

Effects of $\text{ZnO-xV}_2\text{O}_5$ substitution on the microstructure and microwave dielectric properties of ZnNb_2O_6 ceramics

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Abstract The $\text{ZnO-xV}_2\text{O}_5$ substituted ZnNb_2O_6 ceramics with chemical formula $\text{Zn}(\text{Nb}_{0.9}\text{V}_x)_2\text{O}_{5.5+5x}$ ($0 < x \leq 0.10$) were prepared by solid-state reaction route. The densities, microstructures and microwave dielectric properties were investigated according to the different substitution amount of V_2O_5 and sintering temperature. A small amount of substitution of $\text{ZnO-xV}_2\text{O}_5$ was effective to lower sintering temperature of ZnNb_2O_6 ceramics from 1,150 °C to 900 °C. The V_2O_5 substitution led to growth of rod-like grains with the help of liquid phase formed from ZnO and V_2O_5 . The dielectric properties depended largely on the amount of V_2O_5 substitution and sintering temperature. The dense ceramics with $x=0.05$ were obtained at 950 °C, which had excellent dielectric properties: $\epsilon_r=24$, $Q \times f=72,800$ GHz and $\tau_f=-63.5$ ppm/°C. The interface analysis for cofired multilayer composites composed of the present LTCC and metal Ag demonstrated good co-firing chemical compatibility at co-sintering temperature.

Keywords ZnNb_2O_6 · Microwave dielectric ceramics · Dielectric properties · Low temperature sintering · LTCC

1 Introduction

Recently, extensive attention was paid to multilayer microwave devices due to the device miniaturization and

the rapid progress of mobile communication systems. Therefore, the development of low-temperature co-fired ceramics (LTCC) have been stimulated by the benefits offered for the fabrication of miniature multilayer devices involving the co-firing of dielectric and highly conductive metal, such as silver and copper [1, 2]. In addition, investigations on microwave dielectric ceramics with high quality factors have become an important research trend due to their higher applied frequencies, especially in satellite communications.

In previous report, ZnNb_2O_6 ceramics have been found as good candidate dielectrics due to their low sintering temperature (1,150 °C) and excellent dielectric properties ($Q \times f=87,300$ GHz, $\epsilon_r=25$ and $\tau_f=-56$ ppm/°C) [3, 4]. Kim et al. have reported that 5 wt.% CuO could lower the sintering temperature from 1,150 °C to 900 °C [5]. In our previous works, we have found that CaF_2 and $\text{CuO-Bi}_2\text{O}_3\text{-V}_2\text{O}_5$ additions were also effective to lower sintering temperature of ZnNb_2O_6 ceramics [6, 7]. In addition, Wee et al. have reported the microwave dielectric properties of low-fired ZnNb_2O_6 ceramics with BiVO_4 additions [8]. However, too much addition introduced would decrease the microwave dielectric properties, especially the quality factor.

In the present work, we focus on the research of ZnNb_2O_6 ceramics co-doped with different amount of ZnO and V_2O_5 because some compounds in $\text{ZnO-V}_2\text{O}_5$ system have high quality factors and low sintering temperature. Therefore, we supposed that ZnNb_2O_6 ceramics co-doped with ZnO and V_2O_5 may have low sintering temperature combining with excellent microwave properties [9]. In this paper, we investigated the possibility of lowering the sintering temperature of ZnNb_2O_6 ceramics by co-substituting with ZnO and V_2O_5 according to different substitution amount.

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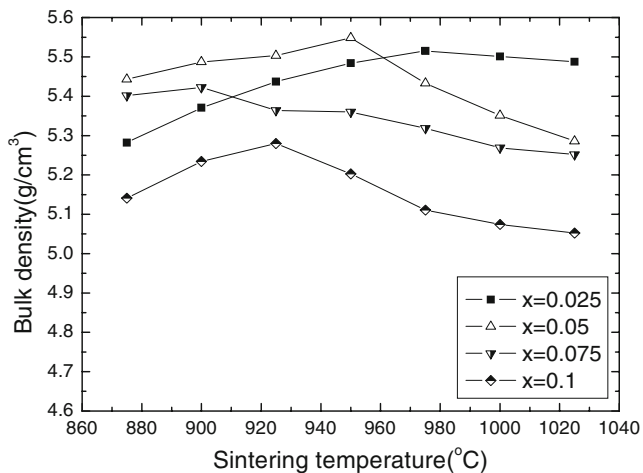


Fig. 1 Bulk densities of substituted ZnNb_2O_6 ceramics with different x as a function of sintering temperature

2 Experimental procedure

The novel $\text{ZnO}-x\text{V}_2\text{O}_5$ substituted ZnNb_2O_6 microwave dielectric ceramics with chemical formula $\text{Zn}(\text{Nb}_{0.9}\text{V}_x)_2\text{O}_{5.5+5x}$ ($0 < x \leq 0.10$), noted as ZNV for short, were prepared by solid-state reaction route. The starting materials were high-purity oxide powders (>99.9%) of ZnO , Nb_2O_5 and V_2O_5 , which were mixed according to the chemical formula above and then calcined at 850°C for 2 h. The resultant powders were ball-milled in a polyethylene bottle for 6 h with zirconia balls using ethanol as medium and

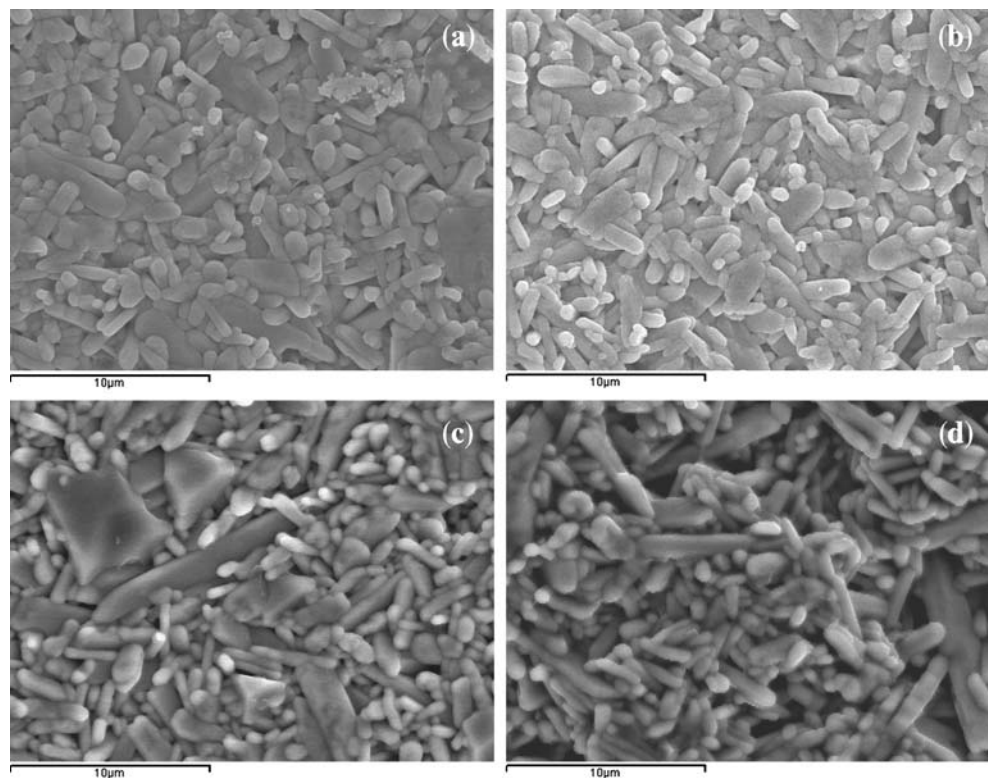
then dried. Then the powders were uniaxially pressed into pellets 4–5 mm thick under the pressure of 100 MPa using a 10 mm diameter die. The samples were sintered at 875°C – $1,025^\circ\text{C}$ for 2 h with a heating rate of 5°C min^{-1} and then cooled to room temperature.

The bulk densities of the sintered ceramics were measured by Archimedes method. The crystal structures of sintered samples were analyzed by X-ray diffractometer (Rigaku D/Max) using $\text{CuK}\alpha$ radiation. The samples were polished and thermal etched at 850°C for 30 min. Then microstructures 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 Courtney et al. by HP8720ES network analyzer in the frequency range of 8–10 GHz [10]. The $Q \times f$ values of sintered samples were measured using transmission cavity method using a brass cavity and a quartz supporter [11]. Temperature coefficients of resonant frequency (τ_f) were measured in the temperature range of 20 to 100°C .

3 Results and discussions

Figure 1 shows the bulk densities of $\text{Zn}(\text{Nb}_{0.9}\text{V}_x)_2\text{O}_{5.5+5x}$ ceramics as a function of sintering temperature. It could be seen that the densities of all the samples first increased with increment of sintering temperature, and then decreased with

Fig. 2 Typical SEM images of $\text{Zn}(\text{Nb}_{0.9}\text{V}_x)_2\text{O}_{5.5+5x}$ ceramics with different x , (a) $x=0.025$, (b) $x=0.05$, (c) $x=0.075$ and (d) $x=0.10$



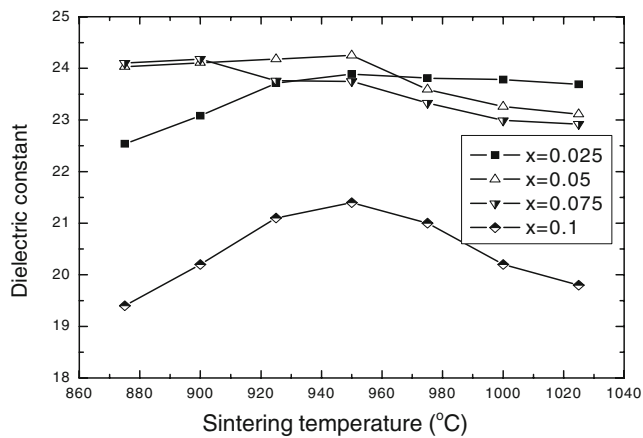


Fig. 3 Dielectric constant of samples with different x as a function of sintering temperature

increasing temperature further. A density maximum appeared for all compositions. It could be also seen that the maximum density shifted towards lower sintering temperature, i.e. from 980 °C for $x=0.025$ to 900 °C for $x=0.075$. Different from above trend, the maximum density appeared at 920 °C for $x=0.1$. These suggested that a small amount of V substitution for Nb was effective to lower the sintering temperature of ZnNb_2O_6 ceramics. This may be attributed to the low melting temperature of $\text{ZnO} \cdot x\text{V}_2\text{O}_5$, which is lower than 800 °C. The densification process could be considered as the liquid phase sintering, in which the process may be promoted by the liquid phase formation from ZnO and V_2O_5 at high temperature. The decrease in densities with increasing temperature further may be attributed to the evaporation of ZnO and V_2O_5 .

XRD analysis showed that all samples with different x were mainly composed of single phase with columbite structure. No secondary phase could be detected in XRD patterns.

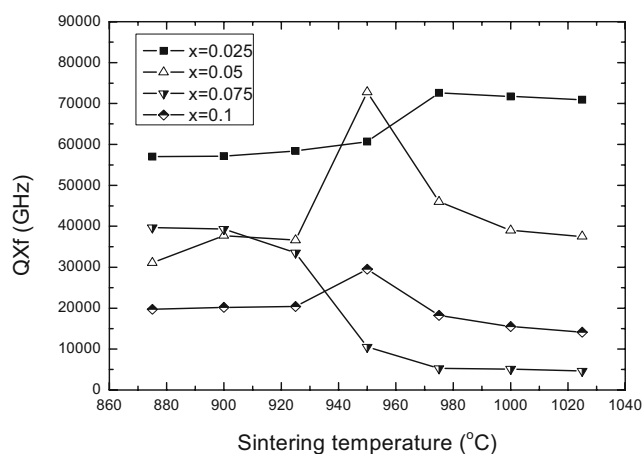


Fig. 4 $Q \times f$ values of samples with different x as a function of sintering temperature

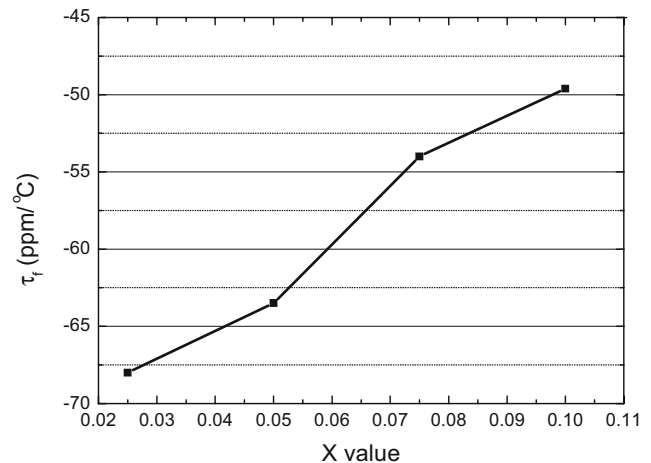


Fig. 5 The temperature coefficient of resonant frequency (τ_f) of samples sintered at 950 °C as a function of x

Figure 2 shows typical SEM images of samples with different x sintered at 950 °C for 2 h. From these images, it could be seen that the introduction of $\text{ZnO} \cdot x\text{V}_2\text{O}_5$ would obviously lead to rod-like grains and the grain size grew larger with more V_2O_5 content. For $x=0.025$ and 0.05, the dense ceramics had rod-like grains with 3–5 μm in length and $\sim 1 \mu\text{m}$ in diameter, while for $x=0.075$ and 0.1, some abnormal rod-like grains with 7–10 μm in length and 2–3 μm in diameter appeared with increased porosity. The formation and growth of rod-like grains demonstrated that the grains grew with the help of liquid phase at sintering temperature. The occurrence of pores was responsible for the decrease in density for $x=0.075$ and 0.1, shown in Fig. 1.

Figure 3 shows the dielectric constant (ϵ_r) of samples with different x as a function of sintering temperature. Compared with Fig. 1, the trend of dielectric constant with

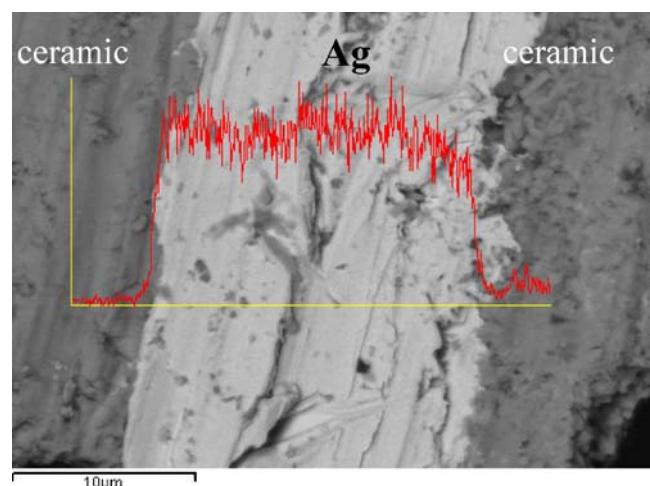


Fig. 6 EDS analysis of Ag distribution across the interface of dielectric and metal Ag in multilayer composites

sintering temperature was similar to that of density, indicating that dielectric constant (ϵ_r) were largely related with sample densification. Therefore, sintering behavior predominated both bulk density and dielectric constant. Among these samples, sample with $x=0.1$ had much lower ϵ_r compared with other samples, suggesting that this dopant composition would have least sintering aid effect and lead to largest deterioration of microwave dielectric properties.

The $Q \times f$ values of samples with different x as a function of sintering temperature were shown in Fig. 4. Once again, samples with $x=0.1$ showed different trend compared with other samples. This sample reached maximum $Q \times f$ values at relatively low temperatures and then decreased remarkably with increasing sintering temperatures. In contrast, $Q \times f$ values of other samples first increased with sintering temperature increment, then decreased gradually after reaching the maximum values. Sample with $x=0.05$ sintered at 950 °C had the largest $Q \times f$ value (72,800 GHz). The large $Q \times f$ values of the present low-temperature sintered ceramics may be benefited from the higher density and better microstructural development.

Figure 5 shows the temperature coefficient of resonant frequency (τ_f) of samples sintered at 950 °C as a function of x . It could be seen that the τ_f values increased towards zero, i.e. from -68 ppm/°C for $x=0.025$ to -50 ppm/°C for $x=0.1$. It has been reported that the τ_f value is related with the titling of octahedrons in perovskite-related structure [12]. These results suggested the V substitution for Nb in ZnNb_2O_6 could cause the titling of octahedrons. This may be attributed to the smaller ionic radius of V^{5+} (0.054 nm) than Nb^{5+} (0.064 nm) and B-site vacancies caused by non-stoichiometric substitution.

To investigate the co-firing chemical compatibility between dielectric and metal electrode, multilayer samples with alternating dielectric and Ag conductor were prepared by tape casting and printing process. After being sintered at 900 °C, the fractured section of samples were polished and characterized by SEM technique. Figure 6 shows the EDS analysis of Ag distribution across the interface of samples with $x=0.075$. It could be seen that Ag-ceramics interface exhibited distinct boundary and showed no obvious chemical reaction and interface diffusion between ceramic and Ag layers, indicating that $\text{ZnO} \cdot x\text{V}_2\text{O}_5$ -doped ZnNb_2O_6 ceramics would be a favorable candidate for LTCC applications.

4 Conclusions

A small amount of substitution of V for Nb in ZnNb_2O_6 as chemical formula $\text{Zn}(\text{Nb}_{0.9}\text{V}_x)_2\text{O}_{5.5+5x}$ ($0 < x \leq 0.10$) was effective to lower sintering temperature of ZnNb_2O_6 ceramics, which could be densified in temperature range 900–950 °C. The $\text{ZnO} \cdot x\text{V}_2\text{O}_5$ substitution led to growth of rod-like grains with the help of liquid phase formed from ZnO and V_2O_5 . The dielectric constant (ϵ_r) and $Q \times f$ values were largely related with sample densification. The τ_f values increased towards zero with increasing V_2O_5 content, i.e. from -68 ppm/°C for $x=0.025$ to -50 ppm/°C for $x=0.1$. The dense ceramics with $x=0.05$ were obtained at 950 °C, which had excellent dielectric properties: $\epsilon_r=24$, $Q \times f=72,800$ GHz and $\tau_f=-63.5$ ppm/°C. The large $Q \times f$ values of the present LTCCs might be benefited from the higher density and better microstructural development. The present LTCC materials have good co-firing chemical compatibility with metal Ag electrode at co-sintering temperature.

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