

# Dielectric properties of ZnNb<sub>2</sub>O<sub>6</sub>-TiO<sub>2</sub> mixture thin films

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**Abstract** ZnNb<sub>2</sub>O<sub>6</sub>-TiO<sub>2</sub> mixture thin films with multilayer structures were fabricated via a sol-gel spin coating process. TiO<sub>2</sub> layers were deposited on the pre-crystallized ZnNb<sub>2</sub>O<sub>6</sub> layers in order to suppress the formation of the ixiolite phase which always forms in the bulk system. The phase constitution of the thin films, confirmed by X-ray diffraction (XRD), could be controlled by the annealing temperatures, which, in turn, influenced the dielectric properties of the thin films. TiO<sub>2</sub> layers crystallized as the anatase phase and then transformed to the rutile phase at temperatures higher than 725°C. Dielectric constants of the mixture thin films, measured at 1 MHz with an MIM (metal-insulator-metal) structure, increased from 27 to 41 with dielectric losses below 0.005 as the annealing temperature increased from 700°C to 900°C. The increase in the dielectric constants was understood to originate from the increasing amounts of the rutile phase. Temperature coefficients of capacitance (TCC) were also measured between 25°C and 125°C, which showed a decreasing manner from positive values to negative values with increasing annealing temperatures. When annealed at 850°C, the TCC of the thin films could be tuned to be approximately 0 ppm/°C with dielectric constant and dielectric loss of 36 and 0.002, respectively.

**Keywords** ZnNb<sub>2</sub>O<sub>6</sub> · TiO<sub>2</sub> · Mixture thin films · Dielectric properties · TCC

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## 1 Introduction

ZnNb<sub>2</sub>O<sub>6</sub>-TiO<sub>2</sub> (ZN-T) systems have been intensively studied for the bulk ceramics since their dielectric properties can be tailored by forming mixtures with various compositions [1–3]. In particular, the temperature coefficients of resonant frequency ( $\tau_f$ ) can be tuned to be 0 ppm/°C for the 0.42·ZnNb<sub>2</sub>O<sub>6</sub>-0.58·TiO<sub>2</sub> system [1]. However, the system is not the mixture of pure ZnNb<sub>2</sub>O<sub>6</sub> and TiO<sub>2</sub> but the mixture of ZnNb<sub>2</sub>TiO<sub>8</sub> (ixiolite) and TiO<sub>2</sub>, since the ixiolite phase always forms in the bulk ceramics [4–6]. Dielectric properties of the ZN-T system will be enhanced if the temperature coefficient can be tuned to be zero without formation of the ixiolite phase since the ixiolite phase exhibits poorer dielectric properties than the pure ZnNb<sub>2</sub>O<sub>6</sub> phase.

In the present study, ZnNb<sub>2</sub>O<sub>6</sub>-TiO<sub>2</sub> mixture thin films with a multilayer structure were prepared via a spin-coating process. The emphasis of this work is to fabricate the mixture thin films without formation of the ixiolite phase and to tailor their dielectric properties. The crystal structure and existence of the ixiolite phase were examined by X-ray diffraction and the dielectric properties, such as the dielectric constants, dielectric losses, and the temperature coefficients of capacitance were tailored by the annealing temperatures.

## 2 Experimental procedures

ZnNb<sub>2</sub>O<sub>6</sub>-TiO<sub>2</sub> mixture thin films with the two-layer structure were prepared via a spin coating process. Two kinds of coating solution were prepared; ZnNb<sub>2</sub>O<sub>6</sub> (ZN) sol and TiO<sub>2</sub> (T) sol. The ZN-sol was prepared via a metalorganic decomposition (MOD) process. Zn-acetate tetrahydrate (99%, High Purity Chemical, Japan), Nb-ethoxide (99.999%, CERAC,

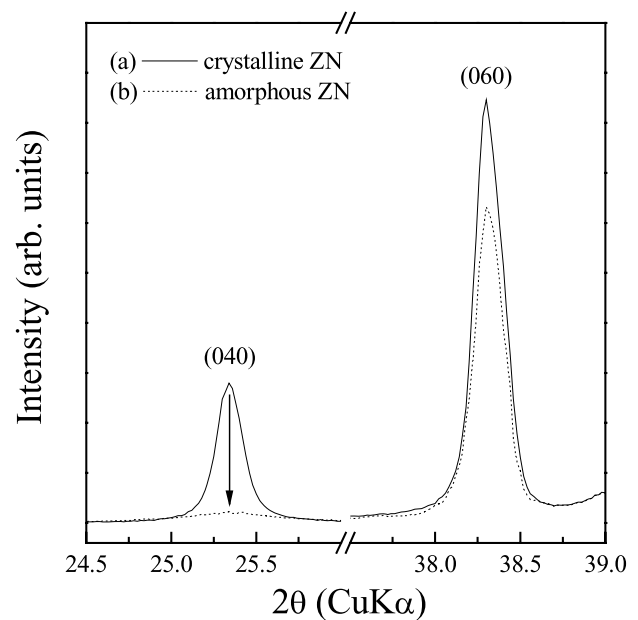
USA), 2-methoxyethanol (MOE; 99%, Aldrich, USA), and diethanolamine (DEA; 97.5%, Aldrich, USA) were selected as the starting materials, solvent, and the stabilizing agent, respectively. 5 mmol of Zn-acetate was dissolved in the MOE (10 cc) and the solution was stabilized with 2 mmol of DEA. In a separate beaker, 10 mmol of Nb-ethoxide was diluted in the MOE (10 cc). Final coating solution was obtained by adding the Nb-solution into the Zn-solution followed by the 2 hour-reaction at room temperatures. The T-sol was prepared via a sol-gel process. After titanium-isopropoxide (TTIP; Aldrich, 97%) was dissolved in dry ethanol (Baker, 99.9%), the resultant solution was partially hydrolyzed with a mixture solution containing distilled water, nitric acid, and ethanol. The molar ratio of TTIP: H<sub>2</sub>O: HNO<sub>3</sub> was 1:2:0.067. This ratio was selected since the sol hydrolyzed at the condition showed the best wetting property during spinning and the best stability against the gelation or precipitation in the previous experiments. The ZN-sol was first coated on the platinized Si substrates at 2500 rpm for 30 seconds. Then, the films were heat-treated at 350°C for 5 minutes to remove the adsorbed alcohol, water, and the organic compounds. The spinning and pyrolysis steps were repeated until the film thickness was approximately 200 nm. As-deposited ZN-films were pre-crystallized at 850°C for 1 hour. The T-sol was coated on the pre-crystallized ZN-films through the same procedures. Thickness of the T-films was also approximately 200 nm. Then, the fabricated ZN-T films were annealed at various temperatures from 700°C to 900°C for 1 hour. To measure the dielectric properties, platinum top electrodes (200 μm in diameter) were sputtered onto the films through a shadow mask.

The crystal structure, morphology, thickness, and the dielectric characteristics (at 1MHz) of thin films were investigated using a X-ray diffraction (XRD; Model M18XHF, Macscience Instruments, Japan), a field emission scanning electron microscopy (FE-SEM; Model JSM-6330F, JEOL, Japan), and a high precision LCR-meter (Agilent 4284A, Agilent, USA), respectively.

### 3 Results and discussions

#### 3.1 Structural properties

As described in the experimental section, TiO<sub>2</sub> thin films were deposited on the pre-crystallized ZnNb<sub>2</sub>O<sub>6</sub> (ZN) layers in order to suppress the formation of the ixiolite phase. The formation of the ixiolite phase can be examined by the existence of the (040) superlattice peak of the columbite (ZN) structure [1]. In general, it is difficult to distinguish the XRD patterns of the ixiolite and the ZnNb<sub>2</sub>O<sub>6</sub> phase due to their similar structures. However, the (040) superlattice peak does not exist in the ixiolite phase since it has a fully disordered



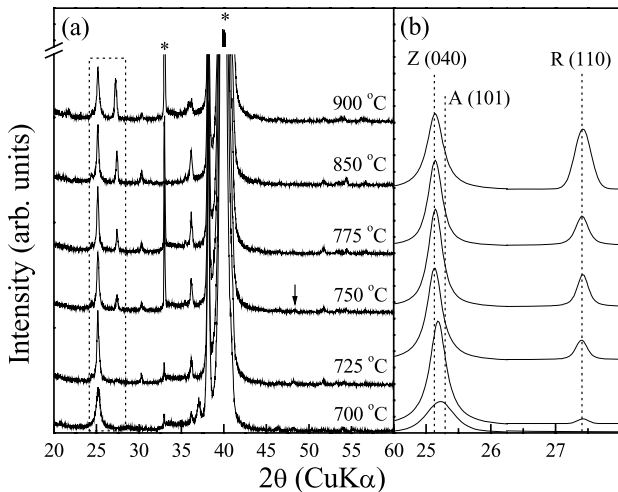
**Fig. 1** XRD diffraction peaks of the ZnNb<sub>2</sub>O<sub>6</sub>-TiO<sub>2</sub> (ZN-T) mixture thin films annealed at 800°C for 1 hour using (a) the pre-crystallized (solid line) and (b) the amorphous (dotted line) ZnNb<sub>2</sub>O<sub>6</sub> (ZN) layers (Figs. (a) and (b) exhibits ZnNb<sub>2</sub>O<sub>6</sub> and ixiolite phase, respectively)

structure compared to the columbite structure. The effects of the pre-crystallization can be elucidated by the XRD patterns shown in Fig. 1. The dotted line shows the XRD pattern of the TiO<sub>2</sub> layer on the amorphous ZN layer and the solid line shows that on the pre-crystallized ZN layer. As can be seen in Fig. 1, the pre-crystallization of the ZN layer successfully suppressed the formation of the ixiolite phase since the (040) superlattice peak remains after annealing at 800°C for 1 hour.

X-ray diffraction patterns of the ZnNb<sub>2</sub>O<sub>6</sub>-TiO<sub>2</sub> (ZN-T) thin films annealed at various temperatures are presented in Fig. 2. The TiO<sub>2</sub> layer crystallizes as the anatase phase at 700°C and gradually transforms to the rutile phase as the annealing temperature increases. The thin films maintain the ternary mixture system of ZN, anatase, and rutile without any secondary phases. The phase transformation seems to be completed above 750°C since the trace of the anatase (200) peak, which is indicated by an arrow, disappears at those temperatures as shown in Fig. 2 (a). The anatase to rutile phase transformation can be also seen in the Fig. 2 (b) which shows the magnified view of the dotted region in Fig. 1 (a) (where ZN, anatase, and rutile phase are denoted as Z, A, and R, respectively). The diffraction patterns were obtained via a step scanning with a step width of 0.006° and a scan rate of 1 sec/step followed by a smoothing process. Although Z (040) and A (101) peaks are located too closely to be separated from each other, the position of the merged peaks shifts from A (101) to Z (040). The shift of the merged peaks can be ascribed to the weakening of the A (101) peaks.

**Table 1** Dielectric properties of the ZnNb<sub>2</sub>O<sub>6</sub>-TiO<sub>2</sub> (ZN-T) mixture thin films (Data of TiO<sub>2</sub> thin films were based on our previous work [8])

Temp. (°C)	Dielectric constant	Dielectric loss (%)	Temp. (°C)	Dielectric constant	Dielectric loss (%)
700	26	0.650	725	27	0.421
750	31	0.392	775	32	0.437
800	34	0.263	850	36	0.247
900	41	0.324	ZnNb <sub>2</sub> O <sub>6</sub>	20	0.400
Anatase	36	1.147	rutile	90	0.111



**Fig. 2** (a) X-ray diffraction patterns of the ZnNb<sub>2</sub>O<sub>6</sub>-TiO<sub>2</sub> (ZN-T) mixture thin films (\* indicates the diffraction peaks of the substrates and ‘↓’ indicates the anatase (200) peak). (b) Magnified view of the dotted region (Z, A, and R represent ZnNb<sub>2</sub>O<sub>6</sub>, anatase, and rutile, respectively)

Considering that the R (110) peaks are strengthened at a fixed position with increasing annealing temperatures, the TiO<sub>2</sub> layer does not seem to react with the ZN layer during the phase transformation.

### 3.2 Morphology

Surface microstructures of the ZN-T thin films annealed at various temperatures are presented in Fig. 3, where only TiO<sub>2</sub> grains are shown in the plan view due to the structure of the mixture thin films. The grain size of the TiO<sub>2</sub> layer increases from 40 to 250 nm as the annealing temperature increases from 725°C to 850°C. Comparing the Figs. 3(a), (b) and (c), it can be seen that the grain size increases abruptly during the phase transformation. This can be understood as a result of the destructive anatase to rutile phase transition. The destructive phase transformation accelerates the mass transportation, which, in turn, promotes the grain growth. This increased grain size has also been reported as being

based on the ‘critical-nuclei-size-effect’ by Kumar et al. [7].

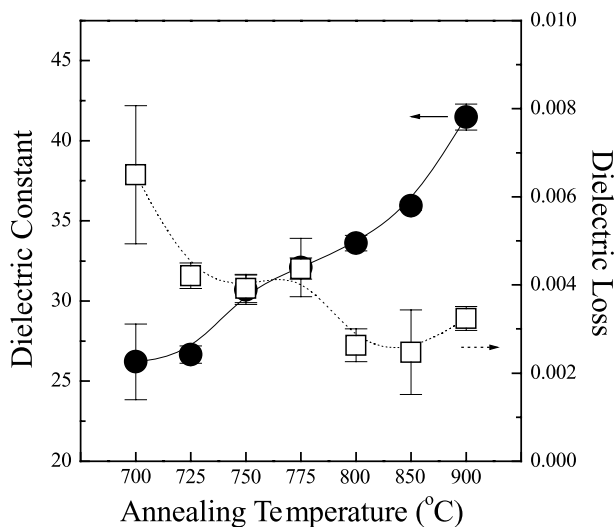
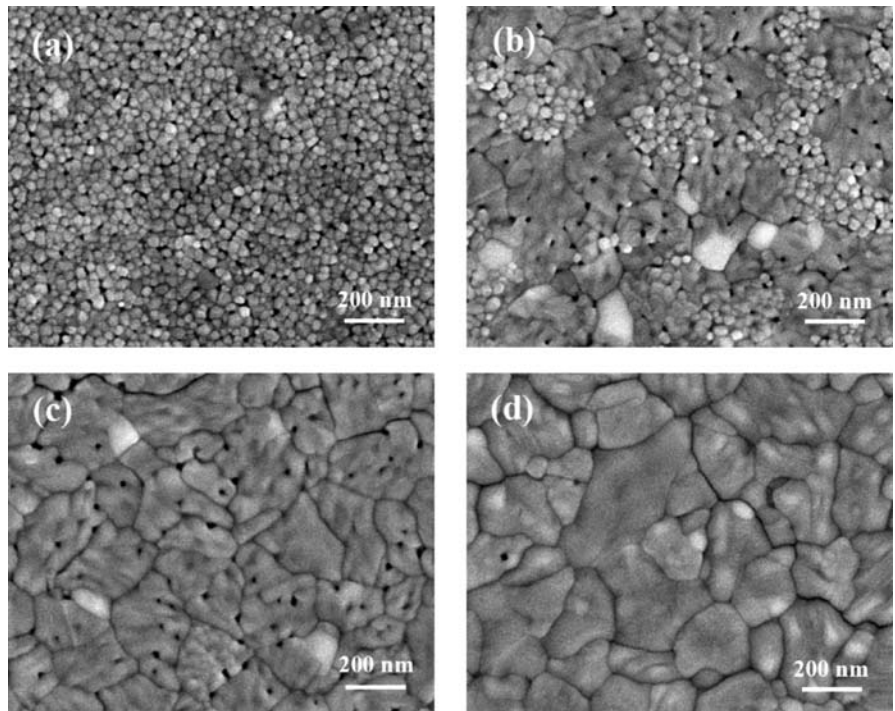
### 3.3 Dielectric properties

As can be observed in Fig. 4, the dielectric properties of ZN-T thin films are strongly dependent on the annealing temperatures, i.e. the relative ratios of the rutile phase. Table 1 summarizes the overall dielectric properties of the ZN-T mixture thin films. The dielectric constants increase from 26 to 41 with the increasing annealing temperatures, while the dielectric losses show an opposite manner. The increasing tendency of the dielectric constants can be ascribed to the increasing amounts of the rutile phase, since the dielectric constant of the rutile phase is higher than the anatase phase (40 for the anatase powders [9] and 100 for the rutile bulk ceramics [10]). The dielectric losses decrease from 0.007 to 0.002 with the increasing annealing temperatures, which can be understood to originate from the removal of the defects like pores and grain boundaries as can be seen in Figs. 3 (a)–(d) and the relaxation of the internal stress at higher annealing temperatures. Low dielectric losses of the mixture thin films can also be ascribed to the suppression of the ixiolite phase formation since the dielectric loss of the ixiolite phase is much larger than ZnNb<sub>2</sub>O<sub>6</sub> phase [1].

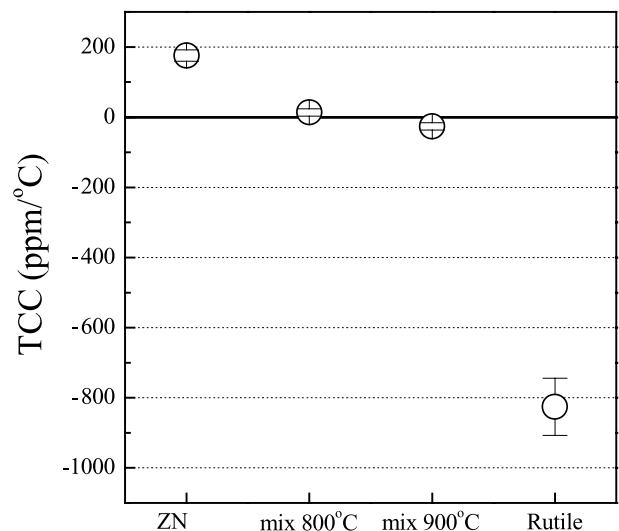
Temperature dependency of the dielectric thin films is one of the most important factors in actual applications as electronic devices like capacitors. Temperature coefficients of capacitance (*TCC*) of the ZN-T mixture thin films, measured from 25°C to 125°C, are shown in Fig. 5. Since the *TCC* of the ZN thin films is positive (176 ppm/°C) while that of the rutile thin films is negative (−826 ppm/°C), it can be tuned to be approximately 0 by the appropriate tailoring of the mixture system. As can be seen in Fig. 5, the *TCC* can be tuned to be zero when the ZN-T thin films are annealed at 850°C and the mixture thin film exhibits the dielectric constant of 36 and the dielectric loss of 0.002 at the same condition.

As a result, it was confirmed that the dielectric properties, particularly the temperature dependency of the mixture thin films could be successfully controlled by a phase design.

**Fig. 3** Surface microstructure of the  $\text{ZnNb}_2\text{O}_6\text{-TiO}_2$  (ZN-T) mixture thin films annealed at (a)  $725^\circ\text{C}$ , (b)  $750^\circ\text{C}$ , (c)  $775^\circ\text{C}$ , and (d)  $850^\circ\text{C}$



**Fig. 4** Dielectric properties of the  $\text{ZnNb}_2\text{O}_6\text{-TiO}_2$  (ZN-T) mixture thin films annealed at various temperatures



**Fig. 5** Temperature coefficients of capacitance ( $TCC$ ) of the  $\text{ZnNb}_2\text{O}_6$  (ZN),  $\text{ZnNb}_2\text{O}_6\text{-TiO}_2$  (ZN-T) mixture, and rutile thin films ( $TCC$  value of the rutile thin film is based on our previous work [8])

#### 4 Conclusions

Structural and dielectric properties of the  $\text{ZnNb}_2\text{O}_6\text{-TiO}_2$  mixture thin films with a multilayer structure were investigated. By depositing the  $\text{TiO}_2$  layer on the pre-crystallized  $\text{ZnNb}_2\text{O}_6$  layer, formation of the ixiolite phase which always forms in the bulk ceramics was successfully suppressed. The  $\text{TiO}_2$  layer crystallized as the anatase phase at  $700^\circ\text{C}$  and transformed to the rutile phase with the increasing annealing temperatures until  $775^\circ\text{C}$ . Dielectric properties of the

mixture thin films were enhanced by suppressing the formation of ixiolite phase whose dielectric properties are poorer than the pure  $\text{ZnNb}_2\text{O}_6$  phase and they could be successfully controlled by the annealing temperatures. The dielectric constants of the  $\text{ZnNb}_2\text{O}_6\text{-anatase-rutile}$  ternary mixture thin films increased with the increasing annealing temperatures, i.e. the increasing amounts of the rutile phase from 26 to 41, while the dielectric losses showed the opposite manner. Temperature coefficients of capacitance ( $TCC$ ) of the  $\text{ZnNb}_2\text{O}_6\text{-TiO}_2$  mixture thin films were also measured and

the *TCC* could be tuned to be zero when the mixture thin films were annealed at 850°C with the dielectric constant of 36 and the dielectric loss of 0.002.

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