

Low-temperature sintering and microwave dielectric properties of ZnTiO₃-based LTCC materials

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Published online: 23 March 2007
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Abstract The low-temperature sintered microwave dielectric ceramics with composition of ZnTiO₃-0.25TiO₂ were prepared by adding a small amount of low-melting compounds CuO-V₂O₅-Bi₂O₃ (CVB). The phase relationship and dielectric properties as a function of sintering temperature and the additional amount were studied. It is demonstrated that the addition of low-melting CVB can suppress the formation of Zn₂TiO₄ at low temperature, but decrease the decomposition temperature of ZnTiO₃. The sintering temperature has a significant effect on the stability of ZnTiO₃ and dielectric properties of sintered ceramics. CVB addition can promote the densification of ceramics through liquid-phase sintering. The dense 2wt% CVB-doped ZnTiO₃-0.25TiO₂ ceramics prepared at 850 °C have excellent dielectric properties of $\epsilon=30$, $Q \times f=32,000$ GHz, and $\tau_f=+12$ ppm/°C.

Keywords ZnTiO₃ ceramics · Microwave dielectrics · Dielectric properties · Low-temperature sintering · LTCC

1 Introduction

Multilayer ceramic technologies based on low-temperature cofired ceramics (LTCC) provide a platform for high level of functional integration. Three crucial factors such as high dielectric constants, high quality factors, and near zero temperature coefficient of resonant frequency are a base for

microwave devices. Another requirement for multilayer devices and passive integration is the cofiring of dielectric ceramics with silver electrode, which has high conductivity and low melting temperature. Thus, the dielectric ceramics must be sintered at temperature lower than 950 °C.

ZnTiO₃ ceramics having excellent dielectric properties and low sintering temperature are promising materials for RF/microwave multilayer devices [1, 2]. However, the decomposition of ZnTiO₃ at >945 °C takes place to form Zn₂TiO₄ and TiO₂, detrimental to the dielectric properties [3]. So, some technique route should be sought to decrease the decomposition of hexagonal ilmenite phase, ZnTiO₃ [4–6].

In the present works, some low-melting compounds of CuO-V₂O₅-Bi₂O₃ (CVB) were added to lower sintering temperature of ZnTiO₃ ceramics, so as to suppress the decomposition of ilmenite phase. The phase relationship and dielectric properties as a function of sintering temperature and addition amount were investigated.

2 Experimental procedure

The low-temperature sintered ZnTiO₃-based ceramics were prepared by solid-state reaction route. The starting materials were high-purity oxide powders (>99.9%) of ZnO and TiO₂, which were mixed according to the chemical composition of ZnTiO₃ + 0.25TiO₂ and then calcined at 850 °C for 2 h. A small amount of low-melting compounds, CVB, was added into the resultant powder, and then ball-milled in a polyethylene bottle for 4 h with zirconia balls using ethanol as medium, and then dried. Then the powders were uniaxially pressed into pellets, 4–5 mm thick and 10 mm in diameter. The samples were sintered at 750–950 °C for 2 h.

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The crystal structures of sintered samples were analyzed by X-ray diffractometer (Rigaku D/Max) using $\text{CuK}\alpha$ radiation. The microstructures of samples were observed by scanning electron microscopy (SEM, Hitachi S450). The microwave dielectric constants were measured using the Hakki-Coleman dielectric resonator method as modified and improved by Courteny [7] by an HP8720ES network analyzer in the frequency range of 8–10 GHz. The quality factor ($Q \times f$) values of sintered samples were measured using transmission cavity method using a brass cavity and a quartz supporter [8]. Temperature coefficients of resonant frequency (τ_f) were measured in the temperature range of 20–100 °C.

3 Results and discussions

To identify the phase formation and its dependence on temperature, the oxides mixture was heat-treated at temperature from 700 to 850 °C. The development of crystal phases in ZnO-TiO₂ system was studied by using X-ray diffraction (XRD) techniques. Figure 1 shows the XRD patterns for heat-treated powders at temperatures from 700 to 800 °C. It could be seen that the resultant powder remains a mixture of ZnO and TiO₂ oxides at 700 °C. At 750 °C, the cubic spinel Zn₂TiO₄ and hexagonal ilmenite ZnTiO₃ were formed. Thus, the resultant powder was a mixture of spinel, ilmenite, and rutile phases. With increasing temperature to 850 °C (shown in Fig. 2), the phase relationship does not change significantly. No solid-solution phase, Zn₂Ti₃O₈, was detected in all temperature range. This result was different from that of Kim et al. [1]; in their report the spinel phase Zn₂TiO₄ was formed from decomposition of Zn₂Ti₃O₈. The present result suggested that the cubic spinel phase, Zn₂TiO₄, was formed at very low temperature, implying that the pure ilmenite phase

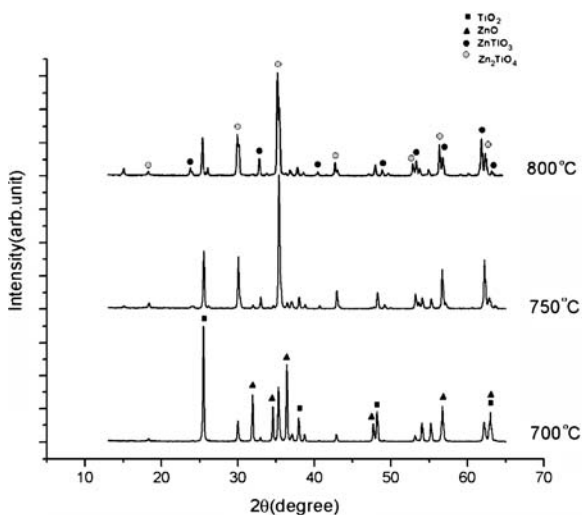


Fig. 1 XRD patterns for calcined powders at different temperatures

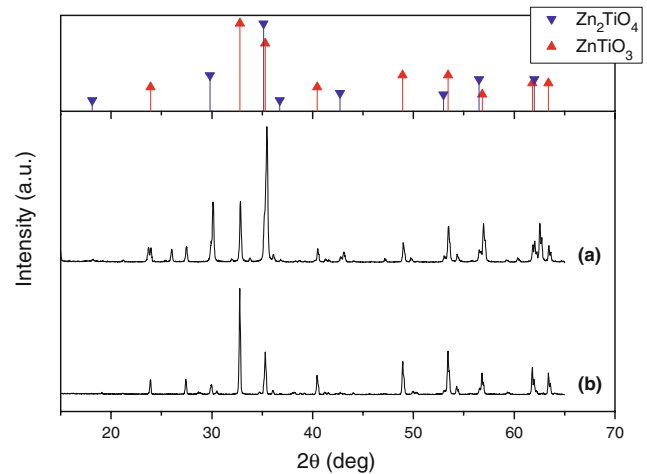


Fig. 2 XRD patterns for calcined powder at 850 °C (a) and sintered samples with CVB addition at 850 °C (b)

ZnTiO₃ was difficult to synthesize via conventional mixed oxides route.

Figure 2 shows the XRD patterns for heat-treated powder at 850 °C and sintered samples with addition of CVB at 850 °C. It is interesting to note that CVB addition can promote the phase transition from spinel to ilmenite. It is therefore demonstrated that the addition of low-melting CVB can suppress the formation of Zn₂TiO₄ in ZnO-TiO₂ ceramics. This result is similar to the observation of Lee and Lee [6] in Bi₂O₃-doped (ZnMg)TiO₃-TiO₂ system, in which Bi₂O₃ addition could suppress the formation of Zn₂TiO₄.

Figure 3 shows the XRD patterns for samples sintered at temperatures from 850 to 950 °C. It could be seen that ZnTiO₃ existed only at temperatures lower than 870 °C. Above 890 °C, however, ZnTiO₃ decomposed completely into Zn₂TiO₄ and TiO₂. The result indicates that the decomposition temperature of ZnTiO₃ decreases from 945

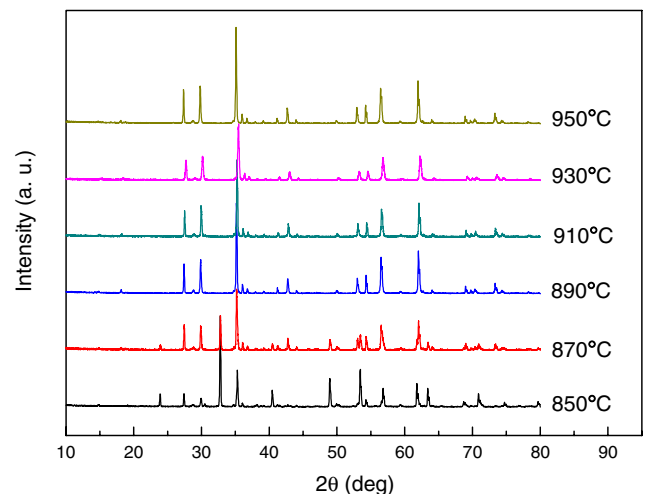
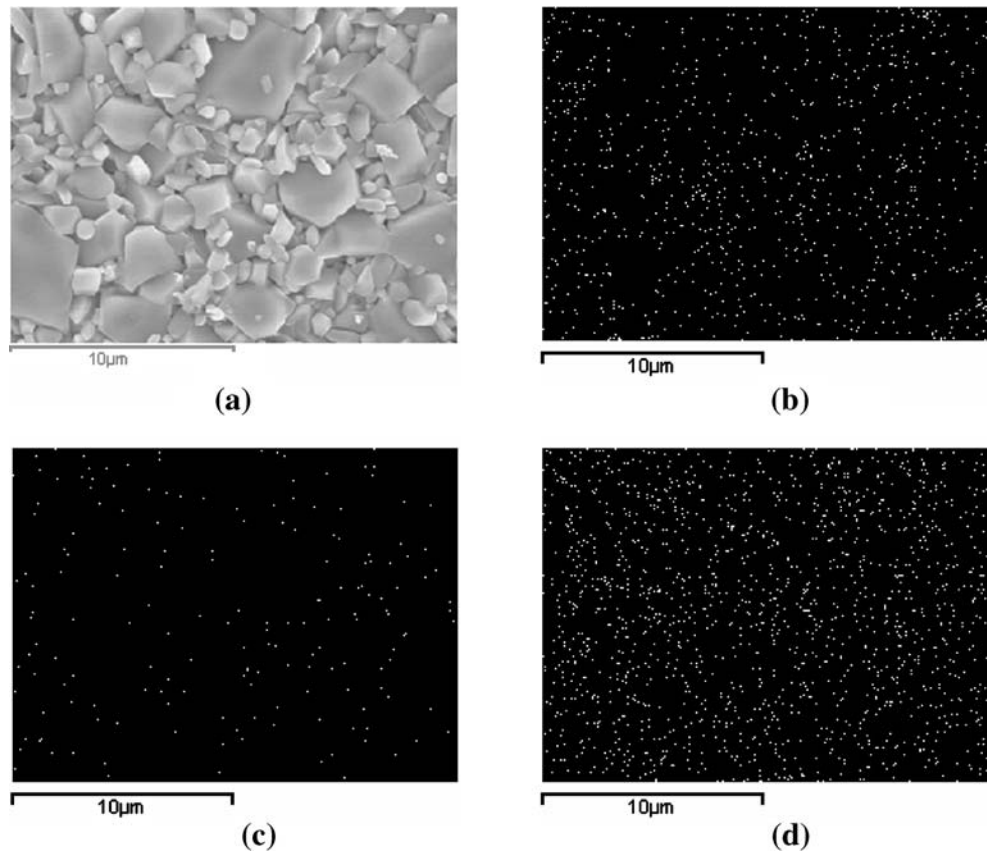


Fig. 3 XRD patterns for samples sintered at temperatures from 850 to 950 °C

Fig. 4 (a) SEM image and element distribution of 4wt% CVB-doped samples (b) Bi, (c) Cu, and (d) V



to 890 °C due to the CVB addition. The decrease in stability of ZnTiO₃ may be caused by the existence of CuO, V₂O₅, and Bi₂O₃. In fact, it was inevitable that these oxides could enter into the lattice of ZnTiO₃ during the sintering. For example, Cu²⁺ and V⁵⁺ could substitute some of the Zn²⁺ and Ti⁴⁺ in ZnTiO₃, respectively, due to the similar ionic size. For V⁵⁺ substitution, some cation vacancies V'_{Zn} may be formed for the charge compensation. These cation vacancies may be responsible for the decrease in stability of ZnTiO₃.

Figure 4(a) shows SEM images of 4wt% CVB-doped samples sintered at 850 °C for 2 h. To determine the distribution of CVB addition in sintered body, the element distribution was recorded by EDS analysis and the results are shown in Fig. 4(b)–(d). It could be seen from Fig. 4(a) that the dense ceramic body could be obtained at sintering temperature of 850 °C, indicating that the CVB addition could effectively promote the densification of ZnTiO₃-TiO₂ ceramics at low temperatures. The distribution of the CVB addition in sintered body was not uniform. It could be recognized that the elements of addition mostly existed at

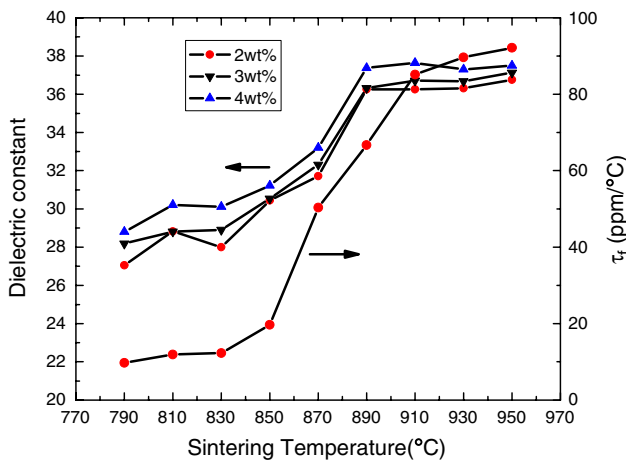


Fig. 5 Dielectric constant and τ_r as a function of sintering temperature

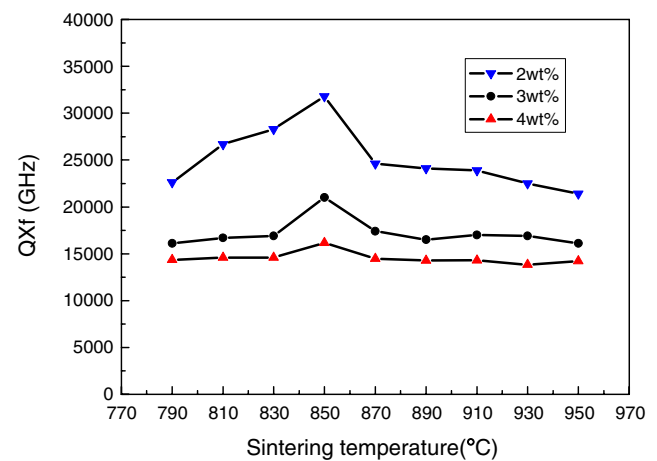


Fig. 6 $Q \times f$ as a function of sintering temperature

grain boundaries. This implies that CVB addition may promote densification by liquid-phase sintering. Relative to Cu and Bi elements, V element distributed more uniformly across the grains and grain boundaries in the sintered body. It suggests that V ions enter into lattice of ZnTiO_3 more easily.

The dielectric constant (ϵ) and temperature coefficient of resonant frequency (τ_f) as a function of sintering temperature are shown in Fig. 5. Due to the phase transition with sintering temperature discussed above, dielectric constant and τ_f depend significantly on sintering temperature. Below 850 °C, dielectric constant and τ_f are almost independent of sintering temperature. In the range from 850 to 890 °C, they increase markedly, i.e., dielectric constant from ~ 29 to 36 and τ_f from $\sim +10$ to $+90$ ppm/°C. Increasing temperature further, both of them do not change with sintering temperature. The marked change of dielectric constant and τ_f with sintering temperature can be attributed to the phase transition. The decomposition of ZnTiO_3 into Zn_2TiO_4 and TiO_2 is responsible for the change in dielectric properties because of high dielectric constant and τ_f value of rutile phase. Therefore, it is necessary to reduce the sintering temperature lower than 850 °C so as to lead ceramics with good dielectric properties.

The $Q \times f$ as a function of sintering temperature is shown in Fig. 6. It can be seen that CVB addition has a remarkable effect on $Q \times f$ value. The $Q \times f$ value decreases obviously as the amount of CVB addition increases from 2 to 4wt%. Relative to dielectric constant and temperature coefficient, the temperature dependence of $Q \times f$ is small, especially for 3 and 4wt% CVB-doped specimens. A $Q \times f$ maximum occurs at sintering temperature of 850 °C for all three compositions. Therefore, for ceramics with 2wt% CVB addition sintered at 850 °C, the favorable microwave dielectric properties $\epsilon_r = 30$, $Q \times f = 32,000$ GHz, and $\tau_f = +12$ ppm/°C were exhibited.

4 Conclusions

The low-melting compounds, $\text{CuO-Bi}_2\text{O}_3\text{-V}_2\text{O}_5$ (CVB), could promote the densification of $\text{ZnTiO}_3\text{-}0.25\text{TiO}_2$ ceramics at a temperature as low as 850 °C through liquid-phase sintering. The CVB addition could be also beneficial to the formation of ZnTiO_3 at low temperature, but decreased the decomposition temperature from ~ 945 °C for pure ZnTiO_3 to 890 °C for 2wt% CVB-doped ZnTiO_3 . Due to the decomposition of ZnTiO_3 at high temperature, the dielectric constant and τ_f depended remarkably on sintering temperature. Therefore, the low-temperature sintering at ≤ 850 °C is favorable for ZnTiO_3 -based LTCC materials.

Acknowledgement This work has been financially supported by the National Major Fundamental Research Project (grant no. 2002CB613307), the National High-Tech Development Project, and Specialized Research Fund for the Doctoral Program of Higher Education (no. 20040003003).

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