Low temperature sintered $ZnNb_2O_6$ microwave dielectric ceramics doped with ZnO-V_2O_5 additions

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Multilayer microwave devices have gained much attention recently due to their wide applications in bandpass filters, resonators, and antenna duplexers for microwave mobile communications. In multilayer structures, dielectric ceramics with low sintering temperature are required as they have to be cofired with low loss conductors such as silver and copper [1]. $ZnNb_2O_6$ ceramics have been found as good candidate dielectrics due to their low sintering temperature (1150 °C) and excellent dielectric properties ($Q\times f = 87\ 300$ GHz, $\varepsilon_r = 25$, and $\tau_f = -56$ ppm/°C) [2, 3]. It has been reported that the sintering temperature of $ZnNb_2O_6$ ceramics could be lowered further to 900 °C by addition of some low-melting compounds such as CuO, CaF_2, CuO-Bi_2O_3-V_2O_5, V_2O_5, and $BiVO_4$ [4–7]. However, too much addition introduced would decrease the microwave dielectric properties, especially the quality factor.

Our works focused on the research of $ZnNb_2O_6$ ceramics doped with different amount of ZnO and V_2O_5 because some compounds in ZnO-V_2O_5 system have high quality factors and low sintering temperature. Therefore, we supposed that $ZnNb_2O_6$ ceramics codoped with ZnO and V_2O_5 may have low sintering temperature combining with excellent microwave properties [8]. In this letter, we investigated the low-temperature sintering of $ZnNb_2O_6$ ceramics by codoping with ZnO and V_2O_5 according to $ZnO\cdot V_2O_5$ and $2ZnO\cdot V_2O_5$, and carried out a comparative study on the influence of two additions on the microstructure and dielectric properties of $ZnNb_2O_6$ ceramics.

The ceramics with chemical formulas of $0.9\,ZnNb_2O_6$-$0.1\,ZnO\cdot V_2O_5$, and $0.9\,ZnNb_2O_6$-$0.1[2ZnO\cdot V_2O_5]$ were prepared by solid-state reaction method. The starting materials were high-purity oxide powders (>99.9%) of ZnO, Nb_2O_5, and V_2O_5. They were mixed, ball-milled in alcohol for 2 hr and dried. The resultant powders were calcined at 800 °C for 2 hr. After ball milling with alcohol for 6 hr and drying, the powders were uniaxially pressed into pellets 4–5 mm thick under the pressure of 100 MPa, and then sintered at temperatures from 850 to 1050 °C.

The microwave dielectric constants (ε_r) and the temperature coefficient of resonant frequency (τ_f) were measured using the Hakki–Coleman dielectric resonator method as modified and improved by Kobayashi and Courteny *et al.* by HP8720ES network analyzer in the frequency range of 6–8 GHz [9–11]. The $Q \times f$ values of sintered samples were measured using transmission cavity method using a brass cavity and a quartz supporter [12]. Temperature coefficients of resonant frequency (τ_f) were measured in the temperature range of 20–100 °C.

The densities of the specimens were measured by the Archimedes method. Fig. 1 shows the bulk densities of $ZnNb_2O_6$ ceramics doped with $ZnO\cdot V_2O_5$ and $2ZnO\cdot V_2O_5$ as a function of sintering temperature. It could be clearly seen that the densification of two compositions was of great difference but had same trends. The samples doped with $2ZnO\cdot V_2O_5$ (ZNV-2 for short) had larger densities compared with samples doped with $ZnO\cdot V_2O_5$ (ZNV-1 for short), suggesting that the additions of $2ZnO\cdot V_2O_5$ had much better effect on the sintering behaviors and promoted the sintering process favorably. The densities of both compositions steadily increased with increasing sintering temperature and saturated at 925–950 °C. The densification temperature of ZNV-1 was lower than that of ZNV-2, which might be attributed to larger ZnO/V_2O_5 ratio.

The crystalline phases of the sintered samples were analyzed by X-ray diffraction (XRD). Fig. 2 shows the XRD patterns of ZNV-1 and ZNV-2 specimens sintered at 950 °C. Analysis suggested that both ZNV-1 and ZNV-2 ceramics were single phase with a columbite structure and no secondary phase could be detected by XRD. This suggested that the solid solution of $ZnNb_2O_6$ with ZnV_2O_6 or $Zn_2V_2O_7$ may be formed during sintering.

The SEM photographs of ceramic surfaces of ZNV-1 and ZNV-2 specimens sintered at 950 °C were taken and shown in Fig. 3. It could be seen clearly that ZNV-2 has much less porosity than ZNV-1, which is in accordance with density curves. Moreover, the grains in both samples turned to be rodlike and the grain size of ZNV-1 was larger than that of ZNV-2. Since the amount of dopant ZnO-V_2O_5 is very limited, it could be speculated that the reason to these phenomenon might be caused by the low melting temperature (627 °C) of $ZnO\cdot V_2O_5$; whereas in ZNV-2, $2ZnO\cdot V_2O_5$ has relatively higher melting

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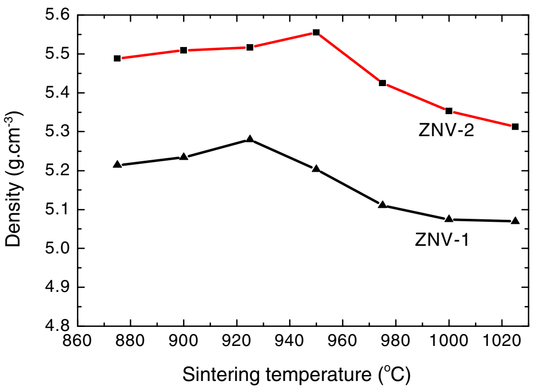


Figure 1 Bulk densities of ZNV-1 and ZNV-2 specimens as a function of sintering temperature.

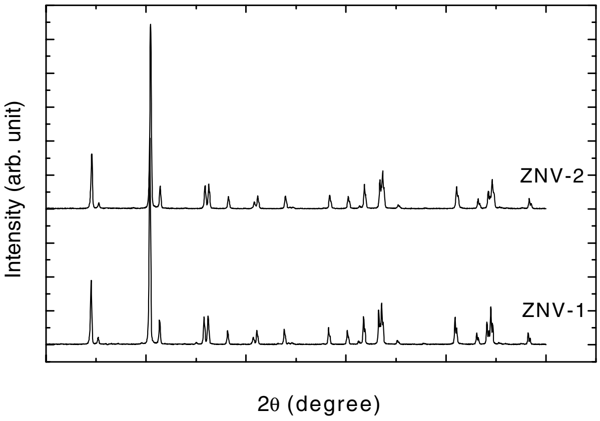


Figure 2 XRD patterns of ZNV-1 and ZNV-2 ceramics sintered at 950 °C for 2 hr.

TABLE I Dielectric constants and $Q \times f$ values of ZNV-1 and ZNV-2 ceramics sintered at different temperatures

ST (°)	ε_r-ZNV-1	ε_r-ZNV-2	$Q \times f$ values -ZNV-1(GHz)	$Q \times f$ values -ZNV-2(GHz)
875	19.4	24.0	20500	31060
900	20.2	24.1	20200	37700
925	21.1	24.2	20400	36600
950	21.4	24.3	29500	72800
975	21.0	23.6	18200	46000
1000	20.2	23.3	15500	39000
1025	19.8	23.2	13400	37500

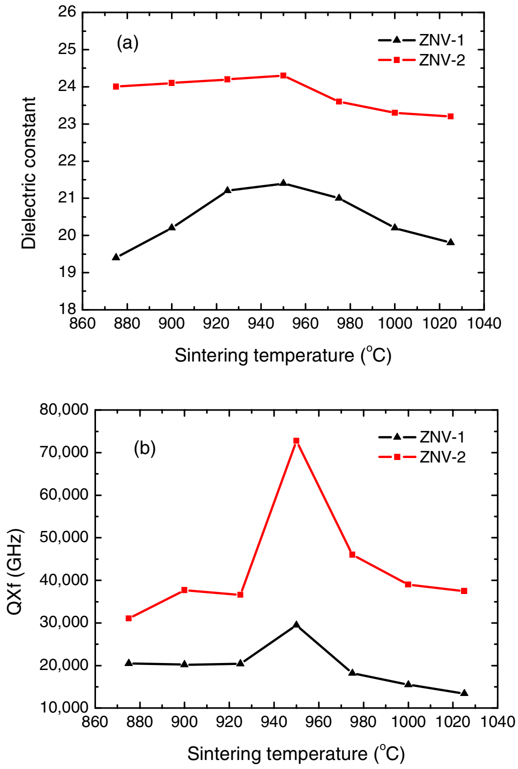
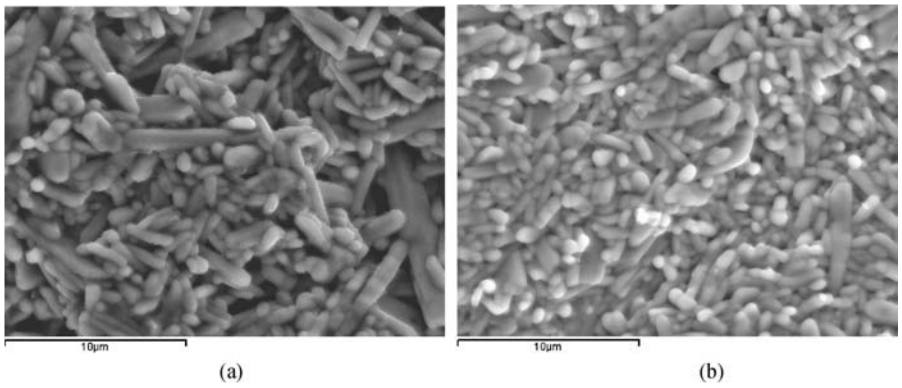


Figure 4 Microwave dielectric properties of two types of samples as a function of sintering temperature: (a) dielectric constant and (b) $Q \times f$ values.

temperature of 874 °C. In ZNV-1, $ZnO \cdot V_2O_5$ would generate liquid phase above 627 °C and promote grain growth much earlier, while $2ZnO \cdot V_2O_5$ in ZNV-2 could have liquid phase until 874 °C. Consequently, larger size of grains were produced in ZNV-1 and lead to more porosity in samples due to their rodlike shape.

The microwave dielectric properties of ZNV-1 and ZNV-2 ceramics sintered at different temperatures are listed in Table I, and shown in Fig. 4. The trends of dielectric constant (ε_r) with sintering temperature were almost consistent with those of densities, showing that ε_r were greatly influenced by densification. The temperature coefficient of resonant frequency (τ_f) of ZNV-1 and ZNV-2 ceramics sintered at 950 °C are –44 ppm/°C and –50 ppm/°C, respectively, showing no significant difference. However, $Q \times f$ values show great difference between ZNV-1 and ZNV-2, with the maximum values of 29 500 GHz and 72 800 GHz, respectively.

It has been reported that three mechanisms can be distinguished for dielectric loss at microwave



(a) (b)

Figure 3 SEM images of samples sintered at 950 °C for 2 hr, (a) ZNV-1, (b) ZNV-2.

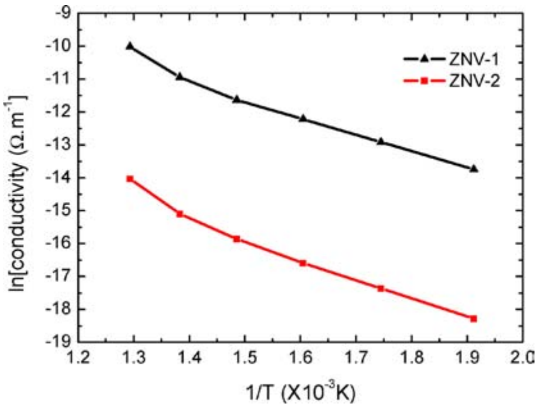


Figure 5 Electrical conductivity of ZNV-1 and ZNV-2 samples as a function of temperature.

frequencies. Intrinsic losses, i.e., losses in perfect (ideal) crystals, could be attributed to anharmonic lattice forces that mediate the interaction between the crystal's phonons [13]. Since the ideal crystal structures of ZNV-1 and ZNV-2 were both columbite structures, the large difference of $Q \times f$ values induced by intrinsic losses could be ignored. In this work, we paid more attention to the losses in real but homogeneous crystals caused by deviations from the perfect lattice periodicity, or defects such point defects, vacancies, or defect pairs that lead to quasi-bonded states. To clarify the possible effect of the concentration of crystal defects on the quality factors of samples, the electrical conductivity of ZNV-1 and ZNV-2 as a function of temperature were measured and shown in Fig. 5. It could be clearly seen that the conductivity of ZNV-2 was two orders of magnitude lower than that of ZNV-1, which indicated that the charged point defects, vacancies, or defect pairs in ZNV-2 were much less than those in ZNV-1. This phenomenon might be induced by the Zn^{2+} ions' volatilization. In ZNV-1 samples, Zn^{2+} ions would vaporize easily in the sintering process due to the lower melting temperature of $ZnO{\cdot}V_2O_5$, resulting in more charged vacancies in $ZnNb_2O_6$. Thus the concentrations of vacancies or defect pairs that might exist in ZNV-1 and ZNV-2 samples show significant difference and lead to different $Q \times f$ values.

Summarizing the above results, it could be concluded that $ZnNb_2O_6$ ceramics codoped with ZnO and V_2O_5 could effectively lower the sintering temperature from 1150 °C of pure $ZnNb_2O_6$ to below 950 °C. The comparative study showed that $2ZnO{\cdot}V_2O_5$-doped $ZnNb_2O_6$ ceramics have better dielectric properties than that of $ZnO{\cdot}V_2O_5$-doped samples. The low-temperature sintered $ZnNb_2O_6$ ceramics with large $Q \times f$ value of 72 800 GHz were obtained at 950 °C, which is a very satisfying result for multilayer microwave devices. The low temperature sintering of the present ceramics may also reduce the cost of the microwave devices.

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