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Crystal structure, mixture behavior, and microwave dielectric properties of novel temperature stable $(1-x)MgMoO_4-xTiO_2$ composite ceramics

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ABSTRACT

Novel temperature stable $MgMoO_4$–TiO_2 microwave dielectric ceramics were prepared by a solid state reaction process at low temperature (950 °C). As TiO_2 content increases, the relative permittivity increases while the $Q\times f$ value decreases, and the variation mechanisms are proposed, respectively. The temperature coefficient of resonant frequency (τ_f) shifts to the positive direction as TiO_2 is added. The mixture mechanisms of τ_f value for two-phase composite materials are supposed. A near-zero τ_f value (3.2 ppm/°C) is obtained when $x=0.3$, with $\varepsilon_r=9.13\pm0.03$ and $Q\times f=11{,}990$ GHz. The $0.7MgMoO_4$–$0.3TiO_2$ composites are considered to be appropriate as a low temperature co-fired ceramic material for microwave wireless communication applications.

1. Introduction

With the rapid development of high frequency communication industry, microwave dielectric ceramics have attracted much attention for a wide range of microwave component applications, including filters, resonators, antennas and waveguides [1–5]. In order to meet the needs of miniaturization and integration of microwave devices, the low temperature co-fired ceramic (LTCC) technology is considered as a promising method from the manufacturing point of view [6–8]. In general, microwave dielectric ceramics with low sintering temperature (<960 °C), high quality factor ($Q\times f$) value, and near-zero temperature coefficient of resonant frequency (τ_f) are required [9–11].

In recent years, $AMoO_4$ (A = Ba, Mg, Mn and Zn) ceramics are found potential candidates for the microwave applications, due to the low sintering temperature (~900 °C), low relative permittivity (7–9), and high quality factor (>30,000 GHz) [12,13]. However, all of them exhibit large negative τ_f value (−46 ppm/°C to −87 ppm/°C), which is not suitable for practical use. A near-zero temperature coefficient of resonant frequency can ensure the thermal stability of the microwave devices at different working temperatures [14]. In order to achieve near-zero τ_f, one of the effective methods is to add other compounds with opposite τ_f value. Rutile TiO_2 with large positive τ_f value (+460 ppm/°C) [15], has been successfully applied in some microwave dielectric ceramics with negative temperature coefficient of resonant frequency [16–20]. Furthermore, the mixture behavior of composite ceramics has significant influence on the adjustment of relative permittivity and τ_f value. Therefore, we have attempted to demonstrate a comprehensive study of $(1-x)MgMoO_4-xTiO_2$ ceramic system.

In this work, the phase composition, microstructure and microwave dielectric properties of $(1-x)MgMoO_4-xTiO_2$ ceramics were investigated as a function of TiO_2 content ($0\le x\le0.4$). The relationship between microstructure and microwave dielectric properties was investigated. The variation mechanisms of relative permittivity, $Q\times f$ value and τ_f value were proposed, respectively.

2. Experimental details

$MgMoO_4$ composition was prepared by a solid state reaction process with reagent-grade MgO and MoO_3 as raw materials. Powdered oxides were weighted in stoichiometry, and subsequently ball milled in ethanol for 6 h. After being dried under an infrared lamp, the mixture was calcined at 700 °C in alumina crucible for 6 h. $MgMoO_4$ and TiO_2 powders were mixed by ball-milling for 12 h according to the following formula: $(1-x)MgMoO_4-xTiO_2$ ($x=0.0$, 0.1, 0.2, 0.3 and 0.4). The final powders were pressed into cylinders of 15 mm in diameter and 7 mm in thickness with 7 wt% wax as

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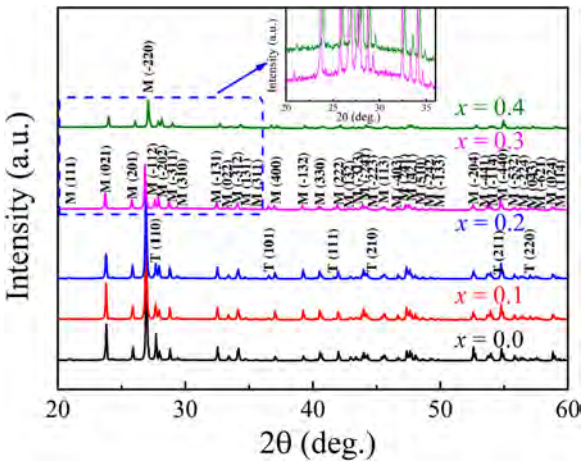

Fig. 1. X-ray diffraction patterns of $(1-x)MgMoO_4-xTiO_2$ ceramics sintered at 950 °C (M: $MgMoO_4$ phase; T: TiO_2 phase).

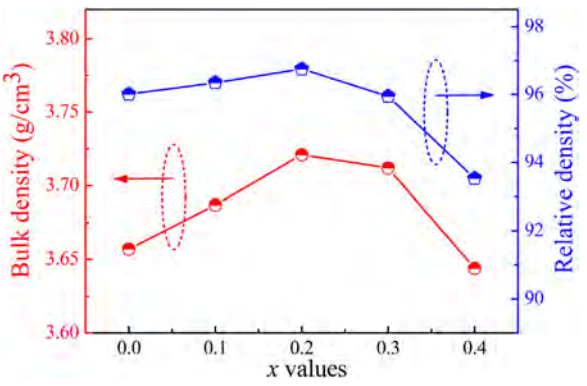

Fig. 2. Bulk density and relative density of $(1-x)MgMoO_4-xTiO_2$ ceramics with various x values.

a binder. After burning off the binder at 550 °C, the samples were sintered at 950 °C in air for 5 h.

The crystalline structures of the samples were identified by an X-ray diffractometer (Rigaku Ultima IV, Japan) with Cu Kα radiation over a 2θ angle from 20° to 60°. The microstructure of polished and etched surfaces was analyzed with field emission scanning electron microscopy (FE-SEM, ZEISS MERLIN Compact, Germany). The bulk density of samples was measured using the Archimedes' method. The microwave dielectric properties of the sintered samples were measured using a network analyzer (Agilent, 8720ES, Santa Clara, California). The relative permittivity and unloaded Q value were measured by the Hakki-Coleman method and shielded cavity method, respectively. The temperature coefficient of resonant frequency was determined in the temperature range of 25 °C–85 °C using the equation:

$$\tau_f = \frac{f_2 - f_1}{f_1(85-25)} \times 10^6 \ (\mathrm{ppm/^\circ C}) \quad (1)$$

where f_1 and f_2 are the resonant frequency at 25 °C and 85 °C.

3. Results and discussion

Fig. 1 illustrates the XRD patterns of $(1-x)MgMoO_4-xTiO_2$ ceramics sintered at 950 °C. No phase other than $MgMoO_4$ (JCPDS #21-0961) is detected for $x=0$, implying that all the raw materials react completely to form a solid solution. $MgMoO_4$ performs monoclinic wolframite structure and belongs to the space group C2/m (no.12) and $Z=8$ [21]. The lattice parameters are $a=10.281$ Å, $b=9.291$ Å, and $c=7.030$ Å. Rutile TiO_2 (JCPDS #21-1276) coexisting with $MgMoO_4$ can be seen from $x=0.1$ to 0.4, which indicates that they behave as a mixture. With the increase of x, the intensities of $MgMoO_4$ diffraction peaks initially increase but subsequently decrease, and become strongest when $x=0.1$. The phenomena suggest that appropriate TiO_2 can promote $MgMoO_4$ in the mass transfer and sintering process, however, excessive TiO_2 will lead to the deterioration of crystal quality for $MgMoO_4$. In addition, a bump can be observed from the inset for $x=0.3$ and 0.4, indicating the appearance of amorphous TiO_2. The relative volume fraction of rutile phase can be defined as the ratio of the most-intense XRD peak height of TiO_2 to the sum of the most-intense peak heights of TiO_2 and $MgMoO_4$ [22]. The calculated proportions of TiO_2 phase are 0.055, 0.077, 0.129, and 0.165 for $x=0.1$, 0.2, 0.3, and 0.4 respectively. The volume fraction of TiO_2 is related to the x value, which obeys the following equation [23]:

$$v_T = \frac{xM_T/\rho_T}{xM_T/\rho_T + (1-x)M_M/\rho_M} \quad (2)$$

where ρ_T and ρ_M are the density of TiO_2 and $MgMoO_4$, respectively. M_T and M_M represent the relative molecular mass of TiO_2 and $MgMoO_4$, respectively. The volume fractions of TiO_2 are 0.040, 0.086, 0.138, and 0.200 for $0.1 \le x \le 0.4$. When $x=0.1$, the obtained content of TiO_2 from XRD is larger than the designed value. This is attributed to the lower actual density of TiO_2. Whereas, the calculated values of others are lower than the designed values, which may be due to the emergence of amorphous TiO_2 and pores in the ceramics.

Fig. 2 exhibits the bulk density and relative density of $(1-x)MgMoO_4-xTiO_2$ ceramics sintered at 950 °C. As TiO_2 content increases, the bulk density gradually increases from 3.657 g/cm^3 to 3.721 g/cm^3 for $0 \le x \le 0.2$, due to the higher theoretical density of TiO_2 (4.230 g/cm^3) than $MgMoO_4$ (3.809 g/cm^3). However, with a further increase of TiO_2 content ($x \ge 0.3$), the bulk density decreases. This may result from the rise in porosity due to the excess TiO_2. To study the relative density of $(1-x)MgMoO_4-xTiO_2$ ceramics, the theoretical density is obtained according to the formula [24]:

$$TD_{M-T} = \frac{W_M + W_T}{W_M/TD_M + W_T/TD_T} \quad (3)$$

where TD_{M-T}, TD_M, and TD_T are the theoretical density of $(1-x)MgMoO_4-xTiO_2$, $MgMoO_4$ and TiO_2, respectively. W_M and W_T represent the weight percentage of $MgMoO_4$ and TiO_2 in the mixture. Eq. (3) is valid since no interaction takes place between $MgMoO_4$ and TiO_2, which is confirmed by the phase analysis. The calculated theoretical densities are 3.827 g/cm^3, 3.846 g/cm^3, 3.869 g/cm^3 and 3.896 g/cm^3 for $x=0.1$, 0.2, 0.3, and 0.4, respectively. The relative density is obtained from

$$\rho_{relative} = \frac{\rho_{bulk}}{\rho_{theoretical}} \times 100\% \quad (4)$$

As shown in Fig. 2, the relative density steadily increases from 96.0% to 96.7% for $0 \le x \le 0.2$, but subsequently decreases to 93.5% for $x=0.4$. The variation trends of bulk density and relative density along with x are consistent with the XRD results.

The microstructures of $(1-x)MgMoO_4-xTiO_2$ ceramics sintered at 950 °C are further analyzed by SEM. As shown in Fig. 3(a), pores are hardly found in pure $MgMoO_4$ sample. However, some indistinct grain boundaries can be observed, which may attribute to the partial melting of the samples sintered at 950 °C. This would have a harmful effect on the grain growth process. When $x=0.1$, rod-shaped TiO_2 grains with a width size of 0.5 μm appear for the

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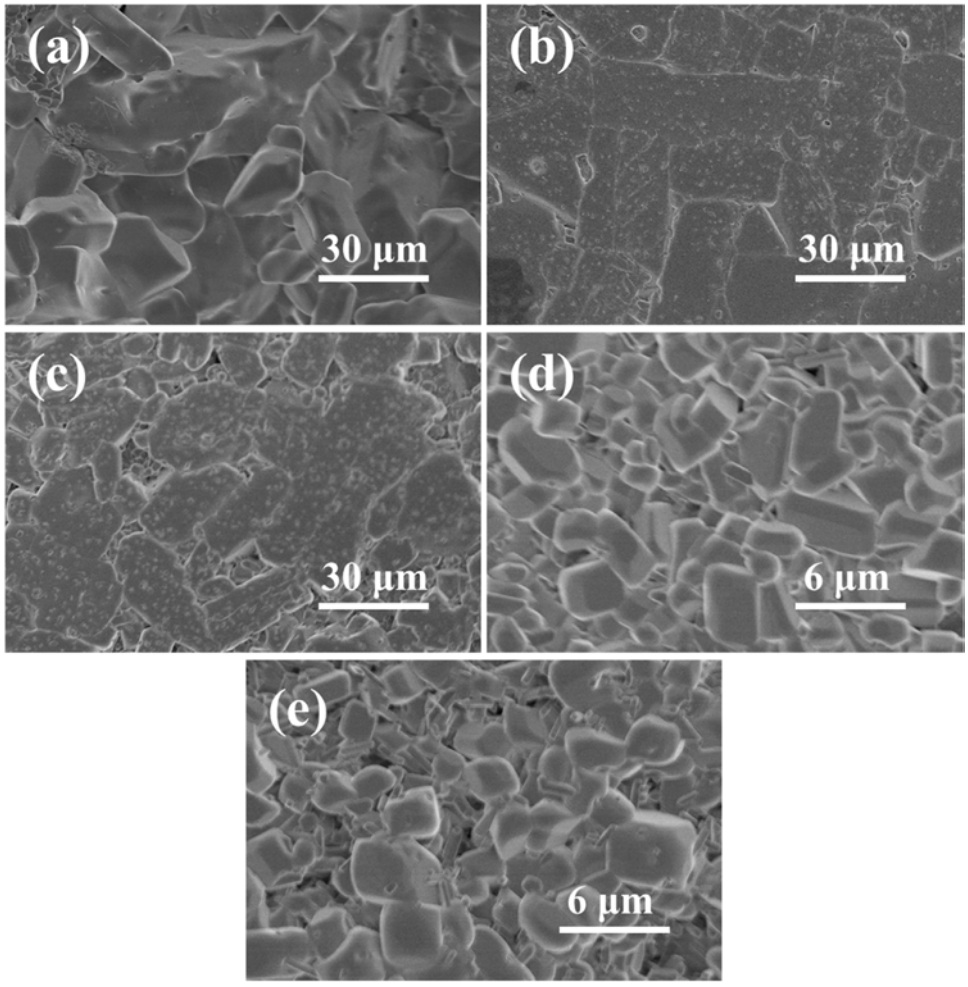

Fig. 3. SEM images of $(1-x)MgMoO_4 - xTiO_2$ ceramics sintered at 950 °C: (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.2$, (d) $x = 0.3$, and (e) $x = 0.4$.

first time in Fig. 3(b), and increase along with x. The two types of grains ($MgMoO_4$ and TiO_2) are randomly distributed, which consists well with the discussions above. The average grain size of $MgMoO_4$ is estimated using linear intercept method as follows [25]:

$$D = \frac{3L}{2MN} \tag{5}$$

where D, L, M and N represent the grain size, the length of test line, the magnification and the number of intercepts which grain boundaries make with the line. The calculated results are 18.3 μm and 23.1 μm for $x = 0$ and 0.1, respectively, indicating that the introduction of TiO_2 can promote the grain growth of $MgMoO_4$. However, with a further increase of x, the average grain size of $MgMoO_4$ decreases from 17.6 μm to 2.6 μm for $0.2 \le x \le 0.4$. It also can be seen from Fig. 3(d) and (e) that, abnormal grains and pores are formed in sintered samples, leading to a decrease of density. This demonstrates that excess TiO_2 have no benefits to the densification of $(1-x)MgMoO_4 - xTiO_2$ ceramics.

Such changes in the microstructure are related to the different physical and chemical properties that depend on different TiO_2 contents of the samples. Pure $MgMoO_4$ ceramics are well sintered at 900 °C [12]. As the sintering temperature increases to 950 °C, the samples are slightly over sintered and a small amount of liquid melt is formed in the grain boundaries. However, the liquid melt can effectively decrease the sintering temperature of TiO_2 by increasing grain boundary motion, diffusion and crystallization kinetics [26]. Therefore, the grain growth of TiO_2 is promoted. At the same time, due to the movement of liquid melt, the crystal quality of $MgMoO_4$ becomes better and the average grain size increases. Evidently, $MgMoO_4$ and TiO_2 can positively influence each other during their sintering process. With a further increase of TiO_2 content, the liquid melt is insufficient for the sintering of excess TiO_2, which exists as amorphous state in $(1-x)MgMoO_4 - xTiO_2$ ceramics. This leads to the deterioration of crystallization for both the two phases and the decrease of density. The discussions correspond well with the variation of microstructure.

Considering the relatively high relative permittivity of TiO_2 ($\varepsilon_r = 105$), the relative permittivity of $(1-x)MgMoO_4 - xTiO_2$ samples is expected to increase along with the TiO_2 content. Fig. 4 depicts the relative permittivity of $(1-x)MgMoO_4 - xTiO_2$ ceramics sintered at 950 °C as a function of x value. It can be observed that as x rises, the measured relative permittivity gradually increases from 6.73 ± 0.04 to 9.97 ± 0.06 for $0 \le x \le 0.4$.

In composite ceramics, the relative permittivity is determined by the permittivity, volume fraction, and complex form of the component material. Many researchers have studied the dielectric response of two-phase compounds and proposed different models and equations [27–29]. The Licktenecher equation is the most widely used empirical equation to predict the relative permittivity of two-phase ceramics by the following relation [30]:

$$\varepsilon^{\alpha} = (1-\nu)\varepsilon_1^{\alpha} + \nu\varepsilon_2^{\alpha} \tag{6}$$

where ε_i is the relative permittivity of the i*th* material and ν represents the volume fraction of material 2. The parameter α varies from −1 to 1, determined by the complex model. The serial model,

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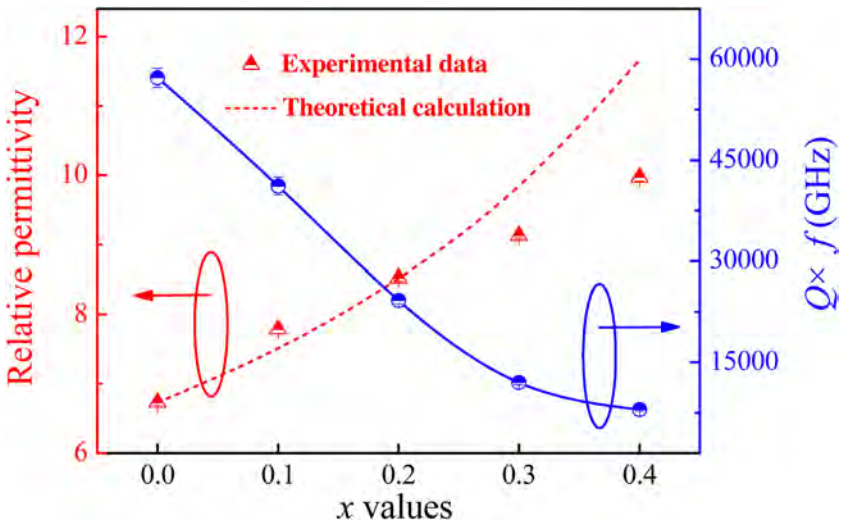

Fig. 4. Relative permittivity and $Q \times f$ value of $(1-x)MgMoO_4 - xTiO_2$ ceramics with various x values.

logarithmic rule model and parallel model correspond to $\alpha = -1$, 0 and 1, respectively. Among the three complex models, the logarithmic rule model is used for randomly distributed composite systems, which better fits the measured data [31].

$$\log\ \varepsilon = (1-\nu)\log\ \varepsilon_1 + \nu\ \log\ \varepsilon_2 \tag{7}$$

The simulation curve is presented in Fig. 4. The relative permittivity of $MgMoO_4$ and TiO_2 are $\varepsilon_1 = 6.73$ and $\varepsilon_2 = 105$, respectively. It can be seen that when $x \leq 0.2$, the calculated relative permittivity is in good agreement with the experimental value. The measured result for $x = 0.1$ is a little higher than the theoretical relative permittivity, which attributes to the larger actual proportion of TiO_2. However, a deviation from the fitting curve can be observed for $x = 0.3$ and 0.4. This is mainly due to the low relative permittivity of amorphous TiO_2 and pores, well consistent with the microstructure analysis results.

The measured $Q \times f$ value of $(1-x)MgMoO_4 - xTiO_2$ ceramics sintered at 950 °C is shown in Fig. 4. It is observed that with increasing the TiO_2 content, the $Q \times f$ value decreases monotonously in the entire composition range. The maximum $Q \times f$ is 57,240 GHz ($x = 0$) and minimum $Q \times f$ is 7980 GHz ($x = 0.4$). In general, the $Q \times f$ value is affected by two parts: intrinsic losses and extrinsic losses. The intrinsic losses are caused by absorptions of phonon oscillation and the extrinsic losses are influenced by many factors, such as impurity, defect concentration, grain size, grain boundaries, and pores, *etc* [32]. In the $(1-x)MgMoO_4 - xTiO_2$ composites, the extrinsic factors are dominated. Because of few impurities and defects, the variation trend of $Q \times f$ value is dependent on other factors. When TiO_2 is added to $MgMoO_4$, the $Q \times f$ value for $x = 0.1$ decreases, owing to the formation of grain boundaries between the two phases. With a further increase of TiO_2 content, the average grain size of $MgMoO_4$ decreases, resulting in the increase of grain boundaries per unit volume. In addition, accompanied with the excess TiO_2, pores are generated for $x \geq 0.3$. These are the sources of loss which will lead to the large dielectric loss, therefore, the $Q \times f$ value decreases along with x.

Fig. 5 shows the temperature coefficient of resonant frequency of $(1-x)MgMoO_4 - xTiO_2$ ceramics sintered at 950 °C. The measured τ_f value shifts from −79.7 ppm/°C to 24.6 ppm/°C with the increase of x from 0 to 0.4, and a near-zero τ_f value (3.2 ppm/°C) is obtained when $x = 0.3$.

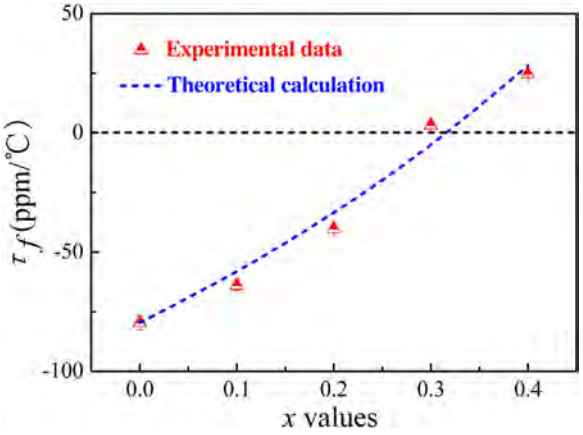

Fig. 5. Temperature coefficient of resonant frequency of $(1-x)MgMoO_4$–$xTiO_2$ ceramics with various x values.

As well known, τ_f is affected by the additive, composition and second phase. It can be written as follows [33]:

$$\tau_f = -(\frac{\tau_\varepsilon}{2} + \alpha_L) \tag{8}$$

where τ_ε and α_L represent the temperature coefficient of relative permittivity and linear thermal expansion coefficient, respectively. In two-phase composite ceramics, the τ_ε can be further defined by a mathematical derivation based on Eq. (7) [34]:

$$\frac{d(log\varepsilon)}{dT} = (1-\nu)\frac{d(log\varepsilon_1)}{dT} + \nu\frac{d(log\varepsilon_2)}{dT} \tag{9}$$

$$\frac{1}{\varepsilon}\frac{d\varepsilon}{dT} = (1-\nu)\frac{1}{\varepsilon_1}\frac{d\varepsilon_1}{dT} + \nu\frac{1}{\varepsilon_2}\frac{d\varepsilon_2}{dT} \tag{10}$$

$$\tau_\varepsilon = (1-\nu)\tau_{\varepsilon_1} + \nu\tau_{\varepsilon_2} \tag{11}$$

where $\tau_{\varepsilon i}$ is the τ_ε value of the i*th* material. Since the linear thermal expansion coefficient of microwave dielectric is about 10 ppm/°C, the α_L value is assumed to be a constant. From Eqs. (8) and (11), the τ_f can be then described as:

$$\tau_f = (1-\nu)\tau_{f_1} + \nu\tau_{f_2} \tag{12}$$

where τ_{f1} and τ_{f2} are the τ_f values of material 1 and material 2. The simulation curve of calculated τ_f value is plotted in Fig. 5. The τ_f of $MgMoO_4$ and TiO_2 are $\tau_{f1} = -79.7$ ppm/°C and $\tau_{f2} = +460$ ppm/°C, respectively. The measured τ_f values are similar to the calculated

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Table 1
Microwave dielectric properties of $0.7MgMoO_4$–$0.3TiO_2$ composites and other molybdate ceramics.

	Relative permittivity	$Q \times f$ (GHz)	τ_f (ppm/°C)	References
$0.7MgMoO_4 - 0.3TiO_2$	~9.1	11,990	3.2	This work
0.7MgMoO4	~6.7	57,273	−79.7	This work
$ZnMoO_4$	8.67	49,900	−87.49	[12]
$BaMoO_4$	9.0	37,110	−90.1	[23]
$MnMoO_4$	8.55	54,100	−73.91	[12]

ones, which indicates that $MgMoO_4$ and TiO_2 are randomly mixed in the $(1-x)MgMoO_4 - xTiO_2$ ceramics. The microwave dielectric properties of $0.7MgMoO_4$–$0.3TiO_2$ composites are listed in Table 1. Compared with other molybdate ceramics, $0.7MgMoO_4$–$0.3TiO_2$ composites present a near-zero temperature coefficient of resonant frequency, which is beneficial for LTCC applications.

4. Conclusions

$(1-x)MgMoO_4 - xTiO_2$ ceramics were prepared by a solid state reaction method. The microstructure and microwave dielectric properties of the samples sintered at 950 °C are investigated. The XRD and SEM analyses reveal that rutile TiO_2 can coexist with wolframite $MgMoO_4$. With the increase of x, the relative permittivity gradually increases from 6.73 ± 0.04 to 9.97 ± 0.06 and the $Q \times f$ value monotonously decreases from 57,240 GHz to 7980 GHz. The deviation between measured relative permittivity and calculated value has a close relationship with the variation of microstructure. The variation mechanisms of relative permittivity and $Q \times f$ value are proposed, respectively. The τ_f value shifts from −79.7 ppm/°C to 24.6 ppm/°C along with the TiO_2 content. The mixture mechanisms of τ_f value for two-phase composite materials are supposed. A near-zero τ_f value (3.2 ppm/°C) is obtained for $x = 0.3$, with $\varepsilon_r = 9.13 \pm 0.03$ and $Q \times f = 11{,}990$ GHz. The $0.7MgMoO_4 - 0.3TiO_2$ composites are considered to be appropriate as a low temperature co-fired ceramic material for microwave wireless communication applications.

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