering temperature. Also, the density decreases with the increase of x value due to a lower density of $ZrTiO_4$. The variation of ε_r was consistent with that of density suggesting the influence of the presence of the second phase on the dielectric constant is almost negligible. In comparison with that of $Zr_{0.3}(Zn_{1/3}Ta_{2/3})_{0.7}TiO_4$ ceramics, the $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ shows not only a higher dielectric constant, but also a lower sintering temperature and a lower cost, which makes it a more promising dielectric for practical applications.

The $Q \times f$ and τ_f values of the $Zr_x(Zn_{1/3}Nb_{2/3})_{1-x}TiO_4$ ceramics sintered at different sintering temperature for 3 h is demonstrated in Fig. 4. The $Q \times f$ of the $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ ceramics sintered at 1110 °C was relatively low due to the low density and porous microstructure, as shown in Fig. 2. By increasing the sintering temperature, the $Q \times f$ value increased to a maximum value of ∼26,600 GHz (measured at 6 GHz) at 1170 °C and decreased thereafter, which may have been caused by the presence of inhomogeneous grain growth induced by the over-sintering. In addition to the high density, the obtained maximum $Q \times f$ is also likely resulting from a fairly uniform grain size distribution leading to a lowering of lattice defects and imperfection. The temperature coefficient of resonant frequency (τ_f) is well-known to be governed by the composition, the additives, and the second phase of the material. It was not sensitive to the sintering temperature but a function of the x value suggesting the variation of τ_f was mainly due to the compositional change. The τ_f value varied from 106 to 51 ppm/°C as the x value increased from 0.1 to 0.4.

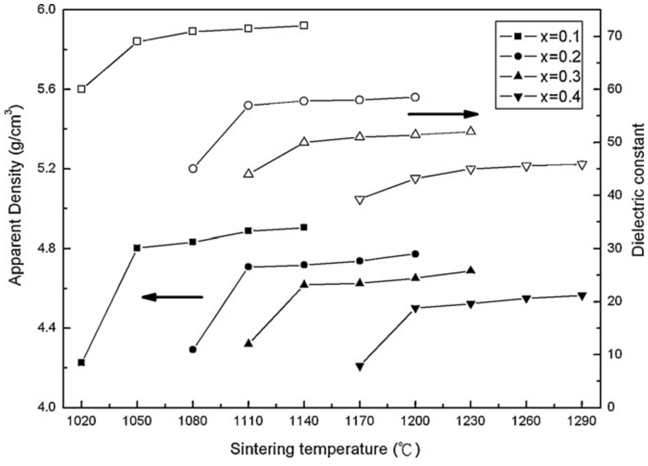

Fig. 3. Apparent density and dielectric constant of $Zr_x(Zn_{1/3}Nb_{2/3})_{1-x}TiO_4$ ceramics sintered at different temperature.

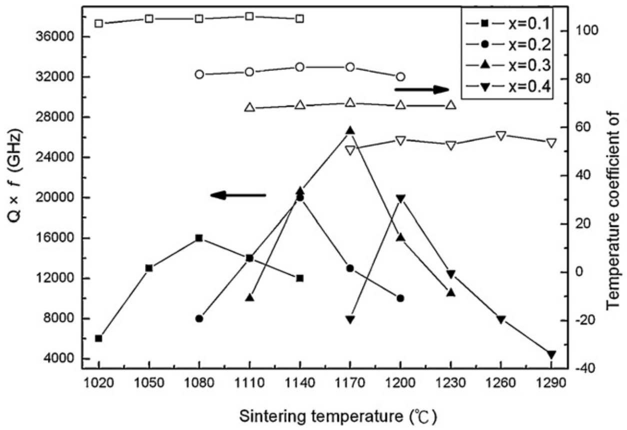

Fig. 4. $Q \times f$ and τ_f values of $Zr_x(Zn_{1/3}Nb_{2/3})_{1-x}TiO_4$ ceramics as a function of sintering temperature.

4. Conclusion

The microwave dielectric properties of $Zr_x(Zn_{1/3}Nb_{2/3})_{1-x}TiO_4$ ceramics were investigated. Compared with $Zr_{0.3}(Zn_{1/3}Ta_{2/3})_{0.7}TiO_4$, a large sintering temperature reduction (130 °C) can be achieved by replacing the Ta with Nb. In this study, $Zr_{0.3}(Zn_{1/3}Nb_{2/3})_{0.7}TiO_4$ sintered at 1170 °C possessed a maximum $Q \times f$ value of 26,600 GHz due to a relatively uniform grain morphology, along with a dielectric constant of 51 and a τ_f value of 70 ppm/°C.

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