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Microwave dielectric properties of $(1-x)ZnTa_2O_6-xMgNb_2O_6$ ceramics

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Abstract

Single phase $MgNb_2O_6$ and $ZnTa_2O_6$ powders were synthesized by solid-state method, and the high quality factor composite ceramics of $(1-x)ZnTa_2O_6-xMgNb_2O_6$ (x=0, 0.05, 0.10, 0.15, 0.20, 0.25 and 1.0) were prepared using the as-synthesized powders. The microwave dielectric properties, microstructure, phase transition and sintering behavior of the composite ceramics were investigated. The X-ray diffraction analysis revealed that solid solution between $ZnTa_2O_6$ and $MgNb_2O_6$ phases appeared in the composite ceramic. SEM results show that the grain sizes of the composite ceramics increased with increasing x values. The temperature coefficient of resonant frequency of $(1-x)ZnTa_2O_6-xMgNb_2O_6$ composite ceramics reaches near-zero of 1.02 ppm/°C with ε_r=35.58 and a high quality factor of 65500 GHz when x=0.20 and sintered at 1350 °C for 2 h.

Keywords: B. Composite; D. Microwave dielectric ceramic; D. $MgNb_2O_6$; D. $ZnTa_2O_6$

1. Introduction

The fast growth of microwave communication demands more and more dielectric ceramics with high performance. The properties required for a high performance dielectric ceramic are high dielectric constant (ε_r), high quality factor ($Q\times f$) and near zero temperature coefficient of resonant frequency (τ_f)[1,2]. However, most of the single phase microwave dielectric ceramics do not have a near zero τ_f and need to be adjusted for practical applications. There are many methods for adjusting microwave dielectric properties of ceramics, such as forming solid solution, use of additives, nonstoichiometry, stacked resonator and forming mixture phases [3–5]. Among those methods, mixing two kinds of single phase ceramics with opposite τ_f values, both have high ε_r and high $Q\times f$ is an effective method to obtain high performance microwave dielectric ceramics [6,7].

Recently, AB_2O_6 (A = Ca, Mg, Mn, Co, Ni, Zn etc. and B = Nb, Ta) compounds were found to be promising candidates for application in microwave devices [8,9]. Among these compounds, both of $MgNb_2O_6$ and $ZnTa_2O_6$ have excellent microwave dielectric properties (ε_r = 19.17, $Q\times f$ = 68,805 GHz for $MgNb_2O_6$ and ε_r = 36.02, $Q\times f$ = 56417 GHz for $ZnTa_2O_6$). However, $MgNb_2O_6$ have a negative τ_f of −70.56 and $ZnTa_2O_6$ have a positive τ_f of 8.94 ppm/°C [10,11]. Therefore, it is necessary to modify τ_f of them to near zero and keep the high quality factors simultaneously for practical applications. In this work, the composite ceramics of $(1-x)ZnTa_2O_6-xMgNb_2O_6$ was prepared and the effects of x values on the microwave dielectric properties and microstructures of the ceramics were investigated.

2. Experimental

$MgNb_2O_6$ and $ZnTa_2O_6$ powders were synthesized by solid-state reaction method. MgO (≥98.5%), ZnO (≥99.0%), Nb_2O_5 (≥99.99%) and Ta_2O_5 (≥99.99%) were used as starting materials. For preparing $MgNb_2O_6$ powders, the stoichiometric ratios of MgO and Nb_2O_5 were mixed and ball-milled in ethanol with zirconia balls for 2 h. After drying, the mixed powders were calcined in covered alumina crucible at 1000 °C for 2 h in air.

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$ZnTa_2O_6$ powders were synthesized in the same way and calcined at 1100 °C for 2 h. $(1-x)ZnTa_2O_6-xMgNb_2O_6$ ($x=0$, 0.05, 0.10, 0.15, 0.20, 0.25 and 1.0) ceramics were prepared from the as-synthesized powders of $MgNb_2O_6$ and $ZnTa_2O_6$. The powders were mixed and remilled for 2 h then pressed into pellets of 10 mm in diameter and 6 mm in thickness at 100 MPa. The pellets were sintered at 1200–1400 °C for 2 h in air.

The crystal structure of the calcined powders and sintered ceramics were examined by X-ray diffraction (XRD, Rigaku, DMAX-RB, Japan) using Cu K_α radiation with a scan speed of 10 °/min. The apparent densities of the sintered samples were measured by Archimedes' method. The microstructures of the ceramics were studied by scanning electron microscopy (SEM, JSM-6480LV). The dielectric properties of the ceramic samples were measured with a HP8720ES network analyzer using Hakki–Coleman's dielectric resonator method, as modified and improved by Courney and Kobayashi et al.[12–14].

3. Results and discussion

Fig. 1 shows the XRD patterns of calcined powders of $MgNb_2O_6$ and $ZnTa_2O_6$. Both of them are single phases and belong to orthorhombic crystal system, columbite for $MgNb_2O_6$ and tri-αPbO_2 for $ZnTa_2O_6$ structure (JCPDS, File No. 88-0708, and No. 76-1826), respectively. The phases of composite ceramics sintered at 1350 °C are shown in Fig. 2, and the similar patterns were obtained when x increased from 0 to 0.25 except slight shift in the position of diffraction peaks. This phenomena is due to the same ionic radii (64 Å) of Nb^{5+} and Ta^{5+} and similar ionic radii of Mg^{2+}(0.72 Å) and Zn^{2+}(0.74 Å) [15], furthermore, both of $MgNb_2O_6$ and $ZnTa_2O_6$ belong to orthorhombic crystal system, it is easily for them to occur chemical reactions and form solid solutions [11]. For $x=0.05$–0.25, the $(1-x)ZnTa_2O_6-xMgNb_2O_6$ composite ceramics exhibit a structure based on $ZnTa_2O_6$ phase because of the high content of $ZnTa_2O_6$, and the shift of diffraction peaks shows the change of lattice parameters.

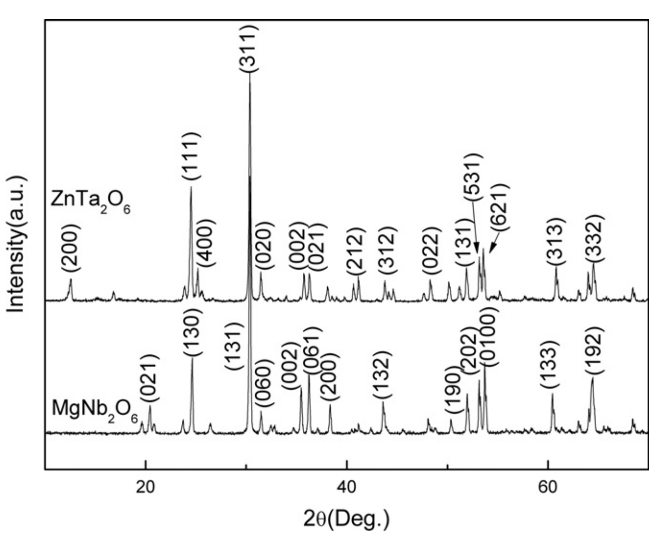

Fig. 1. XRD patterns of calcined powders of $MgNb_2O_6$ and $ZnTa_2O_6$.

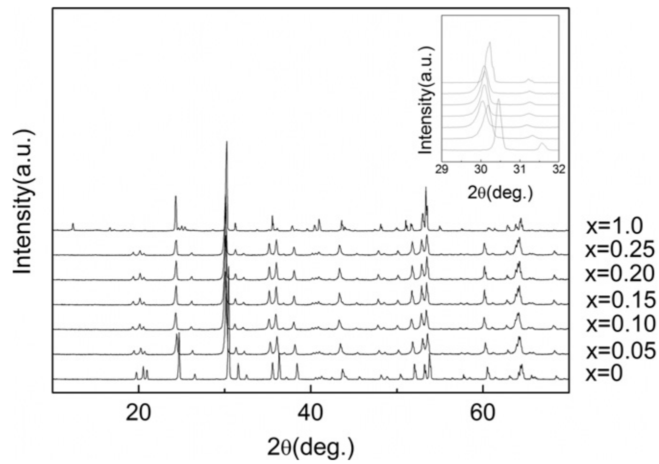

Fig. 2. XRD patterns of sintered samples of $(1-x)ZnTa_2O_6-xMgNb_2O_6$ ceramics ($x=0$, 0.05, 0.10, 0.15, 0.20, 0.25 and 1.0).

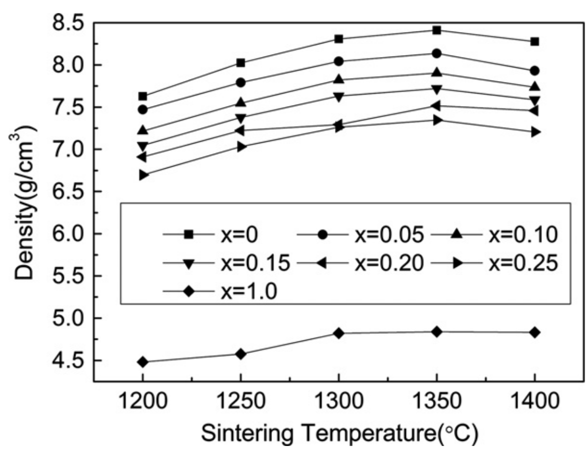

Fig. 3. Densities of $(1-x)ZnTa_2O_6-xMgNb_2O_6$ ceramics ($x=0$, 0.05, 0.10, 0.15, 0.20, 0.25 and 1.0) as a function of sintering temperature.

Fig. 3 shows densities of $(1-x)ZnTa_2O_6-xMgNb_2O_6$ ceramics with different x values as a function of sintering temperature. For all the samples with various x values, although the solid solution is occurred between $MgNb_2O_6$ and $ZnTa_2O_6$ in the sintering process, bulk densities of the composite ceramics increased with increasing sintering temperature, and then declined after reaching a maximum values at 1350 °C. The densities of all samples with different x values sintered at the same temperature decreased with increasing x values. It indicates that $(1-x)ZnTa_2O_6-xMgNb_2O_6$ ceramics can be successfully sintered at 1350 °C when $x=0$, 0.05, 0.10, 0.15, 0.20, 0.25 and 1.0.

The surface micrographs of $(1-x)ZnTa_2O_6-xMgNb_2O_6$ ceramics sintering at 1350 °C were depicted in Fig. 4. The results show that the morphology of sample with $x=0.05$ is similar to that of single phase $ZnTa_2O_6$ due to the low-level of $MgNb_2O_6$. The grain sizes increased with increasing of the content of $MgNb_2O_6$ in the composite ceramic. This phenomenon can be attributed to that the sintering

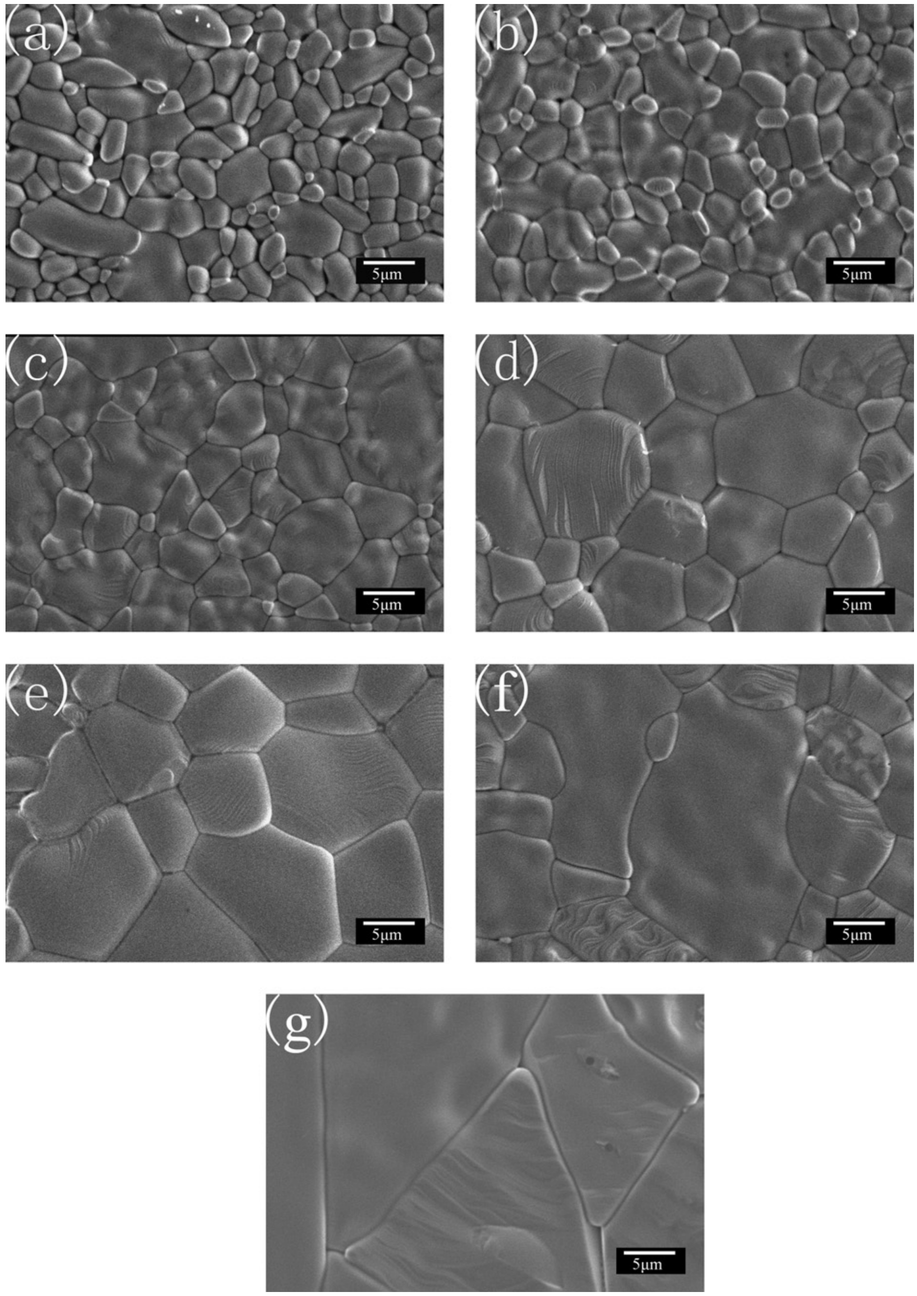

Fig. 4. Surface SEM photographs of $(1-x)ZnTa_2O_6-xMgNb_2O_6$ ceramics sintering at 1350 °C (a) $x=0$, (b) $x=0.05$, (c) $x=0.10$, (d) $x=0.15$, (e) $x=0.20$, (f) $x=0.25$ and (g) $x=1.0$.

temperature of $MgNb_2O_6$ ceramics is lower than that of $ZnTa_2O_6$ ceramics. Fig. 5 presents the element distribution of $0.80ZnTa_2O_6-0.20MgNb_2O_6$ composite ceramics. It can be seen that the elements of Nb and Ta distribute uniformly in all grains, which indicates that Nb^{5+} and Ta^{5+} have substituted each other. The same phenomena can be observed for Mg^{2+} and Zn^{2+}. Those results verified that solid solutions have occurred between $MgNb_2O_6$ and $ZnTa_2O_6$ in the composite ceramics.

Fig. 6 shows the microwave dielectric properties of $(1-x)ZnTa_2O_6-xMgNb_2O_6$ composite ceramics sintered at 1350 °C for 2 h in air. The calculated values of ε_r, $Q\times f$, and τ_f are also given according the empirical equations as follows [16–19]:

$$\varepsilon_r = v_1\varepsilon_1 + v_2\varepsilon_2 \quad (1)$$

$$\tau_f = v_1\tau_1 + v_2\tau_2 \quad (2)$$

$$\frac{1}{Q} = \frac{v_1}{Q_1} + \frac{v_2}{Q_2} \quad (3)$$

where ε_r, τ_f and Q are the dielectric constant, temperature coefficient of resonant frequency and quality factor of the mixture. v_1 and v_2 are volume fractions of the two

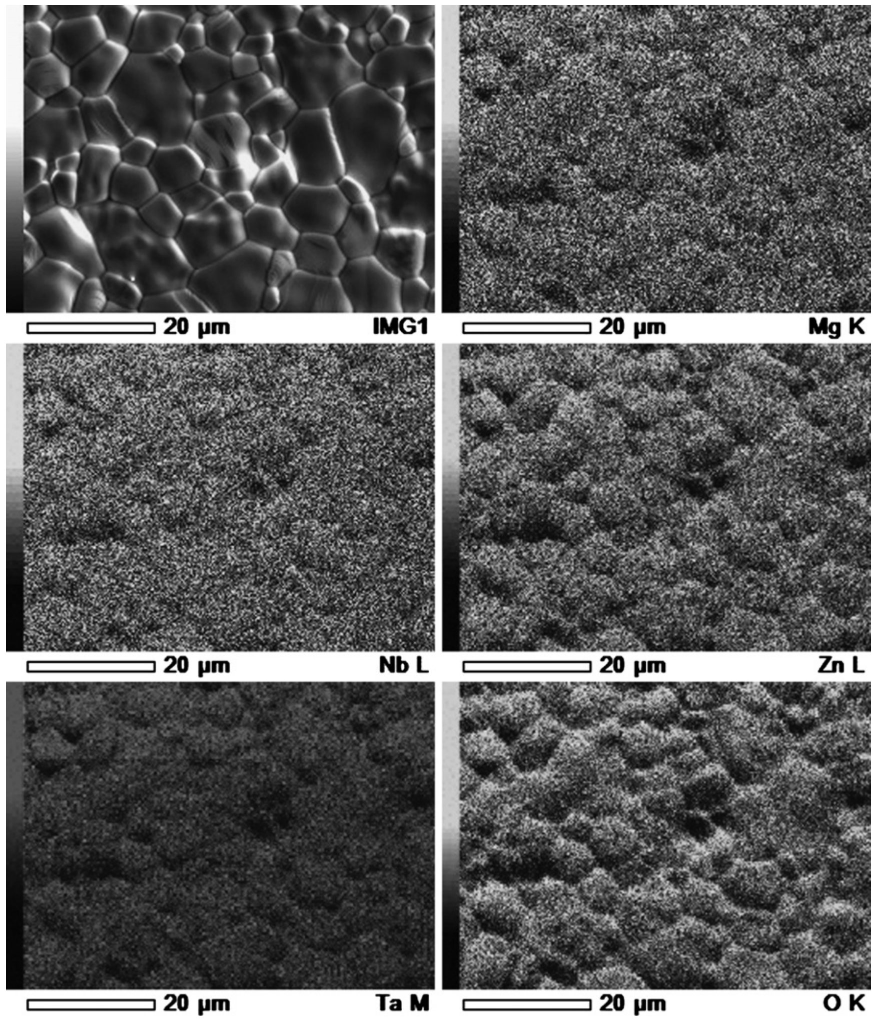

Fig. 5. SEM photographs of $0.80ZnTa_2O_6-0.20MgNb_2O_6$ composite ceramic sintered at 1350 °C and the corresponding elemental mapping.

components. ε_1, ε_2, τ_1, τ_2 and Q_1, Q_2 are their dielectric constants, temperature coefficients of resonant frequency and quality factors of each component, respectively. The empirical equations are based on the fact that every component in the mixture does not have chemical reactions with each other. The measured microwave dielectric properties of single phase $ZnTa_2O_6$ and $MgNb_2O_6$ agree well with those of early studies. However, for $(1-x)ZnTa_2O_6-xMgNb_2O_6$ ceramics with $x=0.05$–0.25, chemical reactions happened between two components in the mixture, and the measured ε_r, τ_f and $Q\times f$ values deviated from the calculated value. The measured ε_r values do not change remarkably, and ranged from 35.57 to 35.71 as x changes from 0.05 to 0.25 due to the composite ceramic exhibit a $ZnTa_2O_6$-like structure. However, the measured $Q\times f$ values are higher than the calculated values, and increased rapidly from 58900 to 64700 GHz as x ranges from 0.05 to 0.15 and then increase near linearly to 66300 GHz when x increasing to 0.25. According to the empirical equation, the calculated τ_f values decreased with increasing x values and could reach 1.07 ppm/°C when $x=0.10$. However, the measured values of τ_f were delayed and reached 1.02 ppm/°C until $x=0.20$, then continuing to decrease to -4.27 ppm/°C when $x=0.25$. These results may attribute to the formation of solid solutions and the change of lattice parameters and thus lead to the changing of τ_f and $Q\times f$ for $x=0.05$–0.25.

4. Conclusions

The single phase of $MgNb_2O_6$ and $ZnTa_2O_6$ powders have been synthesized using solid-state method when the mixture of corresponding oxides calcined at 1000 °C and 1100 °C for 2 h in air, respectively. The $(1-x)ZnTa_2O_6-xMgNb_2O_6$ ($x=0$, 0.05, 0.10, 0.15, 0.20, 0.25 and 1.0) composite ceramics can be well sintered at 1350 °C for 2 h in air. Interdiffusion of elements such as Nb, Ta, Mg and Zn can observe in composite ceramics, which indicates that solid solution is formed between $ZnTa_2O_6$ and $MgNb_2O_6$ ceramics. The interdiffusion and solid solution in composite ceramic lead to the deviation of microwave dielectric properties from the calculated values according to the empirical equations. The temperature coefficient of resonant frequency (τ_f) can reach near-zero of 1.02 ppm/°C with $\varepsilon_r=35.58$ and remains a high

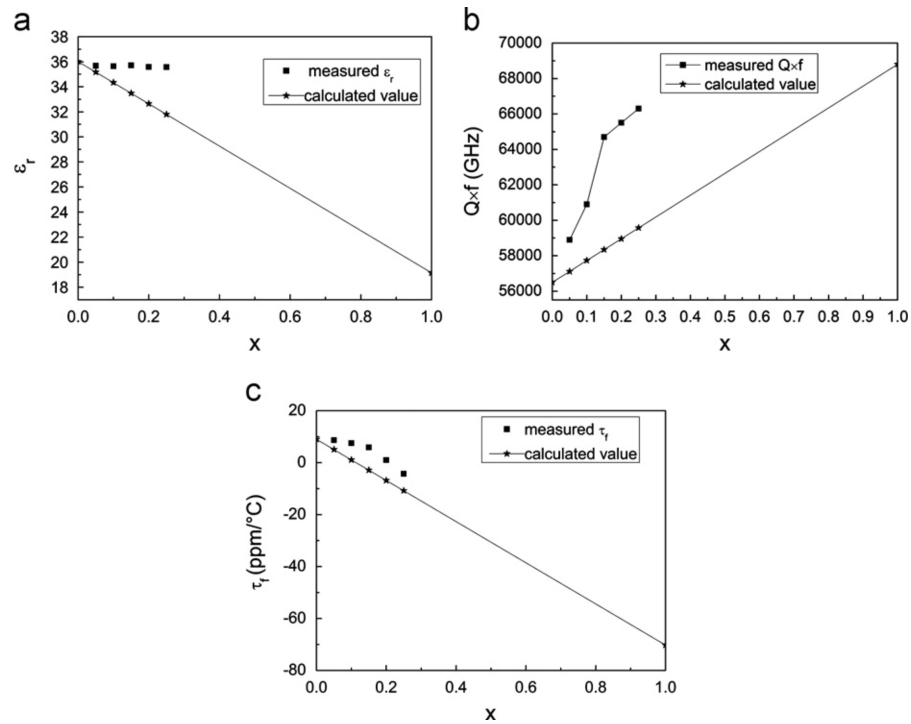

Fig. 6. Microwave dielectric properties of $(1-x)ZnTa_2O_6-xMgNb_2O_6$ ceramics ($x=0$, 0.05, 0.10, 0.15, 0.20, 0.25 and 1.0) sintering at 1350 °C as a function of x, (a) ε_r, (b) $Q \times f$, (c)τ_f.

quality factor ($Q \times f$) of 65500 GHz when $x=0.20$ sintering at 1350 °C for 2 h.

Acknowledgments

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