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Effects of Mn substitution on microwave dielectric properties of trirutile-type ceramics

Zheng Sun [a,b,*], Qiuyang Li [a], Shiyi Xie [a], Wenxu Liu [a], Yemei Han [a,b]

[a] School of Electrical and Electronic Engineering, Tianjin University of Technology, Tianjin 300384, China
[b] Tianjin Key Laboratory of Thin Film Electronics and Communication Devices, Tianjin University of Technology, Tianjin 300384, China

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ABSTRACT

The $(Zn_{1-x}Mn_x)TiTa_2O_8$ ($0 \le x \le 0.1$) ceramics were initially prepared by solid state method. Effects of Mn^{2+} ions on crystal structure and microwave dielectric properties of this trirutile system were investigated. Through the X-ray powder diffraction and SEM micrograph analysis, Mn^{2+} was considered to be used to adjust the phase transformation process between two kinds of rutile-like structures (trirutile and ixiolite) with opposite temperature characteristics, achieving the improvement of temperature stability in this system. With 0.08 mol% Mn^{2+} doped, the composition of $(Zn_{0.92}Mn_{0.08})TiTa_2O_8$ showed a near zero τ_f value of 3.4 ppm/°C, meanwhile the dielectric constant was 40.2 and the $Q \times f$ value was 31,950 GHz, indicating this ceramic system was a promising material for microwave applications.

1. Introduction

In recent decades, microwave dielectric ceramic materials have been investigated for use in wireless communication components, such as resonators, antennas, duplexers, and oscillators. To utilize these at microwave frequencies, the microwave dielectric materials should possess high dielectric constant (ε_r), high quality factor ($Q \times f$), and near-zero temperature coefficient of resonant frequency (τ_f), which are desirable for minimization of the microwave circuit component, maximum signal intensity and adaptation to environmental temperature changes [1–6]. And nowadays many of them have been reported for their excellent microwave dielectric properties.

Recently, the ternary systems of $AO\text{-}BO_2\text{-}C_2O_5$ (A = Zn, Mg, Co, Ni, Mn; B = Ti, Zr; C = Nb, Ta) have attracted much attention because of their good dielectric properties [7–12]. Being one of the most promising dielectric for microwave applications, trirutile-type $ZnTiTa_2O_8$ ceramic possessed considerably high dielectric constant combined with relatively low loss ($\varepsilon_r \sim 46.2$, $Q \times f \sim 36{,}700$ GHz, $\tau_f \sim +74$ ppm/°C) [11,12]. However, the $ZnTiTa_2O_8$ ceramic exhibited relatively high τ_f values, which often limit their practical applications. Usually, the methods to achieve temperature stable microwave dielectric materials are combining two component materials with opposite τ_f values or ions substitution. Compared to the first method, the second method usually would not destroy the microwave dielectric properties of the specimens [13–15]. For example, with partial replacement of Zn^{2+} by Mn^{2+}, the temperature stable microwave dielectric materials $Zn_{0.9}Mn_{0.1}ZrNb_2O_8$ would be obtained [16]. It should be of interest to investigate the effects of Mn^{2+} substitutions on the microwave dielectric properties of $ZnTiTa_2O_8$ ceramic series.

In this study, the crystal structure, microstructure and microwave dielectric characteristics of $(Zn_{1-x}Mn_x)TiTa_2O_8$ ceramics were investigated. The τ_f values have been also studied as a function of the lattice energy.

2. Experimental procedure

$(Zn_{1-x}Mn_x)TiTa_2O_8$ ($0 \le x \le 0.1$) ceramic were proportionately prepared by conventional solid state reaction method with high-purity (≥99%, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) reagents: ZnO (99.9%), TiO_2 (99%), Ta_2O_5 (99.99%), and $MnCO_3$ (99%). The starting powders were weighed in appropriate proportions and ball milled in distilled water for 24 h using zirconia media, the milling rate was 400 rpm/min. The mixtures were dried and calcined at 1050 °C for 3 h, and then pressed into pellets 10 mm in diameter and 5 mm in thickness. The compacts were sintered at 1220 °C for 3 h. The heating rate during calcination was 5 °C/min [17].

The phase identification and the determination of the lattice parameter were carried out by X-ray diffraction method (Rigaku, D/MAX-2500, Tokyo, Japan) using Cu-Kα radiation. The microstructure was observed using the scanning electron micro-

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* Corresponding author.
E-mail address: sz_tjut1986@126.com (Z. Sun).

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scopy (SEM, Philips XL30 ESEM, Netherland). The dielectric constant was measured by the Hakki-Coleman method, and the unloaded Q value was measured by the shielded cavity method [18,19] using a network analyzer (8720ES, Agilent, Santa Clara, CA). The temperature coefficient of resonant frequency was obtained from 25 °C to 85 °C and calculated using Eq. (1):

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \tag{1}$$

where f_1 and f_2 are the $TE_{01\sigma}$ resonant frequency of the samples at 25 °C and 85 °C, respectively.

3. Results and discussion

Fig. 1a shows the XRD patterns of $(Zn_{1-x}Mn_x)TiTa_2O_8$ ceramics sintered at 1220 °C for 3 h. Single phase $ZnTiTa_2O_8$ was obtained for × = 0. $ZnTiTa_2O_8$ performed tetragonal trirutile structure and belonged to the space group *P*42/*mnm* (1 3 6) and Z = 2. The trirutile-type structure consists of close-packed oxygen layers, in which the cations occupy half of the octahedral sites and the occupied octahedra share edges, thus forming ordered linear chains in the *c*-direction, as schematically shown in Fig. 1b. For $x \geq 0.02$, the second phase indexed as orthorhombic ixiolite structure which consists of layered oxygen octahedra and the oxygen octahedra share edges in a zigzag in the *c*-direction (shown in Fig. 1c), was observed, and increased rapidly as the increase of Mn content. In addition, the increase of ixiolite phase decreased the unit cell volume of trirutile phase, which caused the reflections to be shifted toward higher angle.

The SEM micrographs of $(Zn_{1-x}Mn_x)TiTa_2O_8$ $(0 \leq x \leq 0.1)$ ceramics are illustrated in Fig. 2. As shown in Fig. 2, we can see that, in general, all the compositions were well sintered. The grains were homogeneous and the surface was smooth. The average grain sizes tended to increase with increasing *x*, implying the low-level substitution of Zn^{2+} by Mn^{2+} would lower the sintering temperature of $ZnTiTa_2O_8$.

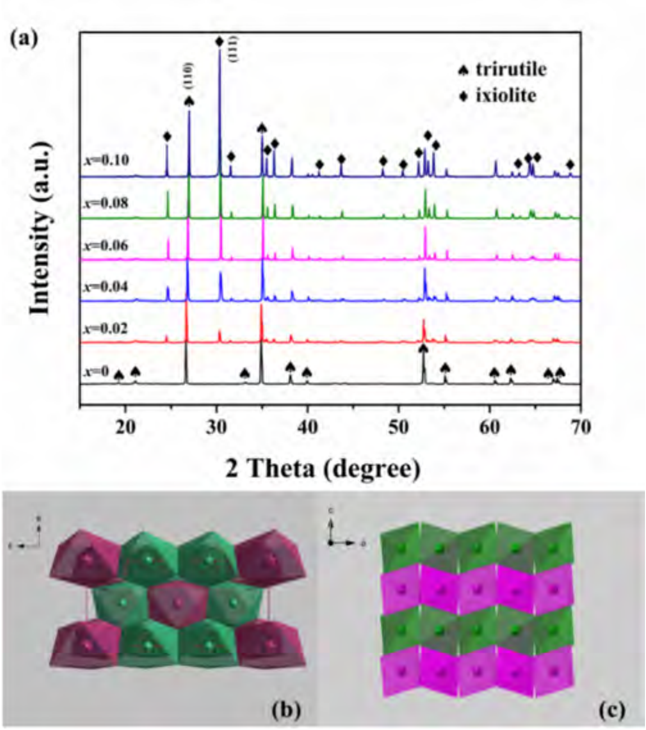

Fig. 1. (a) XRD patterns for the $Zn_{1-x}Mn_xTiTa_2O_8$ ceramics sintered at 1220 °C for 3 h. Schematic illustrations of trirutile-type structure (b), and ixiolite-type structure (c).

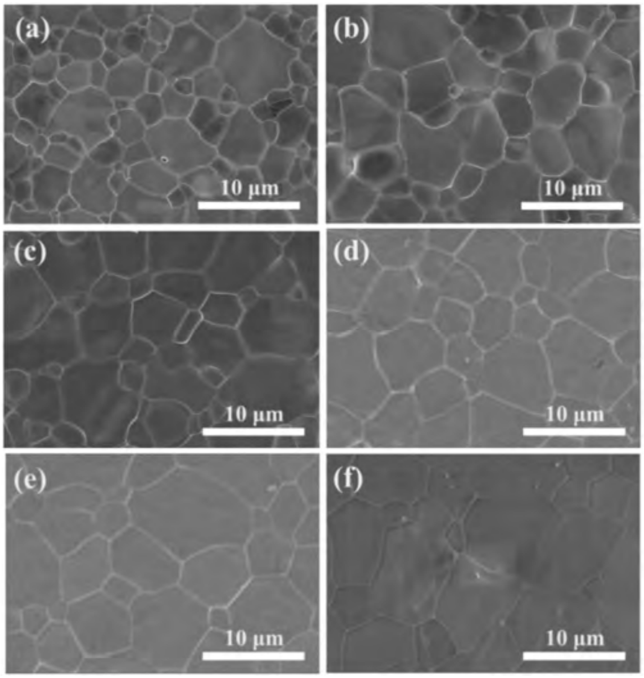

Fig. 2. The SEM micrograph of $Zn_{1-x}Mn_xTiTa_2O_8$ ceramics sintered at 1220 °C for 3 h: (a) $x = 0$, (b) $x = 0.02$, (c) $x = 0.04$, (d) $x = 0.06$, (e) $x = 0.08$ and (f) $x = 0.10$.

The observed relative intensities of ixiolite phase to the trirutile phase in $(Zn_{1-x}Mn_x)TiTa_2O_8$ ceramics are calculated as follows [20]:

$$\%\text{ixiolite} = I_{I(111)}/(I_{I(111)} + I_{T(110)}) \times 100(\%) \tag{2}$$

where $I_{I(1\ 1\ 1)}$ is the intensity of the major peak of the ixiolite phase and $I_{T(1\ 1\ 0)}$ is the intensity of the major peak of the trirutile phase.

Fig. 3 demonstrates the relative volume fraction of ixiolite phase and microwave dielectric properties of the specimen in $Zn_{1-x}Mn_xTiTa_2O_8$ ceramics as functions of Mn content. As shown in Fig. 3a, the volume fraction of ixiolite phase increased with an increasing Mn content, probably owing to the substitution of higher ionic radius elements Mn^{2+} (0.83 Å) in place of lower radius elements Zn^{2+} (0.74 Å) [21]. In general, several factors contribute to the dielectric properties in the range of microwave frequency and these factors can be divided into two parts: intrinsic factors and extrinsic factors. The intrinsic factors are dominated by crystal structure and bonding character, while the extrinsic factors are related to second phases, oxygen vacancies, grain boundaries, and densification or porosity [22,23]. In this work, the microwave dielectric properties were mainly affected by the formation of ixiolite phase. It could be seen that the dielectric constant gradually decreased from 45.9 to 38.8 as increasing the *x* value, in spite of the higher polarizability of Mn^{2+} in comparison with Zn^{2+}. Meanwhile, the decreasing of $Q \times f$ values could be constituted to the extrinsic loss which resulted by the grain boundaries and second phase from Figs. 1 and 2. The τ_f value showed an obvious downtrend with the increase of Mn content. This behavior was ascribed to the negative τ_f value of ixiolite phase [7]. In addition, the $(Zn_{0.92}Mn_{0.08})TiTa_2O_8$ compound shows a ε_r value of 40.2, a relatively high $Q \times f$ value of 31,950 GHz, and a more stable τ_f value of 3.4 ppm/°C. The near-zero τ_f means stabile frequency in harsh environment, which are benefit for the application of microwave dielectric ceramic, such as resonators, filters, and antennas [9].

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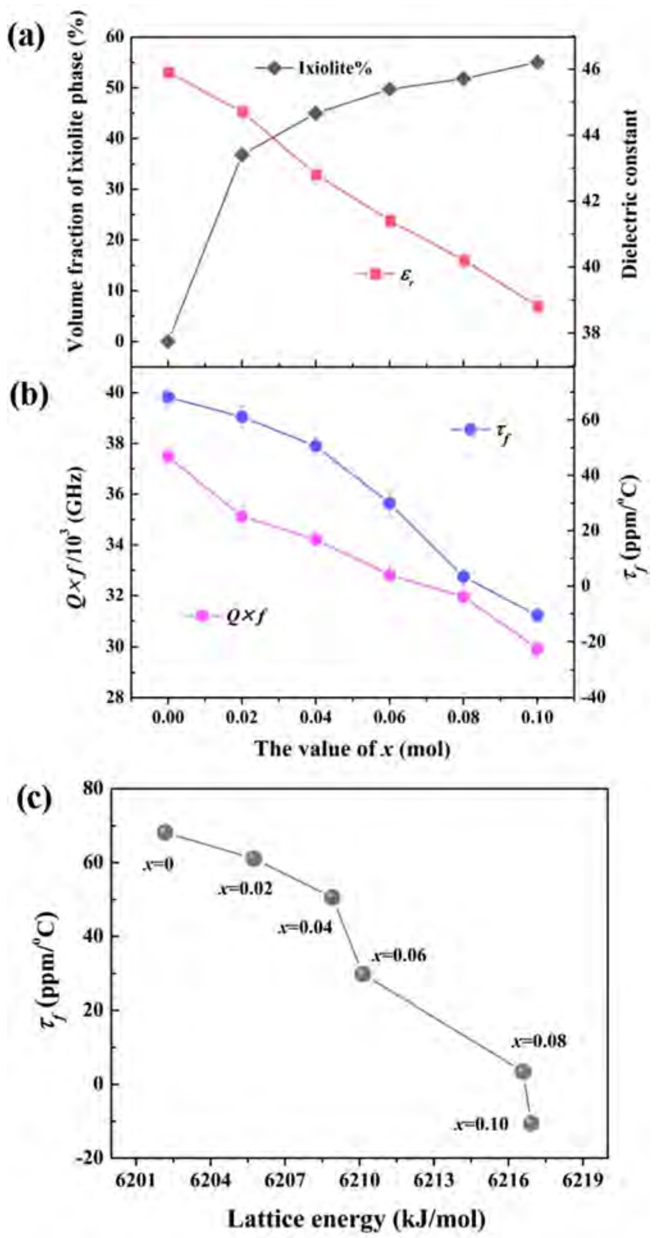

Fig. 3. The relative volume fraction of ixiolite phase, dielectric constant (a), the $Q\times f$ and τ_f values (b) of $(Zn_{1-x}Mn_x)TiTa_2O_8$ $(0 \le x \le 0.1)$ ceramics sintered at 1220 °C for 3 h. τ_f values of $(Zn_{1-x}Mn_x)TiTa_2O_8$ ceramics as a function of lattice energy of trirutile phase (c).

The lattice energy (U), as the intrinsic factor, was also carried out to evaluate the structural stability of $(Zn_{1-x}Mn_x)TiTa_2O_8$ ceramics. For complex ionic crystals, the lattice energy was calculated as follows [24]:

$$U = AI(2IZ/V_{cell})^{1/3} \quad (3)$$

$$2I = \sum_i n_i Z_i^2 \quad (4)$$

where I was the ionic strength, n_i was the number of ions with integer charge Z_i, the summation was taken over all the types of ions in the formula unit. V_{cell} was the unit cell volume respectively. Z was the number of formula units per unit cell. It can be seen that the lattice energy is proportional to the unit cell volume of crystal.

The τ_f value of $(Zn_{1-x}Mn_x)TiTa_2O_8$ ceramics was shown in Fig. 3c as a function of the lattice energy of trirutile phase. The value of τ_f shifted to zero with increasing the lattice energy, which is in agreement with the unit cell volume obtained from XRD patterns. With increase in the lattice energy, the bond strength between cation and oxygen was increased. Higher bond strength would decrease the influence of heat energy on the variation of crystal vibration [25,26]. Therefore, the τ_f value has a negative correlation with the lattice energy.

4. Conclusion

The $(Zn_{1-x}Mn_x)TiTa_2O_8$ ceramics sintered at 1220 °C for 3 h were successfully synthesized by solid state route. Effects of Mn^{2+} substitution on the microstructure and microwave dielectric properties of $(Zn_{1-x}Mn_x)TiTa_2O_8$ were discussed. When $x \ge 0.02$, the ixiolite phase was formed, and dramatically increased. The dielectric constant and $Q\times f$ values gradually decreased as the increase of x, which resulted by the ixiolite phase. The τ_f value dropped significantly with the increase of Mn content and lattice energy. Finally, a new temperature stable ceramic was obtained for $x = 0.08$.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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