

# Influence of Bi<sub>2</sub>O<sub>3</sub> addition on structure and dielectric properties of Ag(Nb<sub>0.8</sub>Ta<sub>0.2</sub>)O<sub>3</sub> ceramics

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The structure and dielectric properties of perovskite  $Ag(Nb_{0.8}Ta_{0.2})O_3$  ceramics were explored. A small amount of  $Bi_2O_3$  was used to modify the dielectric properties of the ceramics. The addition of  $Bi_2O_3$  led the ceramics to a high densification and optimal dielectric properties. With the addition of 4.5 wt%  $Bi_2O_3$ , the permittivity of  $Ag(Nb_{0.8}Ta_{0.2})O_3$  ceramics increased from 470 to 733, the dielectric loss decreased from  $62 \times 10^{-4}$  to  $6.7 \times 10^{-4}$ , and the temperature coefficient of capacitance, TCC, decreased from 2004 ppm/°C to -50 ppm/°C. The high permittivity obtained was due to the high densification and weak Ta-O or Nb-O bond strength in the oxygen octahedron that results from the addition of  $Bi_2O_3$ .

Keywords:  $Ag(Nb_{0.8}Ta_{0.2})O_3$  ceramics;  $Bi_2O_3$ ; dielectric properties; high permittivity; low dielectric loss

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# 1. Introduction

Materials for microwave dielectric resonators should have a high permittivity, a large quality factor Q (Q =  $1/\tan(\delta)$ ) and a stable temperature coefficient of the resonant frequency  $\tau_f$  close to zero [1, 2]. Comprehensive tests on the dielectric properties of microwave ceramics indicated that the Ag(Nb,Ta)O<sub>3</sub> solid solutions were potential materials for wireless telecommunication technology, due to their low dielectric losses and extraordinarily high permittivity [3]. Ag(Nb<sub>0.8</sub>Ta<sub>0.2</sub>)<sub>1-x</sub>Sb<sub>x</sub>O<sub>3</sub> solid solutions were prepared with a permittivity of 825, a dielectric loss of 0.0023, and a TCC of -38.52 ppm/°C [4]. Moreover, M. Valant et al. showed AgNb<sub>0.65</sub>Ta<sub>0.35</sub>O<sub>3</sub>-AgNb<sub>0.35</sub>Ta<sub>0.65</sub>O<sub>3</sub> composition ceramics with a permittivity of 430, a temperature coefficient of permittivity  $< 50 \text{ ppm/}^{\circ}\text{C}$ , and a Q value of 700 [5]. The influence of Bi<sub>2</sub>O<sub>3</sub> on the structure and dielectric properties of Ag(Nb,Ta)O<sub>3</sub> ceramics was studied. The result revealed that the permittivity increased and the dielectric loss decreased significantly as the  $Bi_2O_3$  content was increased [6]. However, these solid solutions showed high dielectric loss or low permittivity, and these properties needed to be improved further.

In the present work,  $Bi_2O_3$  was used to improve the dielectric properties of the Ag(Nb,Ta)O<sub>3</sub> ceramics. The influence of  $Bi_2O_3$  on structure, micromorphology, and dielectric properties of the ceramics were investigated.

# 2. Experimental

Ceramics of Ag(Nb<sub>0.8</sub>Ta<sub>0.2</sub>)O<sub>3</sub> were prepared by the solid-state reaction method, using reagent grade (> 99.99 %) powders Ag<sub>2</sub>O, Nb<sub>2</sub>O<sub>5</sub>, and Ta<sub>2</sub>O<sub>5</sub>. The weighed Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub> were mixed using conventional ball milling in polyethylene jars for 4 h, and pre-reacted to form (Nb<sub>0.8</sub>Ta<sub>0.2</sub>)<sub>2</sub>O<sub>5</sub> solid solution at 1300 °C for 6 h. Ag<sub>2</sub>O and (Nb<sub>0.8</sub>Ta<sub>0.2</sub>)<sub>2</sub>O<sub>5</sub> were weighed according to the formula Ag(Nb<sub>0.8</sub>Ta<sub>0.2</sub>)O<sub>3</sub>, and then mixed with zirconia in distilled water for 4 h. The mixed powders were pressed into disks of 10 mm diameter and

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1 mm thickness, and were then sintered at 1100  $^{\circ}$ C for 3 h. Bi<sub>2</sub>O<sub>3</sub> with the appropriate weight ratio was used as an additive, before granulation.

To minimize the conductor losses, appropriate electrode were chosen, consisting of highly conductive metals like copper or silver. In this work, thin silver electrodes were sputtered on both surfaces of the pellets to form plate capacitors. For better accuracy and reliability of the data, a few samples were prepared and measured for every doping level and they showed similar results.

The microstructures of the sintered samples were examined using a Scanning Electron Microscope (Phillips XL30). The crystal structures of the samples were studied with an X-ray diffractometer (Rigaku 2038) using  $CuK_{\alpha}$  radiation. The density of the sintered samples was measured by Archimedes' Principle (using a Mettler Toledo XS64 Analytical Balance). The dielectric capacitance and dielectric loss were measured at 1 MHz with a capacitance meter (Agilent HP4278A). Raman measurements for the sintered samples were carried out at room temperature (Bruker FS100). The excitation source was the 1064 nm line with 100 mW Raman laser power. The recorded Raman spectra exhibited approximately  $2 \text{ cm}^{-1}$  resolution. The TCC was tested by C-T parameter measurement equipment, consisting of an oven (GZ-ESPEC) and a HM 27002 Capacitor C-T Meter Model. The TCC value was defined by the following relation:

$$TCC = \frac{\Delta C}{60 \times C_{25}} \tag{1}$$

where  $\Delta C = C_{85}$ - $C_{25}$ ,  $C_{85}$  and  $C_{25}$  are the capacitance of a sample tested at 85 °C and 25 °C, respectively.

### 3. Results and discussion

#### **3.1.** Synthesis of (Nb,Ta)<sub>2</sub>O<sub>5</sub> precursor

To reduce the shrink of the final sample and avoid the decomposition of Ag<sub>2</sub>O, the mixture of Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub> was pre-reacted at high temperature (> 1000 °C). And a much more homogeneous Ag(Nb<sub>1-x</sub>Ta<sub>x</sub>)O<sub>3</sub> compound could be synthesized

in this manner. Completely homogeneous solid solutions, Nb<sub>2</sub>O<sub>5(ss)</sub> and Ta<sub>2</sub>O<sub>5(ss)</sub> could be obtained in the concentration range x < 0.25 and x > 0.51, respectively [7, 8].

Fig. 1 shows the XRD pattern of the mixture of Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub> sintered at 1300 °C in air. Single phase Nb<sub>2</sub>O<sub>5</sub> (JCPDS Card No. 37-1468) was formed, which indicated that Ta<sup>5+</sup> entered the lattice of Nb<sup>5+</sup> and formed a solid solution of Nb<sub>2</sub>O<sub>5(ss)</sub>. The condition for forming continuous solid solution is as follows:

$$t = \left| \frac{\mathbf{r}_1 - \mathbf{r}_2}{\mathbf{r}_1} \right| < 15 \%, \tag{2}$$

where  $r_1$  is the radius of large ions, and  $r_2$  is the radius of small ions. For ions with the same valence, if the ionic radii of the solute and the solvent satisfy equation (2), then a continuous solid-solution could be formed. For solvent Nb<sub>2</sub>O<sub>5</sub> and solute Ta<sub>2</sub>O<sub>5</sub> with the same ion valence, t = 7.2 % (< 15 %) is obtained, according to equation (2) ( $r_{Nb5+} = 0.69$  nm and  $r_{Ta5+} = 0.64$  nm). Therefore, continuous solid solutions of Nb<sub>2</sub>O<sub>5(ss)</sub> were formed.

#### **3.2.** Phase structures

Fig. 2 shows the XRD patterns of  $xBi_2O_3$ -doped Ag(Nb<sub>0.8</sub>Ta<sub>0.2</sub>)O<sub>3</sub> ceramics (x = 2.5, 3.5, 4.5, and 5.5 wt%) sintered at 1100 °C in air. The main perovskite Ag(Nb<sub>0.8</sub>Ta<sub>0.2</sub>)O<sub>3</sub> was detected. Weak traces of metallic silver were detected for the sample doped with 5.5 wt% Bi<sub>2</sub>O<sub>3</sub>, indicating that partial Ag<sup>+</sup> was substituted by Bi<sup>3+</sup>. The presence of Ag would deteriorate the dielectric properties of Ag(Nb<sub>0.8</sub>Ta<sub>0.2</sub>)O<sub>3</sub> ceramics. In addition, the diffraction peaks of these samples shifted to different angle ranges. These shifts indicated that the lattice parameter of Ag(Nb<sub>0.8</sub>Ta<sub>0.2</sub>)O<sub>3</sub> was changed and the lattice distortion was induced, which would therefore influence the dielectric properties of the ceramics.

To understand the phenomenon discussed above, the refined lattice parameters of Bi<sub>2</sub>O<sub>3</sub>doped Ag(Nb<sub>0.8</sub>Ta<sub>0.2</sub>)O<sub>3</sub> samples are shown in Fig. 3. The error bars indicate the standard deviation is attributable to the lattice constants a, b, c, and the  $\beta$  measurement, as well as the unit cell volume and the crystallinity. The monoclinic angle  $\beta$ ,



Fig. 1. XRD pattern of the mixture of Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub> sintered at 1300 °C in air for 6 h.



Fig. 2. XRD results of Ag(Nb<sub>0.8</sub>Ta<sub>0.2</sub>)O<sub>3</sub> samples doped with various amounts of Bi<sub>2</sub>O<sub>3</sub> x (x = 2.5, 3.5, 4.5 and 5.5 wt%).

as a function of the composition doped with 4.5 wt%  $Bi_2O_3$ , was smaller than that of other samples. The influence of the  $Bi_2O_3$  content on the XRD patterns of the samples can be observed in the intensity variations and the full-width of medium-height (FWHM) of the diffraction peaks. These characteristics were utilized to determine the degree of

crystallinity. The crystallinity of the samples was estimated on the basis of the integral area of the diffraction peaks. These estimates revealed that the crystallinity degree decreased with the increase in the  $Bi_2O_3$  content. It indicated that the grain size decreased and that some defects were induced.



Fig. 3. XRD results of Ag(Nb<sub>0.8</sub>Ta<sub>0.2</sub>)O<sub>3</sub> samples doped with various amounts of Bi<sub>2</sub>O<sub>3</sub> x (x = 2.5, 3.5, 4.5 and 5.5 wt%).

#### 3.3. Microstructures

The micro-morphology, such as the average grain size, the grain size distribution, the grain morphology and the grain orientation, are important factors affecting dielectric properties, in particular they are important for the dielectric losses [9–11]. SEM micrographs of Bi<sub>2</sub>O<sub>3</sub>-doped Ag(Nb<sub>0.8</sub>Ta<sub>0.2</sub>)O<sub>3</sub> samples are shown in Fig. 4. The fine cubic structures were observed for the pure sample, with grain size ranging between 0.5 to 2.5  $\mu$ m (Fig. 3(a)). However, when Bi<sub>2</sub>O<sub>3</sub> was added to the ceramics, most of the grain structures changed from cubic structures to "spiral-shaped" structures.

The non-doped sample exhibited a porous microstructure with a density,  $\rho$ , of 6.435 g/cm<sup>3</sup>. However, a small amount of Bi<sub>2</sub>O<sub>3</sub>,  $\leq$  3.5 wt%, significantly decreased the porosity of the sintered samples, as shown in Fig. 4(b) and 4(c), which had a density  $\rho$  = 7.082 g/cm<sup>3</sup> and  $\rho$  = 7.091 g/cm<sup>3</sup>, respectively. 4.5 wt% Bi<sub>2</sub>O<sub>3</sub> enabled full densification ( $\rho$  = 7.138 g/cm<sup>3</sup>) at 1100 °C. Further addition of Bi<sub>2</sub>O<sub>3</sub> ( $\geq$  5.5 wt%) resulted in a slight decrease in the final density  $\rho = 7.025$  g/cm<sup>3</sup> (Fig. 4(e)), and all the relative density was less than 90 %.

# **3.4.** Influence of Bi<sub>2</sub>O<sub>3</sub> on the dielectric properties of Ag(Nb<sub>0.8</sub>Ta<sub>0.2</sub>)O<sub>3</sub> ceramics

The dielectric properties of the ceramics are shown in Fig. 5. Increasing the Bi<sub>2</sub>O<sub>3</sub> content caused a decrease in the dielectric loss  $(tan(\delta))$  and an increase in the permittivity  $(\varepsilon)$ , initially. These could be explained by the following equation:

$$Bi_2O_3 \xrightarrow{Ag_2O} 2Bi_{Ag}^{\bullet\bullet} + 4V_{Ag}' + 3Oo$$
(3)

The Ag<sup>+</sup> vacancy was caused by partial substitution of Bi<sup>3+</sup>. Because of the Ag<sup>+</sup> vacancy, the lattice distortion of the oxygen octahedron was induced and the ion relaxation polarization was generated. Furthermore, Bi<sup>3+</sup> was of stronger polarizability, 6.12 Å<sup>3</sup>, leading to the higher permittivity of Ag(Nb<sub>0.8</sub>Ta<sub>0.2</sub>)O<sub>3</sub> ceramics [12].

However, when the  $Bi_2O_3$  content was increased up to 5.5 wt%, the dielectric loss increased while the permittivity decreased. These could be attributed to the presence of metallic silver (Fig. 2).



Fig. 4. SEM micrographs of Ag(Nb<sub>0.8</sub>Ta<sub>0.2</sub>)O<sub>3</sub> ceramics doped with various Bi<sub>2</sub>O<sub>3</sub> contents *x*, and sintered for 5 h at 1100 °C. (a) x = 0 wt%; (b) x = 2.5 wt%; (c) x = 3.5 wt%; (d) x = 4.5 wt%. (e) x = 5.5 wt%.

(e)

According to Fig. 4, the residual porosity indicated by the sintered density, could affect both permittivity and dielectric loss. The effect of porosity on permittivity could be estimated by the law of mixtures approach, e.g. by the Lichtenecker equation:

$$\log \varepsilon_r = \sum \log \varepsilon_i V_i \tag{4}$$

where  $\varepsilon_r$  is the permittivity of the sample,  $\varepsilon_i$  is is the permittivity of the *i*th phase,  $V_i$  is the volume fraction of the *i*th phase and porosity is regarded as a phase with a permittivity of 1. The dielectric loss of a compound is known to be affected by extrinsic factors, such as defect concentration, impurities, grain size, and porosity. Therefore, pores were regarded as lattice defects, increasing the tan( $\delta$ )(Fig. 4(e)). It is assumed that for materials of density  $\rho < 90$  %, theoretically, the increase in dielectric loss, due to increasing porosity, might be attributable to the effects of polarization at the pore surfaces [13].

The TCC values of the Ag(Nb<sub>0.8</sub>Ta<sub>0.2</sub>)O<sub>3</sub> ceramics are plotted in parentheses in Fig. 5. The pure sample had the highest TCC value (2004 ppm/°C) compared with the doped samples. The reason why the pure sample showed a positive TCC value is explained as follows: a weak elastic force between cation and anion was caused by the expansion of the unit cell volume under temperature increment, which resulted in high polarizability.

However, when  $Bi_2O_3$  was added to the ceramics, the TCC values of the ceramics decreased.



Fig. 5. Dielectric properties of Ag(Nb<sub>0.8</sub>Ta<sub>0.2</sub>)O<sub>3</sub> ceramics doped with various Bi<sub>2</sub>O<sub>3</sub> content x (x = 2.5, 3.5, 4.5 and 5.5 wt%); TCC values are written in parentheses.



Fig. 6. Raman spectra for pure ceramic (spectrum A) and 4.5 wt% Bi<sub>2</sub>O<sub>3</sub>-doped Ag(Nb<sub>0.8</sub>Ta<sub>0.2</sub>)O<sub>3</sub> ceramics (spectrum B).

When the  $Bi_2O_3$  content was up to 5.5 wt%, the perovskite ceramic showed negative TCC values. This could be explained as follows: the density of the ceramic decreased (Fig. 4(e)) and the inner electric field was weakened, due to the thermaldependent motion of particles at high sintering temperatures.

#### 3.5. Raman spectrum

Typical Raman spectra of the non-doped  $Ag(Nb_{0.8}Ta_{0.2})O_3$  ceramics (spectrum A) and the sample doped with 4.5 wt%  $Bi_2O_3$  (spectrum B) are illustrated in Fig. 6. Three main frequency ranges could be distinguished in perovskite oxides:

(a) a low-frequency part below  $150 \text{ cm}^{-1}$ ,

(b) an intermediate one between 150 and  $400 \text{ cm}^{-1}$ , and

(c) a high-frequency range above  $400 \text{ cm}^{-1}$ .

For  $Ag(Nb_{0.8}Ta_{0.2})O_3$  systems, the vibrations were classified as internal modes of (Nb,Ta)<sub>2</sub>O<sub>5</sub> octahedron and lattice translations involving motion of the cation [14]. The vibration modes of an ideal (Nb,Ta)2O5 could be expressed as follows:  $v_1 (A_{1g}) \rightarrow A_1; v_2 (E_g) \rightarrow A_1 + A_2; v_3, v_4 (F_{1u}) \rightarrow$  $A_1+B_1+B_2$ ;  $v_5$  ( $F_{2g}$ ) $\rightarrow$   $A_1+B_1+B_2$ ;  $v_6$  ( $F_{2u}$ ) $\rightarrow$  $A_2+B_1+B_2$ . The low-frequency bands mainly involved phonon dispersion in the acoustical and the lowest optical branches, activated from brillouin zone folding [15]. By comparison with crystal LiNbO<sub>3</sub>, the lines at 103  $cm^{-1}$  could be assigned as motion of  $Ag^+$ . The lines at 212 cm<sup>-1</sup> and 251 cm<sup>-1</sup> were assigned to  $v_5$  and  $v_6$  bending. The lines at 415 cm<sup>-1</sup> was assigned to  $v_4$  stretching and bending. The lines at 567  $\text{cm}^{-1}$  and the weak line at 820  $\text{cm}^{-1}$  were assigned to vibrations originating from the  $v_1$  and  $v_2$  stretching.

The Raman signals in spectrum B were of much lower intensity than that in spectrum A. It revealed that the spectrum B contained some noncrystallized materials (Fig. 3), which was presumed to be the factor responsible for the slight deterioration in the dielectric loss factor [16]. However, this did not influence the dielectric loss due to their intrinsic loss and extrinsic loss, such as compact structures.

The large damping coefficient in spectrum B was most probably due to the distortion of the grains in this sample. The vibration modes at 569 cm<sup>-1</sup> was the breathing vibration of the  $(Nb,Ta)_2O_5$  octahedron and was slightly blue-shifted as the concentration of Bi<sub>2</sub>O<sub>3</sub> increased for spectrum B. The phenomenon implied that Ta-O or Nb-O bond strength in the oxygen octahedron was weaker, resulting in larger polarizability and hence higher permittivity for the Ag(Nb<sub>0.8</sub>Ta<sub>0.2</sub>)O<sub>3</sub> ceramic doped with 4.5 wt% Bi<sub>2</sub>O<sub>3</sub>.

# 4. Conclusions

 $Ag(Nb_{0.8}Ta_{0.2})O_3$  ceramics with high-permittivity and low dielectric loss were fabricated by

the solid-state reaction method. The influence of Bi<sub>2</sub>O<sub>3</sub> addition on the structure and dielectric properties of Ag(Nb<sub>0.8</sub>Ta<sub>0.2</sub>)O<sub>3</sub> ceramics was investigated. 4.5 wt% Bi<sub>2</sub>O<sub>3</sub>-doped Ag(Nb<sub>0.8</sub>Ta<sub>0.2</sub>)O<sub>3</sub> ceramics showed high permittivity and low dielectric loss. This was due to the large grain sizes, high densification and the grain morphology. In addition, the Raman spectrum indicated that wavenumber in the high frequency range shifted to the high side as the Bi<sub>2</sub>O<sub>3</sub> concentration increased. It indicated that Ta-O or Nb-O bond strength of Bi<sub>2</sub>O<sub>3</sub>-doped Ag(Nb<sub>0.8</sub>Ta<sub>0.2</sub>)O<sub>3</sub> ceramics was weaker than that of the non-doped sample, due to the Bi<sub>2</sub>O<sub>3</sub> concentration. The optimal dielectric properties of 4.5 wt%-doped Ag(Nb<sub>0.8</sub>Ta<sub>0.2</sub>)O<sub>3</sub> ceramics were obtained:  $\varepsilon = 733$ ,  $\tan(\delta) = 6.7 \times 10^{-4}$ , and TCC =  $-50 \text{ ppm/}^{\circ}$ C. These excellent dielectric properties of Ag(Nb<sub>0.8</sub>Ta<sub>0.2</sub>)O<sub>3</sub> doped with 4.5 wt% Bi<sub>2</sub>O<sub>3</sub> indicated its promising suitability for applications in electronic devices.

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