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Microwave dielectric properties of rutile $(Zn_{1/3}Nb_{2/3})_{0.40}(Ti_{1-x}Sn_x)_{0.60}O_2$ $(0.15 \leq x \leq 0.30)$ ceramics

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Abstract

Microwave dielectric properties of $(Zn_{1/3}Nb_{2/3})_{0.40}(Ti_{1-x}Sn_x)_{0.60}O_2$ ceramics were investigated as a function of SnO_2 content $(0.15 \leq x \leq 0.30)$. A single phase with tetragonal rutile structure was obtained through the entire composition. The unit-cell volume of the specimens was increased with SnO_2 content, due to the larger ionic radius of Sn^{4+} (0.69 Å) than that of Ti^{4+} (0.605 Å) for octahedral site. Dielectric constant (K) of the sintered specimens was affected by the dielectric polarizability. Quality factor (Qf) was dependent on the degree of reduction of Ti^{4+} ion. With an increase of SnO_2 content, the temperature coefficient of resonant frequency (TCF) of the specimens decreased due to the decrease of the octahedral distortion of rutile structure.

Keywords: A. Sintering; C. Dielectric properties; D. TiO_2; Rutile structure

1. Introduction

Recently, the rutile compounds with general formula MO_2 (where M = Ti, Sn, Ge, Si, Pb) type have much interested because of luminescent in electro-optic applications and photo-catalyst [1]. However, rutile compound of MO_2 and their solid solution with other compounds have been rarely studied as microwave dielectric materials.

Many works for the binary niobate compounds with the general formula ANb_2O_6 (where A = Zn, Mg, Ni, Mn, Cu, Co and Ca) have been performed [2,3]. These compounds with a columbite structure showed high dielectric constant (K) and quality factor (Qf). Among those compounds, $ZnNb_2O_6$ exhibits excellent dielectric properties: $K = 25$, $Qf = 83{,}700$ GHz and $TCF = -56$ ppm/°C [2,3]. TiO_2 with rutile structure shows K of 105 and Qf of 9200 at 5GHz [4], however, thermal stability (TCF) is too large (~465 ppm/°C) and the sintering temperature is high (1400 °C).

Thermal stability (TCF) is strongly dependent on the structural characteristics of oxygen octahedra [5]. TiO_6 octahedra in rutile structure is composed of four equatorial Ti–O bond lengths and two apical Ti–O bond lengths, is slightly distorted, with apical Ti–O bonds slightly longer than the other equatorial bonds [6]. In contrast, the two Sn–O apical bond lengths are smaller than the four equatorial bond lengths in SnO_2 with same structure [7]. If SnO_2 was incorporated into TiO_2, it would be possible to control the TCF of TiO_2 due to the structural difference between both TiO_2 and SnO_2.

In this study, the microwave dielectric properties and crystal structure of the $(Zn_{1/3}Nb_{2/3})_{0.40}(Ti_{1-x}Sn_x)_{0.60}O_2$ system were investigated as a function of the amount of SnO_2 $(0.15 \leq x \leq 0.30)$. Dependence of TCF on the octahedral distortion of oxygen octahedra and reduction of TiO_2 was also discussed.

2. Experimental procedure

ZnO, Nb_2O_5, TiO_2, and SnO_2 powders with purity above 99.9% were used as raw materials. The powders were separately prepared according to the desired stoichiometry $ZnNb_2O_6$ and $(Ti_{1-x}Sn_x)O_2$ $(0.15 \leq x \leq 0.30)$, and ground in distilled water for 24 h in a ball mill with ZrO_2 balls. Prepared powders of $ZnNb_2O_6$ and $(Ti_{1-x}Sn_x)O_2$ were dried and calcined at 900 °C for 3 h, and 1200–1350 °C for 3 h, respectively. These calcined powders were mixed according to the formula of $(Zn_{1/3}Nb_{2/3})_{0.40}(Ti_{1-x}Sn_x)_{0.60}O_2$ $(0.15 \leq x \leq 0.30)$. The mixed powders were calcined at 1150 °C for 3 h. The calcined

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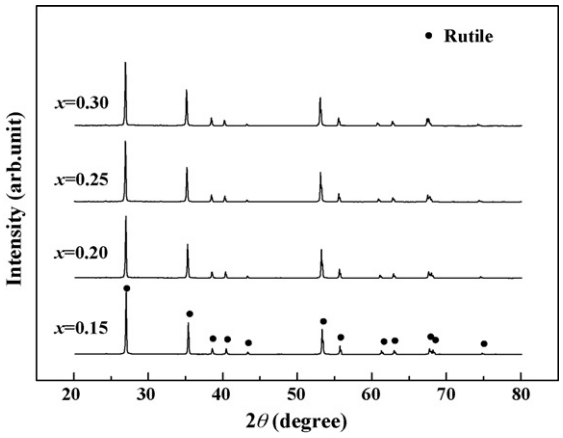

Fig. 1. X-ray diffraction patterns of $(Zn_{1/3}Nb_{2/3})_{0.40}(Ti_{1-x}Sn_x)_{0.60}O_2$ ceramics sintered at 1150 °C for 3 h.

powders were milled again with ZrO_2 balls for 24 h in distilled water and then dried. The dried powders were pressed into 10 mm diameter disk at 1500 kg/cm^2 isostatically. These pellets were sintered at 1150 °C for 3 h in air. The heating rate was 5 °C/min and the cooling rate was 1 °C/min down to 900 °C.

Powder X-ray diffraction analysis (D/Max-3C, Rigaku, Japan) was used to determine the crystalline phase. From the Rietveld refinements of X-ray diffraction patterns, the lattice parameters and unit cell volume of the sintered specimens were determined. Microstructure of polished surface was observed by a scanning electron microscope (JEOL, JSM-6500F).

The dielectric constant, unloaded Q value at frequencies of 5–7 GHz were measured by the post resonant method developed by Hakki and Coleman [8]. *TCF* was measured by the cavity method [9] at the temperature range of 25–80 °C.

The individual bond length (apical and equatorial) of oxygen octahedral was obtained from the lattice parameters and oxygen position parameter of tetragonal rutile structure [11]. From the individual bond length of oxygen octahedra, the octahedral distortion (Δ) was calculated in Eq. (1) [10]:

$$\Delta = \frac{1}{6}\sum\left\{\frac{(R_i - \bar{R})}{\bar{R}}\right\}^2 \quad (1)$$

where R_i is the individual bond length, and $\bar{R}$ is average bond length of oxygen octahedral, respectively.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of $(Zn_{1/3}Nb_{2/3})_{0.40}(Ti_{1-x}Sn_x)_{0.60}O_2$ ($0.15 \le x \le 0.30$) ceramics sintered at 1150 °C for 3 h. The complete solid solutions with the tetragonal rutile structure were obtained, and no secondary phase was detected through the entire composition range. For the $(Zn_{1/3}Nb_{2/3})_{0.40}(Ti_{1-x}Sn_x)_{0.60}O_2$ system, Zn^{2+}, Nb^{5+} and Sn^{4+} cations were easily substituted into the TiO_2 with rutile structure because SnO_2 and $ZnNb_2O_6$ have a same or derived structure [12].

Crystallographic data obtained from a Rietveld refinement for $(Zn_{1/3}Nb_{2/3})_{0.40}(Ti_{1-x}Sn_x)_{0.60}O_2$ ceramics are shown in

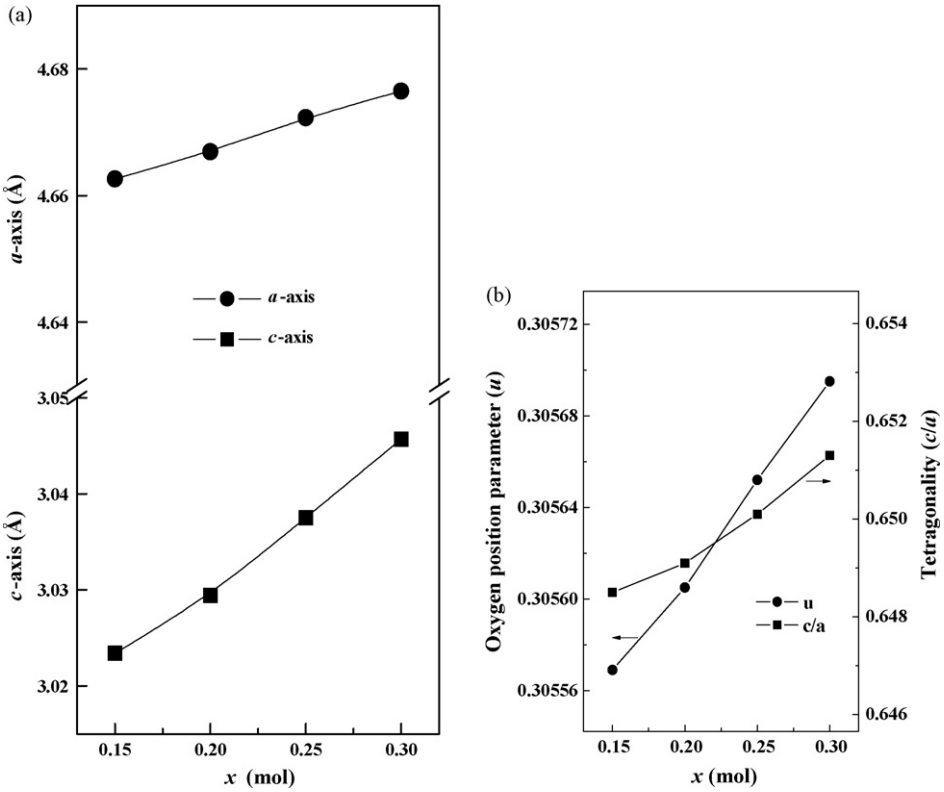

Fig. 2. Crystallographic data of $(Zn_{1/3}Nb_{2/3})_{0.40}(Ti_{1-x}Sn_x)_{0.60}O_2$ ceramics obtained from a Rietveld refinement, as a function of x; (a) lattice parameters, (b) oxygen position parameter and tetragonality.

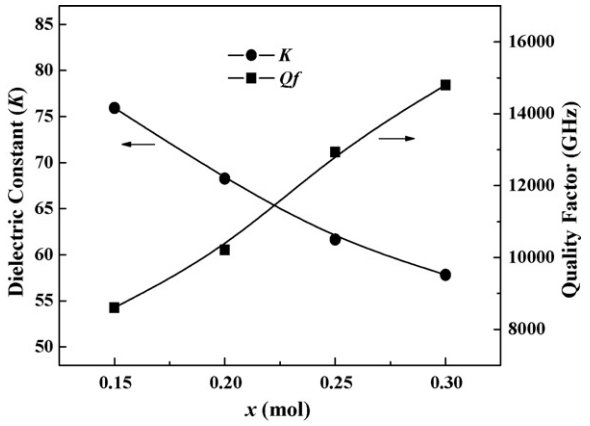

Fig. 3. Microwave dielectric properties (K, Qf) of $(Zn_{1/3}Nb_{2/3})_{0.40}$-$(Ti_{1-x}Sn_x)_{0.60}O_2$ ceramics sintered at 1150 °C for 3 h.

Fig. 2. The rutile structure is defined by three crystallographic parameters, the two lattice parameters a, c, and the oxygen position parameter u. The lattice parameters of solid solution increased with SnO_2 content because of the difference of average ionic radius of Ti^{4+} (0.605 Å) and Sn^{4+} (0.69 Å) [11] at the same coordination number, as shown in Fig. 3(a). Also, SnO_2 has a higher tetragonality (∼0.6725) and oxygen position parameter (∼0.3064) [14] than that of TiO_2. With an increase of SnO_2 content, the tetragonality (c/a) and oxygen position parameter (u) of $(Zn_{1/3}Nb_{2/3})_{0.40}(Ti_{1-x}Sn_x)_{0.60}O_2$ ceramics were increased, as shown in Fig. 3(b).

The apparent density of $(Zn_{1/3}Nb_{2/3})_{0.40}(Ti_{1-x}Sn_x)_{0.60}O_2$ ceramics sintered at 1150 °C for 3 h increased slightly with SnO_2 content up to $x = 0.25$, and then decreased due to the effects of SnO_2 with poor sinterability. The relative density of the specimens in the solid solution range was higher than 89%, and the relative density showed a maximum value at $x = 0.15$.

Fig. 3 shows the microwave dielectric properties of $(Zn_{1/3}Nb_{2/3})_{0.40}(Ti_{1-x}Sn_x)_{0.60}O_2$ ceramics sintered at 1150 °C for 3 h. Dielectric constant (K) was significantly dependent upon the relative density and dielectric polarizability at microwave frequencies. The dielectric constant (K) of the specimens decreased with SnO_2 content due to the decrease of density and the smaller dielectric polarizability of SnO_2 (6.85 Å) than TiO_2 (6.95 Å) [12].

With an increase of SnO_2 content, Qf values of $(Zn_{1/3}Nb_{2/3})_{0.40}(Ti_{1-x}Sn_x)_{0.60}O_2$ specimens increased. It has been reported [13] that Qf values are strongly depended on the density, impurity, secondary phase and grain size. For the specimens with SnO_2, the effect of secondary phase on the Qf value could also be neglected because there was no secondary phase, as confirmed in Fig. 1. With substitution of SnO_2, the grain size decreased and the number and size of pores increased, as shown in Fig. 4. However, Qf values of $(Zn_{1/3}Nb_{2/3})_{0.40}(Ti_{1-x}Sn_x)_{0.60}O_2$ specimens were increased with SnO_2 content.

For the specimens with SnO_2 of $x = 0.15$, the dark gray colors were appeared. With further substitution of SnO_2 gradually changed bright yellow colors. It was related to the reduction of Ti^{4+} ion frequently observed in titanium-containing ceramics, small amounts of Ti^{3+} and oxygen vacancies form during processing [14]. Although there is only a very limited reduction of TiO_2, the reduction is sufficient to cause a severe deterioration in the Qf value. These results are agreed with the report [15] that SnO_2 plays a significant role in increasing the quality factor of the ceramics as an oxidizer. Therefore, the

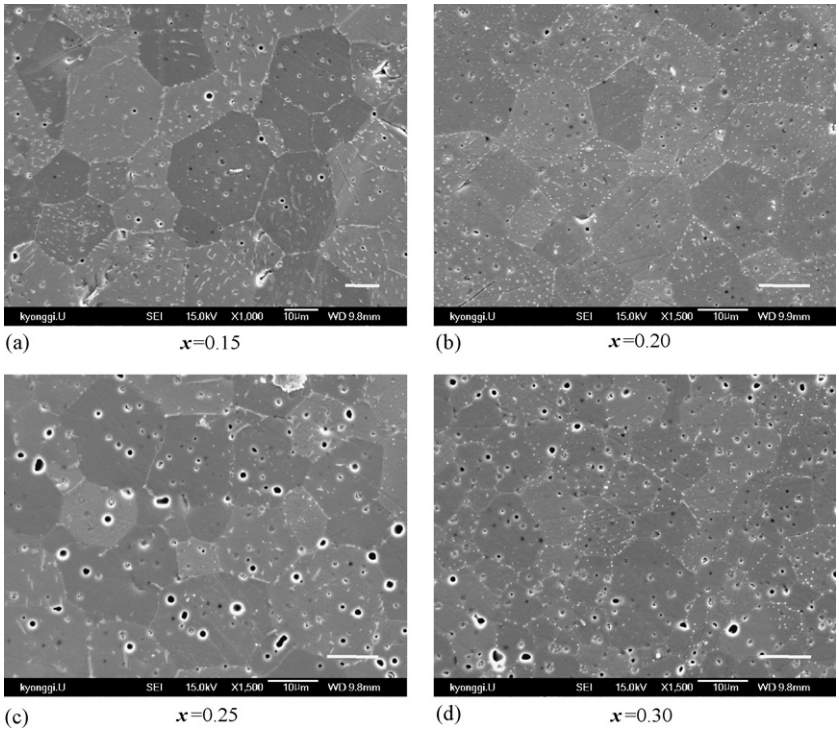

Fig. 4. SEM micrographs of $(Zn_{1/3}Nb_{2/3})_{0.40}(Ti_{1-x}Sn_x)_{0.60}O_2$ ceramics sintered at 1150 °C for 3 h (bar = 10 μm).

Table 1
Octahedral distortion and *TCF* of $(Zn_{1/3}Nb_{2/3})_{0.40}(Ti_{1-x}Sn_x)_{0.60}O_2$ ceramics sintered at 1150 °C for 3 h

x (mol)	Bond length (Å)			Distortion ($\Delta \times 10^5$)	*TCF* (ppm/°C)
	d_{apical}	$d_{equatorial}$	$d_{average}$		
0.15	2.0149	1.9822	1.9931	5.9903	141.44
0.20	2.0170	1.9851	1.9957	5.6843	102.25
0.25	2.0196	1.9889	1.9991	5.2576	77.49
0.30	2.0217	1.9926	2.0023	4.7025	57.91

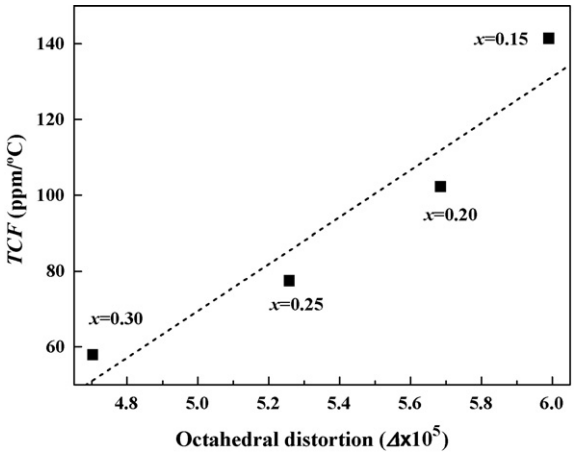

Fig. 5. Dependence of *TCF* on octahedral distortion of $(Zn_{1/3}Nb_{2/3})_{0.40}(Ti_{1-x}Sn_x)_{0.60}O_2$ ceramics sintered at 1150 °C for 3 h.

increase of quality factor (*Qf*) with SnO_2 content is associated with the decrease of reduction of TiO_2.

For the rutile-type structure, there is a close relation between tetragonality (c/a) and oxygen position parameter (u). If the apical and equatorial bond lengths are equal, that is no octahedral distortion, a critical value of u is obtained ($u_{cry} = 1/4[1 + 1/2(c/a)^2]$) [11]. For the complete solid solutions of $(Zn_{1/3}Nb_{2/3})_{0.40}(Ti_{1-x}Sn_x)_{0.60}O_2$, the distortion of oxygen octahedral could be expected because the bond lengths were changed with substitution of SnO_2. Also, the temperature coefficient of dielectric constant (*TCK*) was changed with the tilting of oxygen octahedral in structure. Therefore, *TCF* of compounds with octahedron could be evaluated by the degree of octahedral distortions if the compound has the tilted oxygen octahedral.

Table 1 summarized the oxygen octahedral distortion and *TCF* of $(Zn_{1/3}Nb_{2/3}{}^{5+})_{0.40}(Ti_{1-x}Sn_x)_{0.60}O_2$ ceramics obtained from Eq. (1). The dependence of thermal stability (*TCF*) on the octahedral distortion of $(Zn_{1/3}Nb_{2/3})_{0.40}(Ti_{1-x}Sn_x)_{0.60}O_2$ ceramics is shown in Fig. 5. With an increase of SnO_2 content, *TCF* of $(Zn_{1/3}Nb_{2/3})_{0.40}(Ti_{1-x}Sn_x)_{0.60}O_2$ ceramics decreased due to the decrease of the octahedral distortion of rutile structure resulted that the bond lengths (d_{apical} and $d_{equatorial}$)are tend to same value.

4. Conclusions

For the specimens of $(Zn_{1/3}Nb_{2/3})_{0.40}(Ti_{1-x}Sn_x)_{0.60}O_2$ ($0.15 \leq x \leq 0.30$) sintered at 1150 °C for 3 h, the single phase with tetragonal rutile structure was obtained in the given composition range. Dielectric constant (K) was decreased due to the decrease of dielectric polarizability and density. *Qf* value of specimens with SnO_2 content increased due to the decrease of Ti reduction. Thermal stability (*TCF*) of the specimens was strongly depended on the degree of oxygen octahedral distortion. Typically value of $K = 57.82$, $Qf = 14{,}804$ GHz, $TCF = 57.91$ ppm/°C were obtained for $(Zn_{1/3}Nb_{2/3})_{0.40}$ $(Ti_{0.70}Sn_{0.30})_{0.60}O_2$ ($x = 0.30$) specimens sintered at 1150 °C for 3 h.

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References

[1] A. Nakajima, S. Koizumi, T. Watanabe, K. Hashimoto, Effect of repeated photo-illumination on the wettability conversion of titanium dioxide, J. Photochem. Photobiol. A Chem. 146 (2001) 129–132.
[2] M. Maeda, T. Yamamura, T. Ikeda, Dielectric characteristics of several complex oxide ceramics at microwave frequencies, Jpn. J. Appl. Phys. Suppl. 26 (1987) 76–79.
[3] H.J. Lee, I.T. Kim, K.S. Hong, Dielectric Properties of AB_2O_6 compounds at microwave frequencies (A = Ca, Mg, Mn, Co, Ni, Zn, and B = Nb, Ta), Jpn. J. Appl. Phys. 36 (1996) 1318–1320.
[4] K. Fukada, R. Kitoh, I. Awai, Microwave characteristics of TiO_2–Bi_2O_3 dielectric resonator, Jpn. J. Appl. Phys. 32 (1993) 4584–4588.
[5] I.M. Reany, E.L. Colla, N. Setter, Dielectric and structural characteristics of Ba- and Sr-based complex Perovskites as a function of tolerance Factor, Jpn. J. Appl. Phys. 33 (1994) 3984–3990.
[6] S.D. Mo, W.Y. Ching, Electronic and optical properties of three phases of titanium dioxide: rutile, anatase, and brookite, Phys. Rev. B 51 (19) (1995) 13023–13032.
[7] J.A. Toledo-Antonio, R. Gutierrez-Baez, P.J. Sebastian, A. Vazquez, Thermal stability and structural deformation of rutile SnO_2 nanoparticles, J. Solid Chem. 174 (2003) 241–248.
[8] B.W. Hakki, P.D. Coleman, A dielectric resonator method of measuring inductive capacities in the millimeter range, IRE Trans. Microw. Theory Tech. MTT18 (1970) 476–485.
[9] T. Nishikawa, K. Wakino, H. Tamura, H. Tanaka, Y. Ishikawa, Precise measurement method for temperature coefficient of microwave dielectric resonator material, in: IEEE MTT-S International Microwave Symposium Digest, 1987, 277–280.
[10] R.D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, Acta Crystallogr. A32 (1976) 751–767.
[11] T. Hirata, Oxygen position, octahedral distortion, and bond-valence parameter from bond lengths in $Ti_{1-x}Sn_xO_2$ ($0 \leq x \leq 1$), J. Am. Ceram. Soc. 83 (12) (2000) 3205–3207.
[12] R.D. Shannon, Dielectric polarizabilities of ions in oxides and fluorides, J. Appl. Phys. 73 (1) (1993) 348–366.
[13] W.S. Kim, E.S. Kim, K.H. Yoon, Effect of Sm^{3+} substitution on dielectric properties of $(Ca_{1-x}Sm_{2x/3})TiO_3$ ceramics at microwave frequencies, J. Am. Ceram. Soc. 82 (8) (2000) 2111–2115.
[14] N. Michiura, T. Tatekawa, Y. Higuchi, H. Tamura, Role of donor and acceptor ions in the dielectric loss tangent of $(Zr_{0.8}Sn_{0.2})TiO_4$ dielectric resonator material, J. Am. Ceram. Soc. 78 (3) (1995) 793–796.
[15] W. Guoqing, W. Shunhua, S. Hao, Microwave dielectric ceramics in the BaO–TiO_2–ZnO system doped with $MnCO_3$ and SnO_2, Mater. Lett. 59 (2005) 2229–2231.