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# Microwave dielectric properties of $(1-x)ZnMoO_4$–$xTiO_2$ composite ceramics

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ABSTRACT

$(1-x)ZnMoO_4$–$xTiO_2$ ($x=0.0$, 0.05, 0.158, 0.25, and 0.35) composite ceramics were synthesized by the conventional solid state reaction process. The sintering behavior, phase composition, chemical compatibility with silver, and microwave dielectric properties were investigated. All the specimens can be well densified below 950 °C. From the X-ray diffraction analysis, it indicates that the triclinic wolframite $ZnMoO_4$ phase coexists with the tetragonal rutile $TiO_2$ phase, and it is easy for silver to react with $ZnMoO_4$ to form $Ag_2Zn_2(MoO_4)_3$ phase and hard to react with $TiO_2$. When the volume fraction of $TiO_2$ ($x$ value) increasing from 0 to 0.35, the microwave dielectric permittivity of the $(1-x)ZnMoO_4$–$xTiO_2$ composite ceramics increases from 8.0 to 25.2, the $Q_f$ value changes in the range of 32,300–43,300 GHz, and the temperature coefficient $\tau_f$ value varies from −128.9 to 157.4 ppm/°C. At $x=0.158$, the mixture exhibits good microwave dielectric properties with a $\varepsilon_r=13.9$, a $Q_f=40{,}400$ GHz, and a $\tau_f=+2.0$ ppm/°C.

## 1. Introduction

With the explosive growth of high frequency wireless communication technology, electronic components and substrates are in urgent need of improving performances and realizing miniaturization and integration. It is possible to integrate the passive components to a function module by low temperature cofired ceramic (LTCC) technology. Materials with low sintering temperature (<960 °C), high quality factor ($Q_f$) value and near zero temperature coefficient of resonant frequency ($\tau_f$) are necessary for the applications [1–4]. Recently, a number of new microwave dielectric ceramics have been developed, such as $AWO_4$ and $AMoO_4$ (A = Mg, Mn, Zn, Ca, Sr, and Ba). $AWO_4$ compounds have good dielectric properties: permittivity is 8–17, $Q_f$ value is 32,000–69,000 GHz, and $\tau_f$ value is −53 to −78 ppm/°C [5]. $AMoO_4$ compounds are also suitable for applications of microwave dielectric materials, with low permittivity (7–11), low dielectric loss (37,000–90,000 GHz) and relatively small temperature coefficient of resonant frequency (−57 to −87 ppm/°C) [6]. Compared with $AWO_4$, $AMoO_4$ ceramics have lower sintering temperature, especially $ZnMoO_4$. However, all of them have negative $\tau_f$ values. Normally, there are two methods to design a material with a stable temperature coefficient: (a) composite materials by mixing two or more component materials with opposite $\tau_f$ values, including $ZnAl_2O_4$–$TiO_2$, $Ca_2P_2O_7$–$TiO_2$, $CaWO_4$–$TiO_2$, $Zn_2Te_3O_8$–$TiO_2$, $Zn_2TiO_4$–$TiO_2$, $NiNb_2O_6$–$TiO_2$, and $Bi_2MoO_6$–$TiO_2$ [7–13]; (b) formation of solid solutions, such as complex perovskites and other systems [14–17]. In the recent investigation, $ZnMoO_4$ sintered at 800 °C presents excellent microwave dielectric properties with $\varepsilon_r=8.67$ (permittivity), $Q_f=49{,}900$ GHz, $\tau_f=-87.49$ ppm/°C [6]. In order to compensate the negative $\tau_f$ value of $ZnMoO_4$, rutile $TiO_2$ ($\varepsilon_r=105$, $Q_f=46{,}000$ GHz, $\tau_f=+465$ ppm/°C) [18] was selected to form a $(1-x)ZnMoO_4$–$xTiO_2$ mixture. In this work, the synthesis, sintering behavior, phase composition, chemical compatibility with silver, and microwave dielectric properties of the $(1-x)ZnMoO_4$–$xTiO_2$ mixture ceramics were studied.

## 2. Experimental

All the samples were prepared by the conventional solid state reaction process. ZnO (>99%, Sinopharm Chemical Reagent Co., Ltd., China), $MoO_3$ (>99%, Fuchen Chemical Reagents, Tianjin, China) and rutile $TiO_2$ (>99%, Linghua Co., Ltd., Zhaoqing, China) were used as starting materials. The $ZnMoO_4$ powders were synthesized by calcining in air at 600 °C for 4 h. The $ZnMoO_4$ and $TiO_2$ powders were mixed according to the following stoichiometrics: $(1-x)ZnMoO_4$–$xTiO_2$ ($x=0.0$, 0.05, 0.158, 0.25 and 0.35; ZM, ZMT1, ZMT2, ZMT3, ZMT4 were used for abbreviations). The mixed powders were milled with ethanol and Zirconia milling media (2 mm in diameter) for 4 h using a planet ball-milling system whose running speed is 150 rpm, and then dried. The final powders mixed with PVA binder were pressed into cylinder samples (10 mm in diameter and 4–5 mm in height) and these pellets were sintered in the temperature range from 750 °C to 975 °C for 2 h with a heating rate of 3 °C/min.

The phase compositions of the specimens were identified using X-ray diffraction with Cu Kα radiation (Rigaku D/MAX-2400 X-ray diffractometry, Tokyo, Japan). The microstructure was observed with a scanning electron microscope (JSM-6460, JEOL, Tokyo, Japan). The bulk densities of the specimens were measured by Archimedes' method. The microwave dielectric properties were measured using the $TE_{01\delta}$ method with a network analyzer (8720ES, Agilent, Palo Alto, CA) and a temperature chamber (Delta 9023, Delta Design, Poway, CA). The temperature coefficient of resonant frequency ($\tau_f$) can be obtained by the following equation:

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

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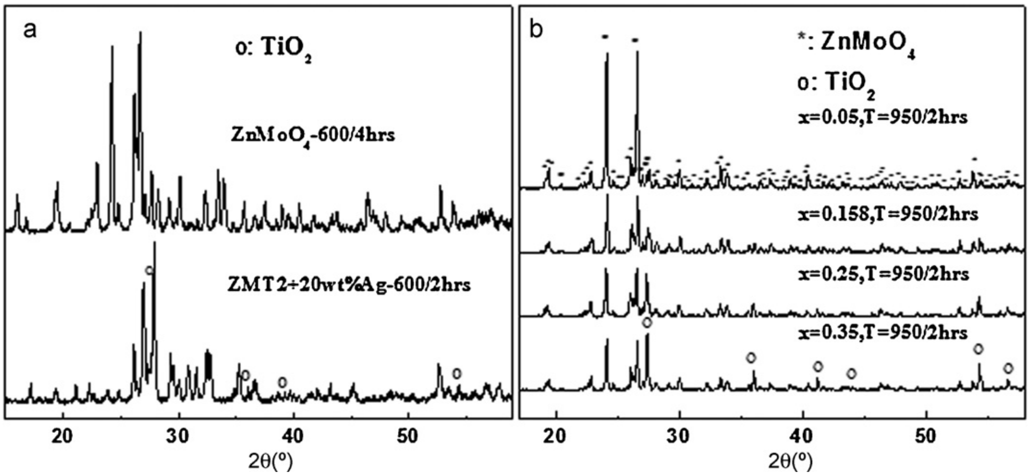


**Fig. 1.** XRD patterns of calcined $ZnMoO_4$ powders, ZMT2 cofired with 20 wt% Ag and sintered $(1-x)ZnMoO_4$–$xTiO_2$ composites (*, triclinic $ZnMoO_4$ phase; O, tetragonal rutile phase).

where $f_{85}$ and $f_{25}$ were the resonant frequencies at 85 °C and 25 °C, respectively.

## 3. Results and discussions

Fig. 1(a) shows the X-ray diffraction patterns of calcined $ZnMoO_4$ powders, $ZnMoO_4$–$TiO_2$ composites cofired with 20 wt% Ag and Fig. 1(b) shows the XRD patterns of $(1-x)ZnMoO_4$–$xTiO_2$ mixed phases sintered at 950 °C. The $ZnMoO_4$ with triclinic wolframite structure was obtained when calcined at 600 °C for 4 h. From Fig. 1(b), it can be concluded that $TiO_2$ coexists with $ZnMoO_4$. When the content of $TiO_2$ increasing, the intensity of the reflections of $TiO_2$ increases greatly. Finally, a study of the chemical compatibility of $ZnMoO_4$–$TiO_2$ compounds with Ag powders has been made. As shown in Fig. 1(a), Ag can form the $Ag_2Zn_2(MoO_4)_3$ phase with $ZnMoO_4$ easily, and seems not to react with $TiO_2$.

Fig. 2 presents the backscattered electron image of the surface of $0.65ZnMoO_4$–$0.35TiO_2$ sample. From the micrograph, it is seen that there are two types of grains in the specimen and the grain size is in the range of 1–6 μm. The EDS analysis shows that the light grains as B belong to $ZnMoO_4$ phase and the dark ones as A belong to the $TiO_2$ phase. Since the sintering temperature of pure $TiO_2$ ceramic is about 1300 °C [10], the $TiO_2$ grains in the compounds are smaller than those of pure $TiO_2$ phase.

Fig. 3(a) presents the densities of the $(1-x)ZnMoO_4$–$xTiO_2$ ceramics. It can be seen that the densities of all the samples are larger than 4.06 g/cm$^3$, which indicates that all the specimens' relative densities are over 94%. Therefore, all the composite ceramics are well densified below 950 °C. The microwave dielectric properties of the $(1-x)ZnMoO_4$–$xTiO_2$ ceramics are shown in Fig. 3(b) and (c). In the composite, the permittivity is determined by the permittivity, volume fraction and the complex form of the composing material [19]. If the composite material is aligned parallel to the electric field, the $\varepsilon$ is given as [19]

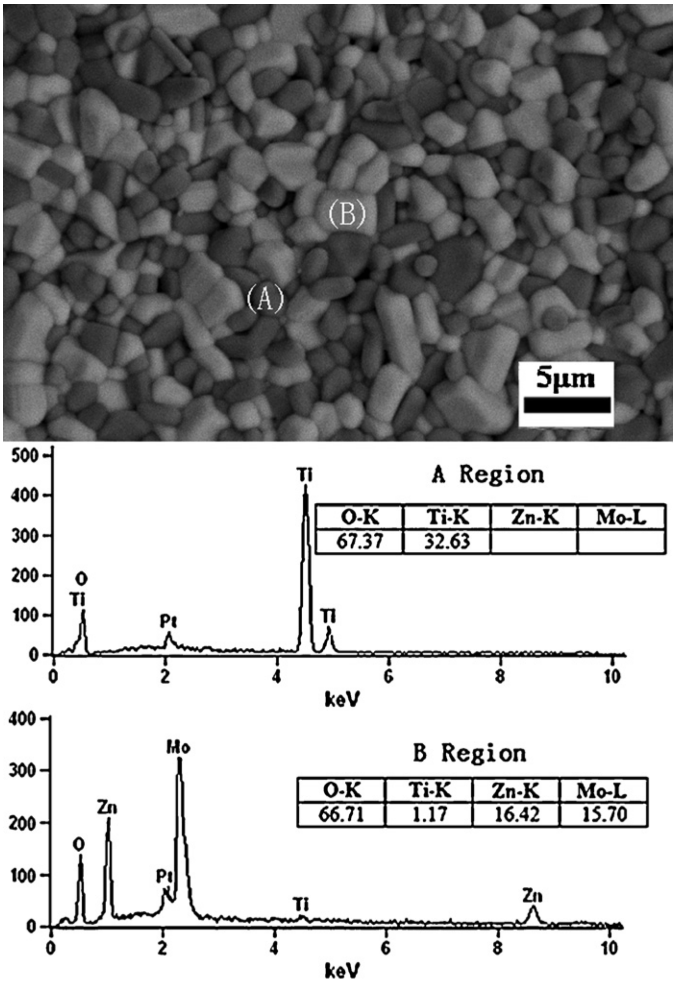
$$\varepsilon = y_1\varepsilon_1 + y_2\varepsilon_2 \tag{2}$$

where $\varepsilon_1$ and $\varepsilon_2$ are permittivities of material 1 and material 2, respectively; $y_1$ and $y_2$ are the volume fractions. When the composite material is aligned in series with the electric field, the $\varepsilon$ can be obtained as follows [19]

$$\frac{1}{\varepsilon} = \frac{y_1}{\varepsilon_1} + \frac{y_2}{\varepsilon_2} \tag{3}$$

In case the composite material is aligned randomly, the $\varepsilon$ follows the empirical logarithmic rule [19]

$$\log\varepsilon = y_1\log\varepsilon_1 + y_2\log\varepsilon_2 \tag{4}$$



A Region

| O-K | Ti-K | Zn-K | Mo-L |
|---|---|---|---|
| 67.37 | 32.63 | | |

B Region

| O-K | Ti-K | Zn-K | Mo-L |
|---|---|---|---|
| 66.71 | 1.17 | 16.42 | 15.70 |

**Fig. 2.** The backscattered electron micrograph and EDS analysis of $0.65ZnMoO_4$–$0.35TiO_2$ specimen sintered at 975 °C for 2 h: (a) A region, $TiO_2$ and (b) B region, $ZnMoO_4$.

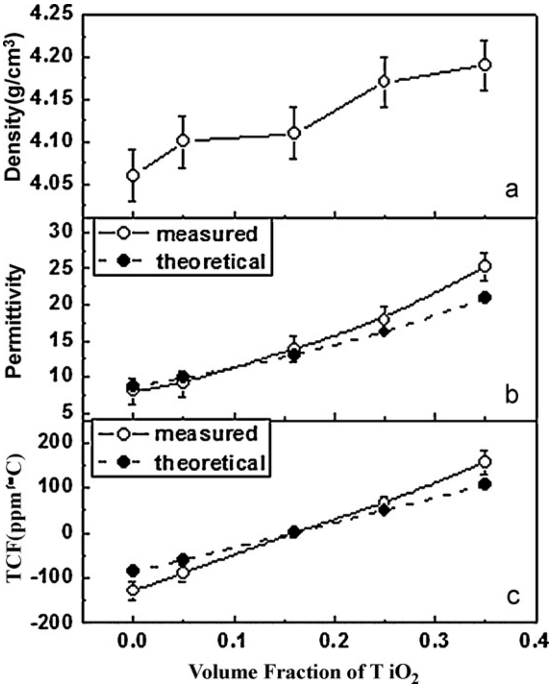


**Fig. 3.** Densities and microwave dielectric properties of $(1-x)ZnMoO_4$–$xTiO_2$ compounds sintered at their optimal temperatures for 2 h with $x = 0$, 0.05, 0.158, 0.25, and 0.35.

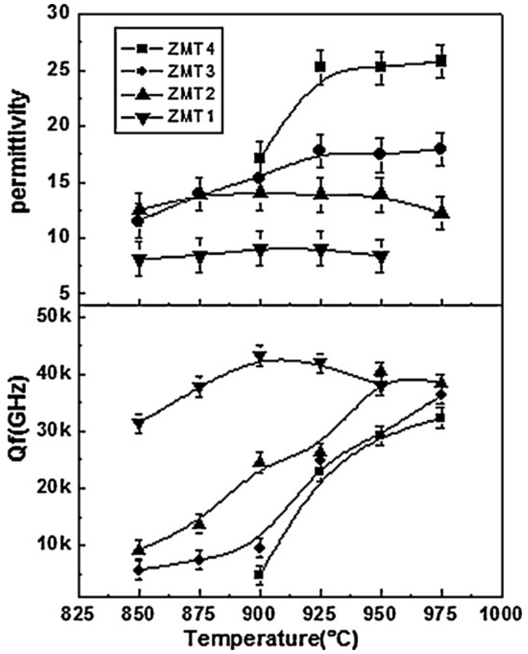


**Fig. 4.** Microwave dielectric properties of $(1-x)ZnMoO_4$–$xTiO_2$ ceramics as a function of sintering temperature.

In the $(1-x)ZnMoO_4$–$xTiO_2$ ceramics, the triclinic wolframite $ZnMoO_4$ phase and tetragonal rutile $TiO_2$ phase are distributed randomly. So the theoretical permittivity of the mixed ceramic can be gained by logarithmic rule. Fig. 3(b) shows that the permittivity of the composite ceramic increases from 8.0 to 25.2 when the volume fraction of $TiO_2$ increasing from 0 to 0.35. Although the measured permittivity is a little higher than the theoretical value, it generally accords to the logarithmic rule.

According to the empirical logarithmic rule, the $\tau_f$ of the mixed ceramic can be obtained as follows: [13]

$$\tau_f = y_1\tau_{f1} + y_2\tau_{f2} \tag{5}$$

where $\tau_{f1}$ and $\tau_{f2}$ are the $\tau_f$ values of material 1 and material 2, respectively. The theoretical and measured $\tau_f$ values are plotted in Fig. 3(c). The measured $\tau_f$ value shifts from −128.9 to 157.4 ppm/°C as $x$ value increasing from 0 to 0.35. Compared with the previous reports [6,18], the measured $\tau_f$ value of pure $ZnMoO_4$ is a little lower and the measured $\tau_f$ value of rutile $TiO_2$ is a little larger, which may be caused by the different calcination temperatures. The $\tau_f$ values of $(1-x)ZnMoO_4$–$xTiO_2$ ceramics agree well with the mixture function (5) and the near-zero $\tau_f$ value is obtained at $x = 0.158$.

The permittivities and $Q_f$ values of the composite ceramics as a function of sintering temperature are plotted in Fig. 4. It is seen that the $(1-x)ZnMoO_4$–$xTiO_2$ ceramics have good $Q_f$ values at low temperatures. The $0.35ZnMoO_4$–$0.65TiO_2$ composite has a minimum $Q_f$ value (32,300 GHz) and $0.05ZnMoO_4$–$0.95TiO_2$ composite has a maximum $Q_f$ value (43,300 GHz). The $0.842ZnMoO_4$–$0.158TiO_2$ composite with a near-zero $\tau_f$ possesses a $Q_f$ value about 40,400 GHz.

## 4. Conclusion

This study introduced a new dielectric material system $(1-x)ZnMoO_4$–$xTiO_2$ with good microwave dielectric properties. All the samples can be well densified below 950 °C. The X-ray analysis reveals that the triclinic wolframite $ZnMoO_4$ phase can coexist with the tetragonal rutile $TiO_2$ phase. Silver reacts with $ZnMoO_4$ easily to form the $Ag_2Zn_2(MoO_4)_3$ phase, and seems not to react with $TiO_2$. When the volume fraction of $TiO_2$ was 0.158, the $\varepsilon_r$, $Q_f$ value, and $\tau_f$ value of the compound were 13.9, 40,400 GHz, and +2.0 ppm/°C, respectively.

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