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Effects of V_2O_5 addition on the phase-structure and dielectric properties of zinc titanate ceramics

Xiangchun Liu · Feng Gao · Lili Zhao · Ming Zhao · Changsheng Tian

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Abstract V_2O_5-doped zinc titanate ceramics ($ZnTiO_3$) were prepared by conventional mixed-oxide method combined with a semi-chemical processing. The effects of V_2O_5 addition on the phase-structures and the dielectric properties of $ZnTiO_3$ ceramics were investigated. The results show the sintering temperature of zinc titanate ceramics could be lowered from 1,150 to 930 °C by reducing the size of starting powders using a semi-chemical processing; and with adding V_2O_5 addition, the densification temperature of $ZnTiO_3$ ceramics could be reduced to 875 °C. Also the phase transition temperature from hexagonal $ZnTiO_3$ phase to cubic Zn_2TiO_4 was lowered by adding V_2O_5. The best properties were: ε_r=20.6, $Q \times f = 8,873$ GHz, when the ceramics was sintered at 900 °C, which is a promising candidate in the field of multi-layer devices requiring low sintering temperature (≤900 °C).

Keywords Low-temperature sintering · Semi-chemical processing · Dielectric properties · Phase transformation · $ZnTiO_3$

1 Introduction

Low-temperature cofired ceramics (LTCCs) are receiving increasing attention in the research community because the application of novel multilayer communication modules involving the integration of passive components. In multilayer structure, it is necessary to lower the sintering temperature of the dielectrics in order to co-fire with low melting point and highly conductive internal electrode metals, such as silver, copper, and their alloys [1]. Three classes of LTCCs compositions have been investigated [2]. The first type includes "low-fire materials," generally Bi-based, such as Bi pyrochlores and sillenites. The second type includes glass-ceramic composites with high glass contents (~45%). These two approaches are combined in the third class, which uses ceramics with relatively low sintering temperatures (1,100–1,150 °C) and adds small amount of glass or sintering aids into ceramics. In this paper, zinc titanates ($ZnTiO_3$) system was chosen as a host material because of its low sintering temperature (1,150 °C) and promising dielectric properties [3–5]. However, its sintering temperature is still higher than the melting temperature of Ag (961 °C) and Cu (1,064 °C) used as inner electrodes of LTCCs.

A semi-chemical route combined with vigorous microbeads milling [6] and sol–gel method [5] were used to lower the sintering temperature of zinc titanates ceramics to 900 °C, but these methods need special equipment and expensive reagents. So, to seek a simple technique using cheap raw materials may be of particular interest to the researchers. Three methods are commonly used for reducing the sintering temperature of zinc titanates dielectric ceramics [7] adding low-melting glass addition, applying a chemical processing, and using starting materials with smaller particle size. In present work, a microwave dielectric ceramics based on the $ZnTiO_3$ system was prepared by conventional mixed-oxide method combined with a semi-chemical processing. Fine particle powders were prepared by semi-chemical processing to activate the formation of $ZnTiO_3$. V_2O_5 addition was selected as sintering aid to improve the sinterability because V_2O_5 has a relatively low melting point (680 °C), and $Zn_3V_2O_8$ has a eutectic

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X. Liu (✉) · F. Gao · L. Zhao · M. Zhao · C. Tian
School of Materials Science and Engineering,
Northwestern Polytechnical University,
Xi'an 710072, People's Republic of China
e-mail: liuxc@126.com

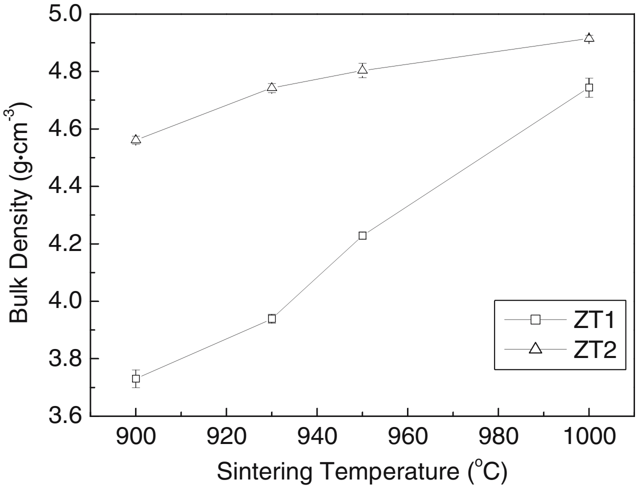


Fig. 1 Bulk density of zinc titanate ceramics prepared with different raw materials vs. the sintering temperature

reaction with ZnO at about 890 °C, thus the formed low-temperature liquid phase during sintering process can directly or indirectly accelerate the reaction with the matrix phase, and accelerate the solution and precipitation of grains [8]. The phase transition and the dielectric properties of the V_2O_5-doped $ZnTiO_3$ ceramics depend on sintering temperatures were investigated.

2 Experimental procedure

$ZnTiO_3$ powder was prepared via a semi-chemical route with Analytical Reagent (Abbreviate to A.R.) zinc hydroxide carbonate ($Zn_5(CO_3)_2{\cdot}(OH)_6$) and anatase ($TiO_2$, 10–30 nm). Zinc hydroxide carbonate was heat-treated at 350 °C for 2 h in air to obtain ZnO with high active energy as starting materials. Anatase nanopowder was mixed with ZnO powder using planetary milling with zirconia balls in ethanol for 24 h. The mixture was dried and then calcined at 750 °C for 2 h. After different amounts of V_2O_5 were respectively added to the mixture, the calcined powders were milled for 12 h. The resultant powders were granulated with 2 wt% poly vinyl alcohol (PVA) solution and then pelleted to 12 mm diameter and ~6.0 mm thick disks. The disks were sintered at 850–1,000 °C for 4 h.

The crystalline structure of the samples was investigated using X-ray diffractometry (XRD, X′ Pert MPD PRO, Holland). The bulk density of the samples was measured by the Archimedes method, and each data point represents a mean value of five specimens. The ceramic microstructure observations of the thermal etched ceramics were performed by scanning electron microscopy (SEM, JEOL JSM-5800, Japan), and energy dispersive spectroscopy (EDS) was used to investigate the function of the addition.

The microwave dielectric properties were measured using the resonant $TE_{01\delta}$ mode of the sample. The dielectric resonance techniques are widely used to measure the dielectric properties of dielectric ceramics because of high accuracy of dielectric properties measurements, especially for dielectric loss measurement, in comparison to other methods [9]. The TE_{011} mode was examined using a network analyzer (HP-8720 ES). The dielectric constants were measured by the Hakki–Coleman dielectric resonator method [10], and calculated from the TE_{011} resonator mode value [11]. The Q values are corrected for losses due to the measurement equipment, and can be assumed to be the Q of the dielectric ceramic [12]. Measurements were made on the as-fired samples, at room temperature. The results are given as $Q\times f$, where f is resonant frequency, between 5 and 8 GHz in all cases. In present work, the measurement errors of the dielectric constant and the Q factors were ±0.7 and ±5.3%, respectively.

3 Result and discussion

Zinc titanate ceramics prepared with A.R. ZnO and A.R. TiO_2 by conventional mixed-oxide method is designated as ZT1; those prepared with zinc hydroxide carbonate and nano-sized TiO_2 powder by conventional mixed-oxide method combined with a semi-chemical processing is designated as ZT2. The bulk densities of ZT1 and ZT2 are shown in Fig. 1, respectively. It can be seen that the densification temperature of ZT2 is far lower than that of ZT1, i.e., 930 °C for ZT2 and 1,000 °C for ZT1. The driving force for densification is the reduction in surface energy as the free surfaces of particles disappear. The surface energy of a solid is the amount of energy needed to create a unit area of new surface. ZnO obtained by decomposing zinc hydroxide carbonate was very small, only 50–70 nm, which resulted in high surface energy. Such

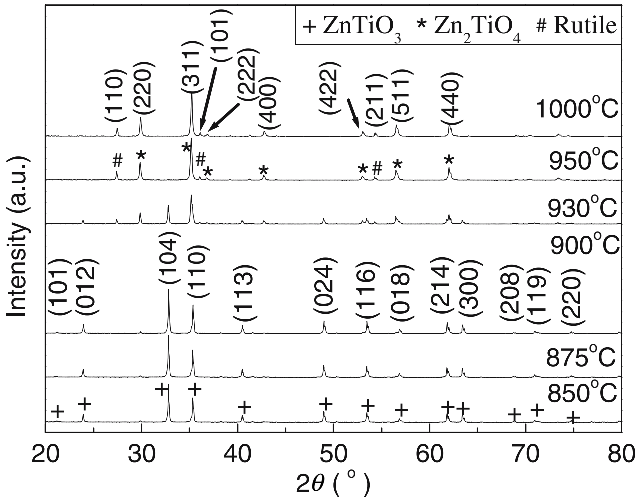
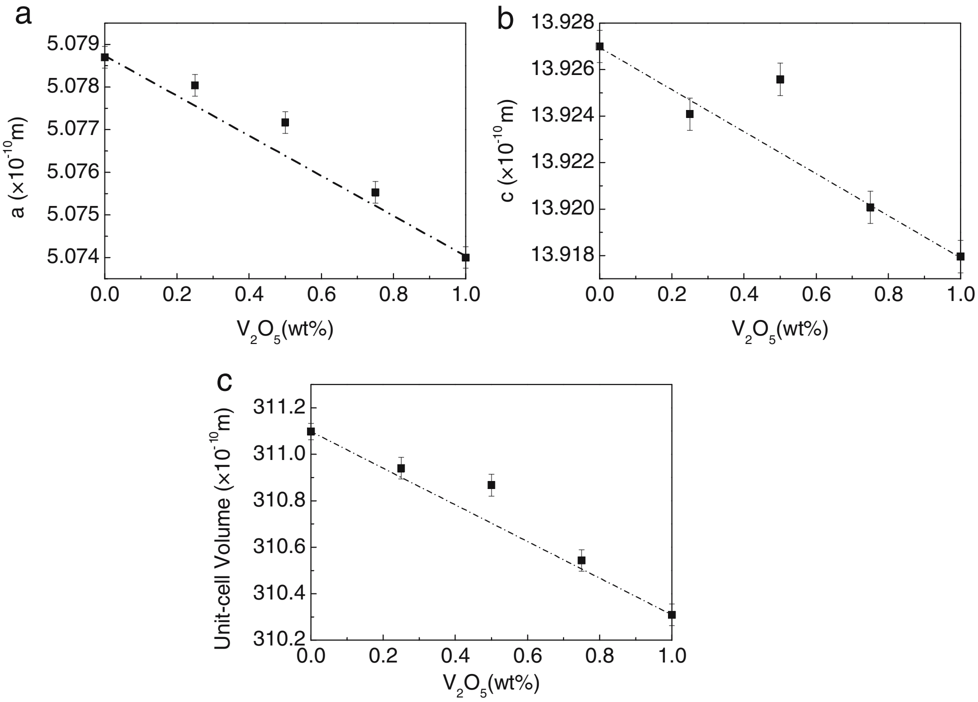


Fig. 2 XRD patterns of the $ZnTiO_3$ ceramics with 1 wt% V_2O_5 addition sintered at different temperature for 4 h

Fig. 3 Lattice parameter as a function of V_2O_5 content



high-surface-energy particles are easy to overcome sintering obstacle and lower the densification temperature. This result indicates that the sinterability of zinc titanate ceramics is strongly dependent on the size of starting powders. Nano-sized particles have shown potential for low-temperature sintering. The sintering temperature of zinc titanate ceramics could be lowered from 1,150 to 930 °C by conventional mixed-oxide method combined with a semi-chemical processing.

Figure 2 shows the XRD patterns of $ZnTiO_3$ ceramics with 1 wt% V_2O_5 addition at different sintering temperatures. It was observed that small amount of the cubic Zn_2TiO_4 phase appeared in the samples sintered at 850 °C, and the relative intensity of the Zn_2TiO_4 peak enhanced with the increase of sintering temperature. This result suggests that the decomposition of hexagonal $ZnTiO_3$ phase started at about 850 °C. Hexagonal $ZnTiO_3$ phase has been reported to be maintained below 945 °C [13]. Actually, according to Kim's reports [3, 4], the decomposition of $ZnTiO_3$ starts at about 900 °C and completes near 945 °C. So, it was concluded that the addition of 1 wt% V_2O_5 lowered the temperature of phase transition from hexagonal $ZnTiO_3$ to cubic Zn_2TiO_4.

Lattice parameter of hexagonal ilmenite phases in V_2O_5-doped zinc titanate ceramics was calculated by the software (MDI Jade 5.0) according to the refined diffraction data including 2θ and the locations of a few low-angle peaks with known Miller indices, the results are shown in Fig. 3. The lattice parameters of hexagonal ilmenite phases decreased on the whole as the amount of V increased. The ionic radii of V^{5+} and Ti^{4+} are 0.59 and 0.68 Å, respectively. Therefore V^{5+} may be substitute for Ti^{4+} according to Experience Expression of Solid Solution. The decrease in lattice parameter can be attributed to several factors; however, the data indicated V substitution into the ilmenite structure. Strictly speaking, the decrease in lattice parameter was not linear with V content. It implies the formation of a crystal lattice distortion, which resulted in the decrease of activation energy of structure unit and lead to the increase of diffusion rate so that the sintering

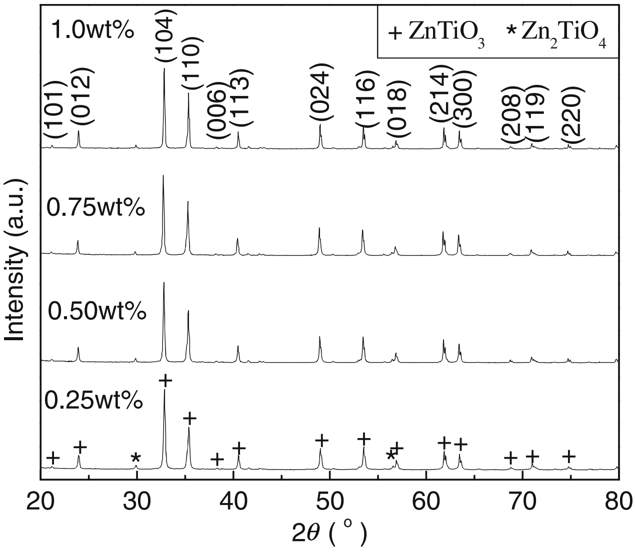


Fig. 4 XRD patterns of the $ZnTiO_3$ ceramics with various amounts of V_2O_5 addition sintered at 900 °C for 4 h

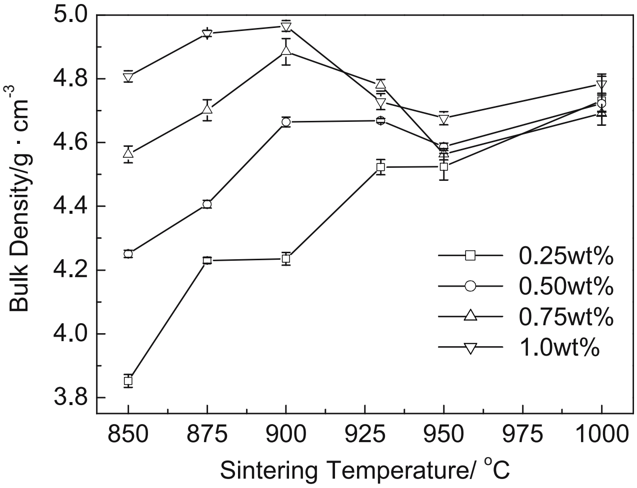


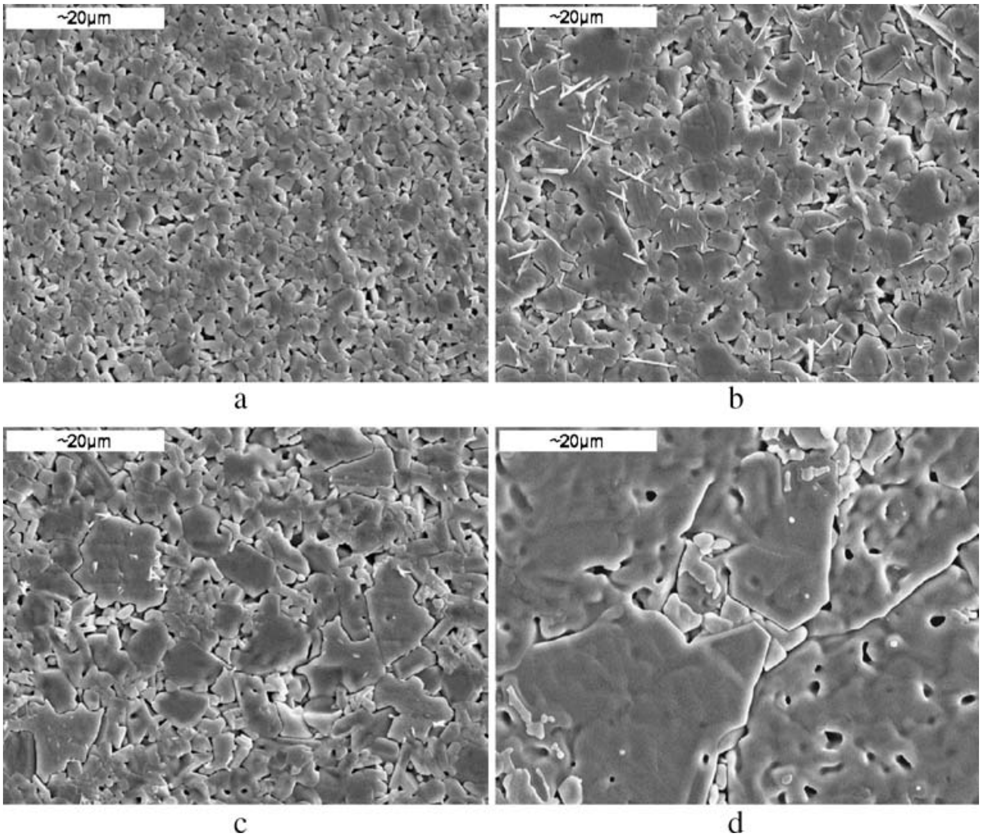
Fig. 5 The bulk densities of $ZnTiO_3$ ceramics with different amount of V_2O_5 added vs. the sintering temperature

temperature was lowered. $ZnTiO_3$ structure is metastable at 900 °C; therefore the crystal lattice distortion and solid-phase reaction resulting from the substitution of V^{5+} accelerated the transition of metastable $ZnTiO_3$ to stable Zn_2TiO_4 structure.

Figure 4 demonstrates the XRD patterns of the $ZnTiO_3$ specimens sintered at 900 °C with 0.25, 0.5, 0.75 and 1 wt% V_2O_5 additions, respectively. It was found that even 0.25 wt% V_2O_5 addition could result in the decomposition of hexagonal $ZnTiO_3$ phase at 850 °C. No apparent difference can be observed from the XRD patterns with further increasing V_2O_5 addition.

Figure 5 shows the bulk density of various amounts of V_2O_5-doped $ZnTiO_3$ ceramics as a function of the sintering temperature. It can be seen that the bulk density of $ZnTiO_3$ ceramics with various amounts of V_2O_5 addition increased as the sintering temperature increased from 850 to 900 °C. After reaching a maximum value at 900 °C, the densities of the ceramics decreased with the sintering temperature increasing from 900 to 950 °C. Then, as the sintering temperature increased to 1,000 °C, the densities of the ceramics enhanced again. Generally, the effectiveness of sintering aids depended on several factors such as sintering temperature, viscosity, solubility and glass wettability [14, 15]. The bulk density of specimens showed a clear increase with sintering temperature increasing from 850 to 900 °C. These results are due to the increase of liquid phases by adding V additions, which were melted at about 680 °C; moreover, ZnO has a eutectic reaction with $Zn_3V_2O_8$ at about 890 °C [16], which proves that the V-rich liquid phase can wet and dissolve Zn. From Fig. 2, it can be concluded that the phase decomposition was a slow reaction process at below 900 °C, but an acute phase decomposition reaction occurred above 900 °C, as a result,

Fig. 6 SEM micrographs of the $ZnTiO_3$ ceramics with 0.75 wt% V_2O_5 addition sintered at **a** 875 °C, **b** 930 °C, **c** 950 °C and **d** 1,000 °C for 4 h (bar=20 μm)



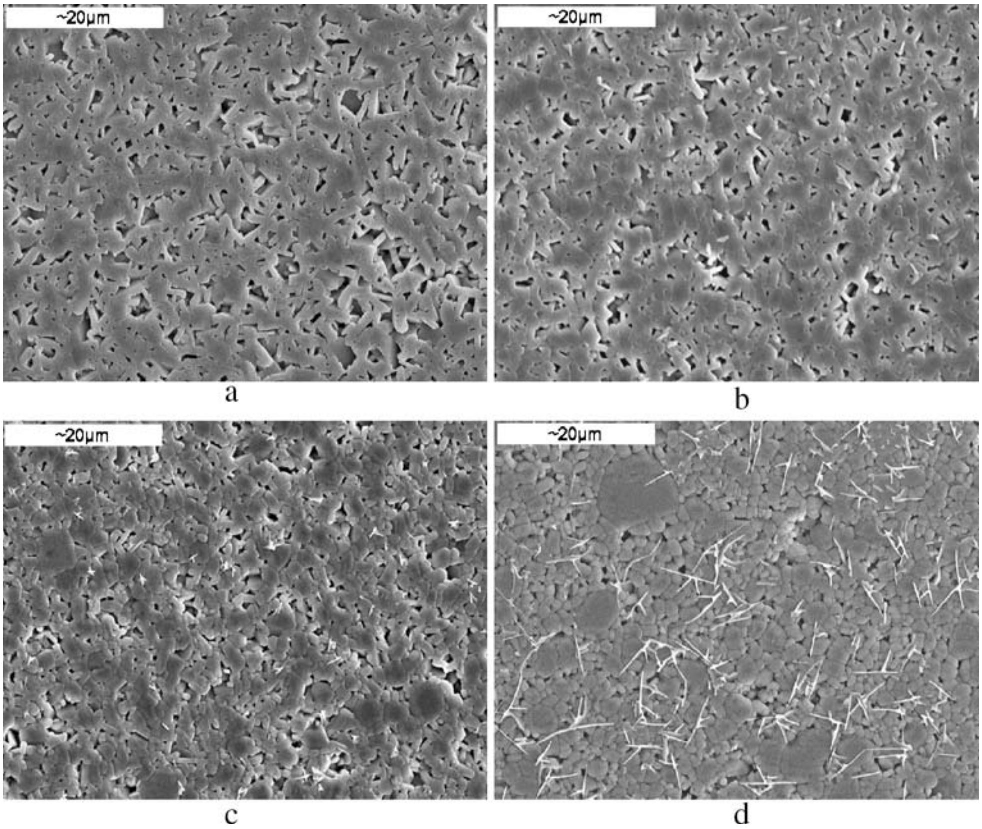


Fig. 7 SEM micrographs of the $ZnTiO_3$ ceramics sintered at 900 °C for 4 h with **a** 0.25 wt%, **b** 0.50 wt%, **c** 0.75 wt% and **d** 1 wt% V_2O_5 addition (bar=20 μm)

the ceramics became loose and the densification decreased from 900 to 950 °C. Another reason for the densification decrease could be attributed to TiO_2 (rutile), which has a lower density (4.25 g/cm^3) than those of $ZnTiO_3$ (5.17 g/cm^3) and Zn_2TiO_4 (5.33 g/cm^3), coming from the decomposition of $ZnTiO_3$. At a designated sintering temperature, the density of the ceramics increased with the V_2O_5 additions increasing. The highest density of the $ZnTiO_3$ ceramics (4.97 g/cm^3, 96.1% theoretical density) was obtained at 900 °C when the amount of V_2O_5 addition reached 1 wt%.

Figure 6 illustrates the SEM images of the $ZnTiO_3$ ceramics with 0.75 wt% V_2O_5 addition at different sintering temperatures; the SEM photographs of the zinc titanates ceramics sintered at 900 °C with different amounts of V_2O_5 additions are shown in Fig. 7, and the EDS analysis of the zinc titanate ceramics with 0.75 and 1 wt% V_2O_5 are shown in Fig. 8, and Table 1. The white needle-like structures observed in Fig. 6, and Fig. 7, was concluded to be the deposit of V volatilization which formed in course of thermal etching. When the samples were etched by HF and HCl acid solution, no white needle-like structures were found. In addition, the EDS analysis of white needle-like structures observed in Fig. 6, and Fig. 7, showed that small amount of V was detected in them, as shown in Table 1. As

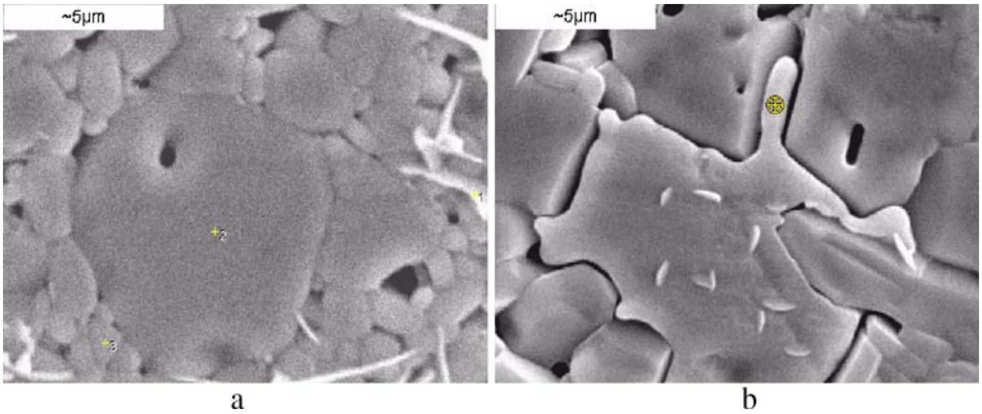


Fig. 8 EDS analysis of ZnO–TiO_2 ceramics with **a**1 wt% V_2O_5 sintered at 930 °C, **b** 0.75 wt% V_2O_5 sintered at 950 °C

Table 1 EDS quantum analysis of zinc titanate ceramics with (a) 1 wt% V_2O_5 sintered at 930 °C, (b) 0.75 wt% V_2O_5 sintered at 950 °C.

Spectrum	In stats.	O (wt%)	Ti (wt%)	V (wt%)	Zn (wt%)	Total
Spectrum 1 in Fig. 8a	yes	14.39	27.71	0.88	57.02	100
Spectrum 2 in Fig. 8a	yes	2.50	40.18	–	57.32	100
Spectrum 3 in Fig. 8a	yes	1.28	39.37	–	58.45	100
Spectrum in Fig. 8b	yes	8.57	20.52	10.36	60.55	100

is shown in Fig. 6, a non-polygon curly grain boundary appears in the samples sintered at the temperature higher than 930 °C, which is clear observed especially in Fig. 8b. This indicates that liquid phases presented in the ceramics during the sintering process. Valant and Suvorov [16] stated that a liquid disappeared or was resident in the final stage of liquid phase sintering; accordingly, a non-polygon curly grain boundary would form. When the samples were sintered at 900 °C, it can be seen in Fig. 6, that the short and bar-shaped grains decreased with increasing the amount of V_2O_5 addition and the granular grains increased at the same time, which may be attributed to the substitution of V^{5+} for Ti^{4+} of $ZnTiO_3$ structure and the decomposition of hexagonal $ZnTiO_3$ phase. When the sintering temperature was higher than 900 °C, the grain morphology took on amorphism because excessive liquid phase formed and then recrystallized during the cooling stage of the sintering. The similar phenomenon was found in B_2O_3 doped $ZnTiO_3$ system by Kim et al. [17].

As is shown in Figs. 6, 7 and 8, an exaggerated grain growth is observed in the samples sintered at temperature ranging from 900 to 1,000 °C. Moreover, the size and the amount of exaggerated grain increase with increasing the sintering temperature and V_2O_5 concentration. In these large grains, a few closed pores come into being. Both the large size of these grains and the high concentration of closed porosity in the grains indicate a fast growth kinetics that can be explained only by the presence of a liquid phase during the sintering. The grain growth rate is higher at higher sintering temperature and at larger amount of liquid phase. All the above results demonstrate that the addition of V_2O_5 addition not only decreased the sintering temperature but also improved the grain growth of ceramics.

An EDS analysis of the zinc titanate ceramics was performed to investigate the formation of the abnormal grain dependence of V_2O_5 addition. The results are shown in Fig. 7 and Table 1. It was noticed that V enriched in the residua of liquid phase, which recrystallized in the boundary of the exaggerated grains as shown in Fig. 8b and Table 1; while not be detected in the inner of exaggerated grains and small grains. For example, the concentration of V in the residua of liquid phase reached 10.36 wt% as shown in Table 1. It can be concluded that liquid phase formed in the V-rich grain boundaries during sintering. V-rich liquid phase accelerated the solution and precipitation process of grains, and effectively helped the grains to move easily. As a result, small grains near V-rich grain boundaries dissolved more easily than big grains because of their high surface energy, and then became smaller and smaller; the dissolved grains moved through the liquid phase and precipitated in the surface of big grains with low surface energy, then the big grains became bigger and bigger. At last, the exaggerated grains formed. From the EDS analysis, it can be found that the amount of Zn was always large in the V-rich grains, which indicates V_2O_5 accelerated the decomposition of hexagonal $ZnTiO_3$ to cubic Zn_2TiO_4 and rutile.

The microwave dielectric properties of V_2O_5-doped $ZnTiO_3$ ceramics fired at 900 °C for 4 h were also investigated, the results are shown in Table 2. Due to the experimental limitations, the value of τ_f is not available. In the report of Umemura et al. [18], a negative τ_f value (−108.2 ppm/°C) can be obtained in $(Mg_{3-x}Zn_x)(VO_4)_2$ system. In addition, TiO_2 has a positive τ_f value (~450 ppm/°C) [19], which appeared in V_2O_5-doped $ZnTiO_3$ ceramics sintered at 900 °C because of the decomposition of $ZnTiO_3$. Single-phase $ZnTiO_3$ ceramics has a negative τ_f value (−55 ppm/°C) [5]. In V_2O_5-doped $ZnTiO_3$ ceramics, the amounts of the second phases, such as TiO_2 and $Zn_3V_2O_8$, were so small that they were not detected by

Table 2 Dielectric properties of V_2O_5-doped $ZnTiO_3$ ceramics.

Composition	Sintering temperature (°C)	ε_r	F	$Q\times f$ (GHz)
$ZnTiO_3$+0.25 wt%V_2O_5	900	19.5	7.349	2,746
$ZnTiO_3$+0.5 wt%V_2O_5	900	20.3	7.763	5,240
$ZnTiO_3$+0.75 wt%V_2O_5	900	20.6	8.169	8,873
$ZnTiO_3$+1.0 wt%V_2O_5	900	21.3	8.887	8,061

XRD, so it can be deduced that V_2O_5-doped $ZnTiO_3$ ceramics sintered at 900 °C exhibited a negative τ_f value. But an assured τ_f value needs further experiments.

Q value was found to decrease for V_2O_5-doped zinc metatitanate-based ceramics in microwave region as compared with single-phase hexagonal $ZnTiO_3$ ceramics. Microwave dielectric loss is mainly caused by second phases, oxygen vacancies, grain sizes and densification or porosity [20, 21]. From Fig. 4, it had been noticed that the volume fraction of the second phase Zn_2TiO_4 was 7% in the samples sintered at 900 °C with 1 wt% V_2O_5 addition (the value was calculated from the intensities of the major peak of each phase by a profile-fitting program). The cubic spinel Zn_2TiO_4 ceramics have fairly bad microwave dielectric properties; its $Q\times f$ is only 2,200 GHz. Hence, even a small quantity of Zn_2TiO_4 was sufficient to cause deterioration in the dielectric properties of zinc metatitanate-based ceramics. The merit of conventional mixed-oxide method combined with a semi-chemical processing lies in simple processes and using inexpensive reagents as compared with sol–gel processing. The best properties were: ε_r=20.6, $Q\times f = 8,873$ GHz, when the 0.75 wt%-V_2O_5 doped ceramics was sintered at 900 °C. Golovchansky et al. [5] prepared single-phase hexagonal $ZnTiO_3$ ceramics by sol–gel processing. When sintered at 920 °C, The best properties were: ε_r=19, $Q\times f = 33,000$ GHz, τ_f=−55 ppm/°C. The sintering temperature of 920 °C is believed still higher for LTCCs using Ag as inner electrodes; because the melting temperature of Ag will be decreased to <920 °C by organic paste in industrial scale [22]; moreover, Ag and Pd can not only diffuse into the ceramics, but also be incorporated into the oxide lattice during the high-temperature sintering and changing the properties of the materials [23], so lowering the sintering temperature of ceramics is important. In addition, sol–gel processing needs especial equipment and expensive raw materials. In present investigation, the low-fired (≤900 °C) zinc titanate ceramics with V_2O_5 addition combined with a semi-chemical processing can be prepared by simple techniques, and the raw materials used corresponding to Zn and Ti are relatively cheaper compared to other Ta or Nb-based materials [24, 25]. Therefore, the 0.75 wt%-V_2O_5 doped zinc titanate ceramics is a promising candidate in the field of multi-layer devices requiring low sintering temperature (≤900 °C).

4 Conclusions

The sintering temperature of zinc titanate ceramics could be lowered from 1,150 to 930 °C by using a semi-chemical processing; and with adding V_2O_5 addition, the densification temperature of $ZnTiO_3$ ceramics could be reduced to 875 °C. Zinc titanate ceramics with 1 wt% V_2O_5 addition can be well-sintered to approach 96% theoretical density below 900 °C due to liquid phase sintering. At the same time, the addition of V_2O_5 lowered the phase transition temperature from hexagonal $ZnTiO_3$ phase to cubic Zn_2TiO_4. The second phase and the nonuniformity of grain morphology affect the dielectric properties. The Q value decreases for V_2O_5-doped zinc metatitanate-based ceramics in microwave region as compared to single-phase hexagonal $ZnTiO_3$ ceramics. The best properties were: ε_r=20.6, $Q\times f = 8,873$ GHz, when the 0.75 wt%-V_2O_5 doped ceramics was sintered at 900 °C.

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