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# Influence of $V_2O_5$ substitutions to $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ pyrochlore on sintering temperature and dielectric properties

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**Abstract**

The dielectric properties of the monoclinic zirconolite-like structure compound, $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ ($0 \leq x \leq 0.1$), were investigated. We found a small vanadium substitution ($x$) to $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ ceramics lowered sintering temperature from 950 to 850 °C. Low-temperature sintered $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ maintained high dielectric constant ($\varepsilon_r$), ∼80 and $Qxf$ value, ∼3000 at 6 GHz. By increasing $x$, second phase, bismuth vanadate ($Bi_4V_2O_{11}$) was detected. The formation of second phase is accompanied by a significant decrease in dielectric loss. It was found that $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ had two phases, one was for the stoichiometric composition and the other was for Bi-deficient composition. The chemical compatibility of silver electrode and $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ ($x = 0.005$) has also been investigated using SEM micrograph and EDS line scan of the interface between a silver electrode and the ceramic body, for low-temperature cofired ceramics (LTCC) applications.


*Keywords:* A. Sintering; B. X-ray methods; C. Dielectric properties; E. Capacitors

## 1. Introduction

Multilayer microwave components have been investigated to miniaturize passive devices for volume efficiency and low-temperature cofired ceramics (LTCC) are required for manufacturing multilayer components. In the case of LTCC, low-melting-point glasses are frequently added as sintering aids and the resulting ceramic-glass dielectrics can be cofired with low-resistivity conductor layers, such as silver. By the way, $V_2O_5$ has been also used as a sintering aid for the materials, such as $BiNbO_4$, $SrBi_2Nb_2O_7$, and $Pb(Zr,Ti)O_3$, etc. [1–3] because $V_2O_5$ has low melting temperature of ∼690 °C.

Recently, bismuth-based dielectric ceramics have been studied for its relatively low sintering temperature (less than 1000 °C) and high dielectric constant [4]. $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ ceramics with a dielectric constant in the range of 80–210, dielectric losses ($\tan\delta$) as low as $1 \times 10^{-4}$ at frequency of 1 MHz, were reported [5,6]. But not much work has been done on the sintering behaviors and related dielectric properties as LTCC materials.

In our study, as a way of lowering sintering temperature, Nb ion was substituted with V ion in $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ sample with $0 \leq x \leq 0.1$. The sintering behavior, phase, and microwave dielectric properties of low-temperature sintered $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ were examined.

## 2. Experimental procedure

The powders were prepared by conventional mixed oxide method. $Bi_2O_3$, ZnO, $Nb_2O_5$ and $V_2O_5$ (High Purity Chemical Lab., Japan) powders with 99.9% purity were weighed and mixed for 24 h with stabilized zirconia media and ethanol. The mixed powders were calcined at 800–900 °C for 2 h and then ball milled for 24 h. The milled powders were pressed into disks 8 mm in diameter and 2–4 mm thick under a pressure of 1000 kg/cm$^2$. Pellets were sintered at 750–1000 °C for 2 h in air with a heating rate of 5 °C/min. The bulk density of the sintered specimens was determined by the Archimedes method. Shrinkage of the specimens

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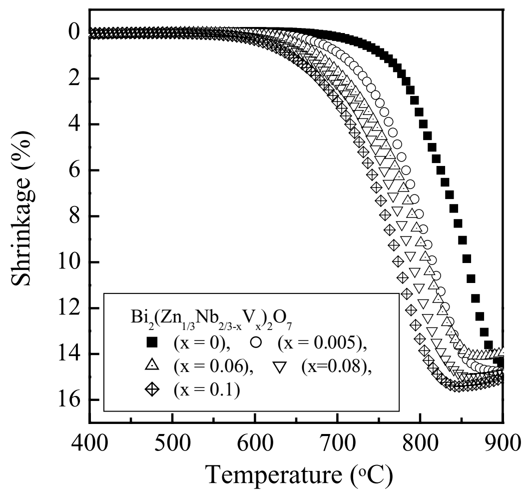



Fig. 1. Shrinkage curves of $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ samples as a function of sintering temperature.

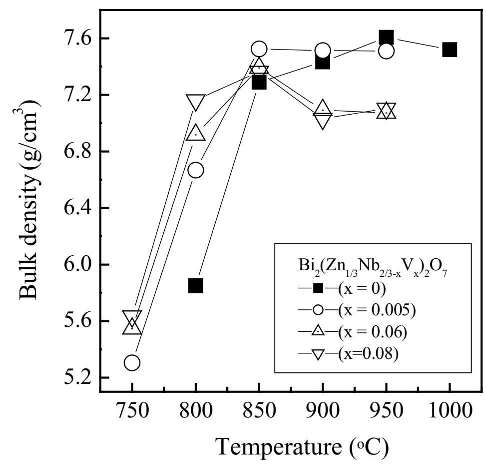



Fig. 2. Bulk density of $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ samples as a function of sintering temperature.

during heating was measured using a horizontal-loading dilatometer with $Al_2O_3$ rams and boats (Model DII, 420C, Netzsch Instruments, Germany). The formation of second phase was investigated using powder X-ray diffractometer (XRD: Model M18XHF, Mac Science Instruments, Japan). Polished and thermally etched surfaces of sintered specimens were examined using scanning electron microscopy (SEM: Model XL20, Philips, The Netherlands). EDS line scan was used to characterize the diffusion of silver and the interface reactions. The microwave dielectric properties of sintered samples were measured at *x*-band frequencies (8–10 GHz) using a network analyzer (model HP8720C, Hewlett Packard, Palo Alto, CA). To determine the dielectric properties in the frequency range from 1 kHz to 10 MHz, the capacitance and $\tan\delta$ were measured using an impedance/grain-phase analyzer (Model HP 4194A, Hewlett Packard, USA).

## 3. Results and discussion

### 3.1. Sintering behavior of $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$

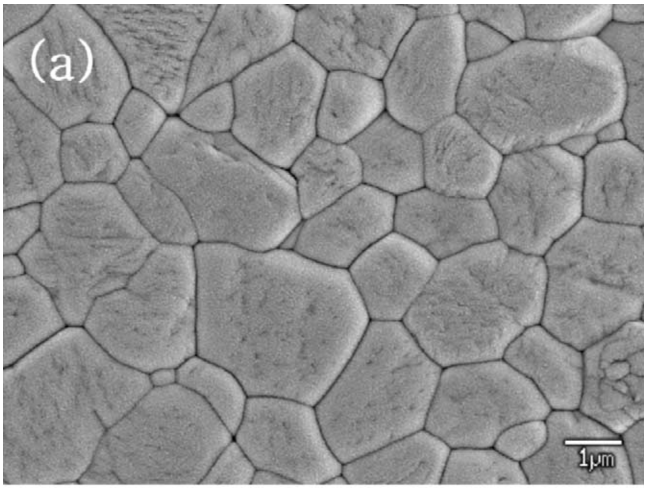
Fig. 1 shows shrinkage curves of the green compact of pure $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ (BZN) and $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ (BZNV). As can be seen in the figure, a rapid shrinkage occurred near 700 °C in the case of BZNV specimens. The onset of shrinkage occurred at lower temperatures as *x* increased. Shrinkage was initiated at approximately 800 °C for pure BZN specimen. This demonstrates that V substitution lowered the sintering temperature about 100 °C.

Generally, $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ is known to be sintered above 950 °C [4], but the bulk density of $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ with $x = 0.005$ sintered at 850 °C for 2 h reaches ~97% of the theoretical density of $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$, as shown in Fig. 2. Therefore, these results reveal that sintering of $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ below 900 °C is possible by $V_2O_5$ substitution, which indicates that cofiring with silver inner electrode can be done.

Fig. 3 shows scanning electron micrographs of BZN sintered at 950 °C and BZNV ($x = 0.005$) sintered at 850 °C for 2 h. The dense microstructure of BZNV ($x = 0.005$) was observed. No second phase or liquid phase was observed, and sintered $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ samples containing $V_2O_5$ had a smaller grain size (0.4–1 μm) compared with pure $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ sample sintered at 950 °C for 2 h.

### 3.2. Phase analysis

Fig. 4 shows the XRD patterns of the specimens of $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ ($x = 0.0 \sim 0.08$) sintered at 850 °C for 2 h. The structure of $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ belongs to a monoclinic zirconolite-like structure [*C*2/*c* (No. 15) space group, $a = 13.1037(9)$ Å, $b = 7.6735(3)$ Å, $c = 12.1584(6)$ Å, $\beta = 101.318(5)°$], reported by Levin et al. [7]. The range of solid-solution formation for $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ was very narrow ($x \approx 0.005$). Second phase of $Bi_4Vi_2O_{11}$ and $BiNbO_4$ were found at the specimens of $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ with $x \geq 0.01$. It is of interest that the splitting of the fundamental reflections near 27, 34, 37, 47, and 49° was abruptly decreased with increasing *x* (Fig. 5). One of the changes found with increasing *x* is the formation of Bi-based second phases, which indirectly indicates that the matrix phase of $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ was bismuth deficient state. In order to confirm this hypothesis, Bi-deficient phase of $Bi_{2-\delta}(Zn_{1/3}Nb_{2/3})_2O_{7-(3/2\delta)}$ ($\delta = 0.1$) was prepared and its XRD data is shown in Fig. 5. As can be seen in the figure, $Bi_{1.9}(Zn_{1/3}Nb_{2/3})_2O_7$ exhibited almost same fundamental reflections with $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ ($x = 0.08$). Therefore, it can be said that $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ exhibit two phases determined by the Bi stoichiometry.



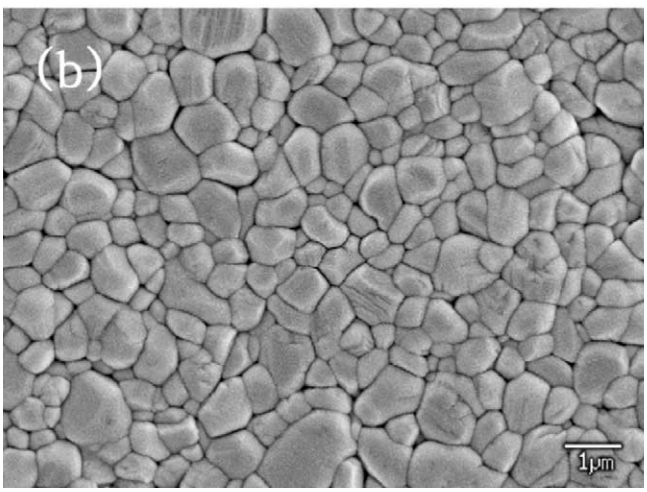




Fig. 3. SEM micrograph of the $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ specimen with (a) $x = 0.0$ sintered at 950 °C for 2 h, (b) $x = 0.005$ sintered at 850 °C for 2 h.

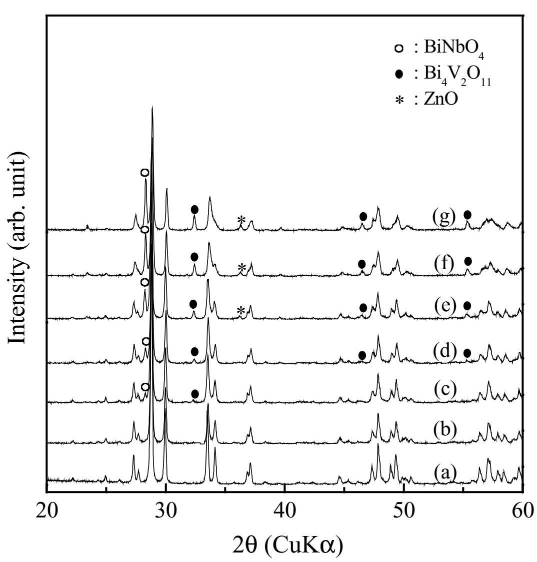



Fig. 4. XRD patterns of $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ sintered at 850 °C for 2 h: (a) $x = 0.0$, (b) $x = 0.005$, (c) $x = 0.01$, (d) $x = 0.02$, (e) $x = 0.04$, (f) $x = 0.06$, (g) $x = 0.08$.

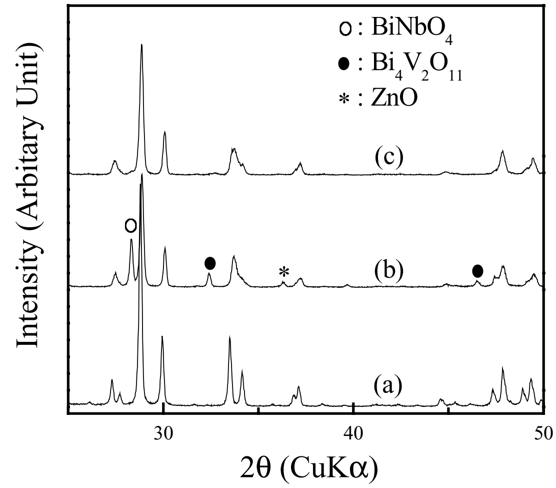



Fig. 5. XRD patterns of $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ for: (a) $x = 0.0$ sintered at 950 °C for 2 h, (b) $x = 0.08$ sintered at 850 °C for 2 h, (c) $Bi_{1.9}(Zn_{1/3}Nb_{2/3})_2O_{6.85}$ sintered at 850 °C for 2 h.

### 3.3. Microwave properties of low-fired $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$

The dielectric properties of $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ are summarized in Tables 1 and 2. $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ ($x = 0.001$) sintered at 850 °C had a dielectric constant ($\varepsilon_r$) of 78 and a $Qxf$ value of 3800 measured at x-band. By the way, the dielectric loss was increased at $x = 0.01$ and exhibited large increase at the specimens with $x \geq 0.02$. Because of large dielectric loss, dielectric properties of the specimens with $x \geq 0.02$ were measured at 1 MHz. This increase of dielectric loss was related to the formation of

Table 1
Microwave properties of $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ for $x = 0.0 \sim 0.1$

| Samples | Sintering temperature (°C/2 h) | $Qxf$ (GHz) | $\varepsilon_r$ | Bulk density (g/cm$^3$) |
|---|---|---|---|---|
| BZN | 950 | 2981 | 76.23 | 7.6059 |
| BZNV (0.001) | 850 | 3799 | 78.55 | 7.5479 |
| BZNV (0.003) | 850 | 3486 | 78.62 | 7.5371 |
| BZNV (0.005) | 850 | 3143 | 78.01 | 7.5238 |
| BZNV (0.01) | 850 | 2200 | 78.37 | 7.5121 |

Table 2
Dielectric properties of $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ for $x = 0.02 \sim 0.08$ and $Bi_4V_2O_{11}$ at 1 MHz

| Samples | Sintering temperature (°C/2 h) | tan $\delta$ (1 MHz) | $\varepsilon_r$ | Bulk density (g/cm$^3$) |
|---|---|---|---|---|
| BZNV (0.02) | 850 | 0.00024 | 72.723 | 7.5141 |
| BZNV (0.04) | 850 | 0.00154 | 72.526 | 7.3938 |
| BZNV (0.06) | 850 | 0.00185 | 72.337 | 7.3910 |
| BZNV (0.08) | 850 | 0.00276 | 67.817 | 7.3648 |
| $Bi_4V_2O_{11}$ | 750 | 0.089 | 87.329 | 7.2143 |

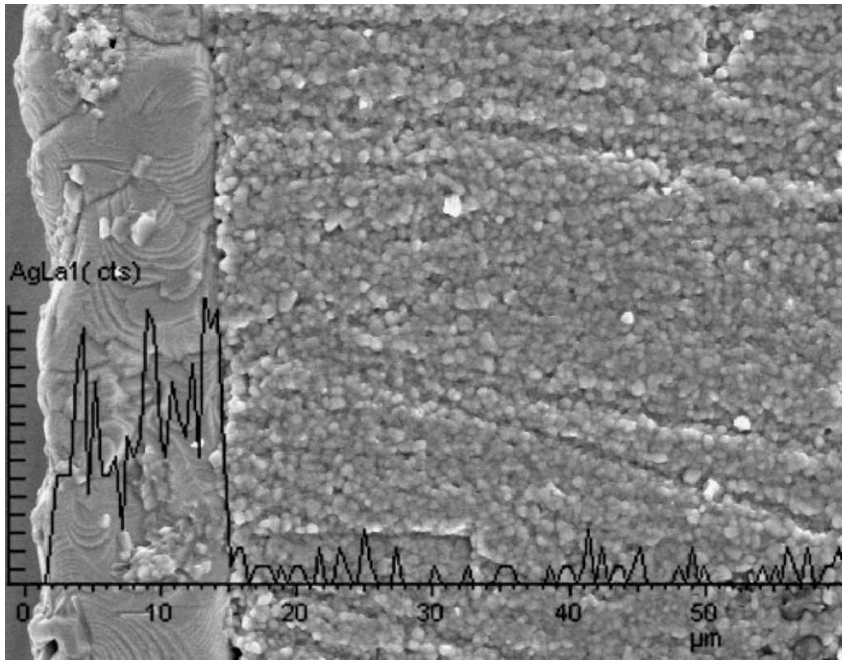



Fig. 6. SEM micrograph and EDS line scan of the interface between a silver electrode and $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ ($x = 0.005$) cofired at 850 °C for 2 h.

second phase $Bi_4V_2O_{11}$ since $Bi_4V_2O_{11}$ ceramic exhibited large dielectric loss; $\tan\delta$ value of ~0.089.

Fig. 6 shows an SEM micrograph and EDS line scan results of the interface between the silver electrode and $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ ($x = 0.005$) cofired at 850 °C for 2 h. The silver profile decreases sharply at the interface, which indicates that the reaction of $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ with silver electrode did not occur.

Consequently, $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ with small amount of $V_2O_5$ substitution can be selected as a suitable candidate for low-temperature cofired ceramics (LTCC) because of its high dielectric constant and compatibility with silver electrode.

## 4. Conclusions

Influence of $V_2O_5$ substitution to $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ on sintering and dielectric properties were investigated. Substitution of vanadium ion induced two structural changes. One is the formation of Bi-based second phase $Bi_4V_2O_{11}$ and $BiNbO_4$. The other is the change of $Bi_2(Zn_{1/3}Nb_{2/3})_2O_7$ phase from stoichiometric form to Bi-deficient form. The $Bi_2(Zn_{1/3}Nb_{2/3-x}V_x)_2O_7$ ($x = 0.001$) sintered at 850 °C for 2 h exhibited good microwave dielectric properties: $Qxf = 3800$ at 6 GHz, $\varepsilon_r = 78.6$ and this composition showed compatibility with silver inner electrode.

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