

Relationships between crystal structure and microwave dielectric properties of $(\text{Zn}_{1/3}\text{B}_{2/3}^{5+})_x\text{Ti}_{1-x}\text{O}_2$ ($\text{B}^{5+} = \text{Nb}, \text{Ta}$) ceramics

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Abstract

Dependence of microwave dielectric properties on the crystal structure of $(\text{Zn}_{1/3}\text{B}_{2/3}^{5+})_x\text{Ti}_{1-x}\text{O}_2$ ($\text{B}^{5+} = \text{Nb}, \text{Ta}$) ceramics was investigated as a function of $\text{Zn}_{1/3}\text{B}_{2/3}^{5+}\text{O}_2$ ($\text{B}^{5+} = \text{Nb}, \text{Ta}$) content ($0.4 \leq x \leq 0.7$). Dielectric constant (K) and the temperature coefficient of resonant frequency (TCF) of sintered specimens were strongly dependent on the structural characteristics of oxygen octahedra in rutile structure. Cation rattling and the distortion of oxygen octahedra were dependent on the bond length ratio of apical (d_{apical})/equatorial ($d_{\text{equatorial}}$) of oxygen octahedra. The quality factor (Qf) was dependent on the reduction of Ti ion as well as the microstructure of the sintered specimens.

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1. Introduction

Microwave dielectric properties are affected by the crystal structure and the interactions between cation and anion of the compound. At microwave frequencies, the dielectric constant was found to be affected by the rattling effect as well as the dielectric polarizability, and the temperature coefficient of resonant frequency was closely related with the temperature coefficient of dielectric constant (TCK), which is depended on the distortion of oxygen octahedral [1]. On the other hand, the rattling effect and the octahedral distortion were largely dependent on the bond strength and bond length of the composing ions.

It has been reported [2] that Ti^{4+} ions of TiO_2 can be substituted by Nb^{5+} or Ta^{5+} as well as monovalent, divalent, or trivalent cation. The extensive new rutile solid solutions of $(\text{A}_{1/3}\text{B}_{2/3}^{5+})_x\text{Ti}_{1-x}\text{O}_2$ have been prepared in which Ti^{4+} was replaced by a divalent and a pentavalent cation. The substitution of Ti^{4+} ions of TiO_2 by other ions would affect the microwave dielectric properties and the crystal structures of the specimens. The ionic size differences between Zn^{2+} ion (0.74 Å), Nb^{5+} ion (0.64 Å) and/or Ta^{5+} ion (0.64 Å) and Ti^{4+} ion (0.605 Å) are not much at the same coordination number (C.N. = 6) [3].

Therefore, tetravalent Ti^{4+} ion in the TiO_2 could be substituted by one third of Zn^{2+} ion and two third of Nb^{5+} and/or Ta^{5+} ions for the charge compensating.

In the rutile structure, the cation is coordinated to six oxygen ions and each oxygen ion is coordinated to three cations. These octahedra form chains, cross-linked by sharing corners at each cation–oxygen bond. The TiO_6 octahedra in rutile TiO_2 consisted of four equatorial Ti–O bonds and two apical Ti–O bonds, is slightly distorted with longer apical Ti–O bonds slightly than the other equatorial bond [4]. The distortion of the oxygen octahedral surrounding each Ti atom is decided by the oxygen position parameter u , the axial ratio c/a , and lattice parameter of a -axis. As to solid solutions between TiO_2 and $\text{Zn}_{1/3}\text{B}_{2/3}^{5+}\text{O}_2$ ($\text{B}^{5+} = \text{Nb}, \text{Ta}$), the octahedral distortion should be changed with the compositional variations of $(\text{Zn}_{1/3}\text{B}_{2/3}^{5+})_x\text{Ti}_{1-x}\text{O}_2$.

In this study, the microwave dielectric properties and crystal structure of the $(\text{Zn}_{1/3}\text{B}_{2/3}^{5+})_x\text{Ti}_{1-x}\text{O}_2$ ($\text{B}^{5+} = \text{Nb}, \text{Ta}$) system were investigated as a function of the amount of $\text{Zn}_{1/3}\text{B}_{2/3}^{5+}\text{O}_2$ ($\text{B}^{5+} = \text{Nb}, \text{Ta}$) ($0.4 \leq x \leq 0.7$). Dependence of dielectric constant on the rattling effects and the dependence of TCF on the octahedral distortion of oxygen octahedra were also discussed.

2. Experimental procedure

ZnO , Nb_2O_5 , Ta_2O_5 , and TiO_2 powders with reagent-grade were used as starting materials. They were weighed

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according to the compositions of $\text{ZnB}_2^{5+}\text{O}_6$ ($\text{B}^{5+} = \text{Nb}, \text{Ta}$), and then milled with ZrO_2 balls for 24 h in distilled water. Powders with a composition of ZnNb_2O_6 and/or ZnTa_2O_6 were calcined at 900°C and/or 1200°C for 3 h, respectively. These calcined powders were mixed according to the formula of $(\text{Zn}_{1/3}\text{B}_{2/3}^{5+})_x\text{Ti}_{1-x}\text{O}_2$ ($\text{B}^{5+} = \text{Nb}, \text{Ta}$, $0.4 \leq x \leq 0.7$). Mixtures with $\text{B}^{5+} = \text{Nb}$ and/or Ta were calcined at 1100°C and/or 1200°C for 3 h, respectively. The calcined 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 from 1050°C to 1250°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 , and then furnace cooled to room temperature.

Crystalline phases of the specimens were identified with the powder X-ray diffraction patterns (D/Max-3C, Rigaku, Japan). The sintered specimens was pulverized and weighted with a 10 wt.% of internal standard Si powder to correct 2θ . From the Rietveld refinements of X-ray diffraction patterns, the lattice parameters and unit cell volume of the sintered specimens were determined. Microstructure was observed using a scanning electron microscope and energy dispersive spectrometer (JEOL, JSM-6500F). The dielectric constant, unloaded Q value at frequencies of 5–7 GHz was measured by the post-resonant method developed by Hakki and Coleman [5]. TCF was measured by the cavity method [6] at the temperature range of $25\text{--}80^\circ\text{C}$.

From the lattice parameters and oxygen position parameter of tetragonal rutile structure, the individual bond length [7] of oxygen octahedral was obtained from Eqs. (1)–(3):

$$d_{\text{apical}} = au\sqrt{2} \quad (1)$$

$$d_{\text{equatorial}} = 0.5a \left[2(2u - 1)^2 + \left(\frac{c}{a} \right)^2 \right]^{1/2} \quad (2)$$

$$u = \frac{2 - (4 - 2(1 - (d_{\text{equatorial}}/d_{\text{apical}})^2)((c/a)^2 + 2))^{1/2}}{4(1 - (d_{\text{equatorial}}/d_{\text{apical}})^2)} \quad (3)$$

where a and c are the lattice parameters and u is the oxygen position parameter in oxygen octahedral. From the individual bond length of oxygen octahedra, the octahedral distortion (Δ) was calculated in Eq. (4) [3]:

$$\Delta = \frac{1}{6} \sum \left\{ \frac{R_i - \bar{R}}{\bar{R}} \right\}^2 \quad (4)$$

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

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of $(\text{Zn}_{1/3}\text{B}_{2/3}^{5+})_x\text{Ti}_{1-x}\text{O}_2$ ($\text{B}^{5+} = \text{Nb}, \text{Ta}$) sintered specimens. The specimens with $\text{B}^{5+} = \text{Nb}$ and/or $\text{B}^{5+} = \text{Ta}$ were sintered at 1100°C and/or 1200°C for 3 h, respectively. For the specimens with $\text{Zn}_{1/3}\text{Ta}_{2/3}\text{O}_2$, tetragonal rutile solid solutions were obtained through the entire composition, while the ixiolite $\text{ZnTiNb}_2\text{O}_8$ was detected as a secondary phase of $(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.7}\text{Ti}_{0.3}\text{O}_2$, along with rutile phase, and these solid solution limits depend on substituted B^{5+} ion [8]. Fig. 2 shows the crystal structure of rutile solid solution. In the $(\text{Zn}_{1/3}\text{B}_{2/3}^{5+})_x\text{Ti}_{1-x}\text{O}_2$ ($\text{B}^{5+} = \text{Nb}, \text{Ta}$) system, the Zn^{2+} and B^{5+} cations are substituted into the rutile structure, and then distributed at random over the octahedral Ti^{4+} sites [2].

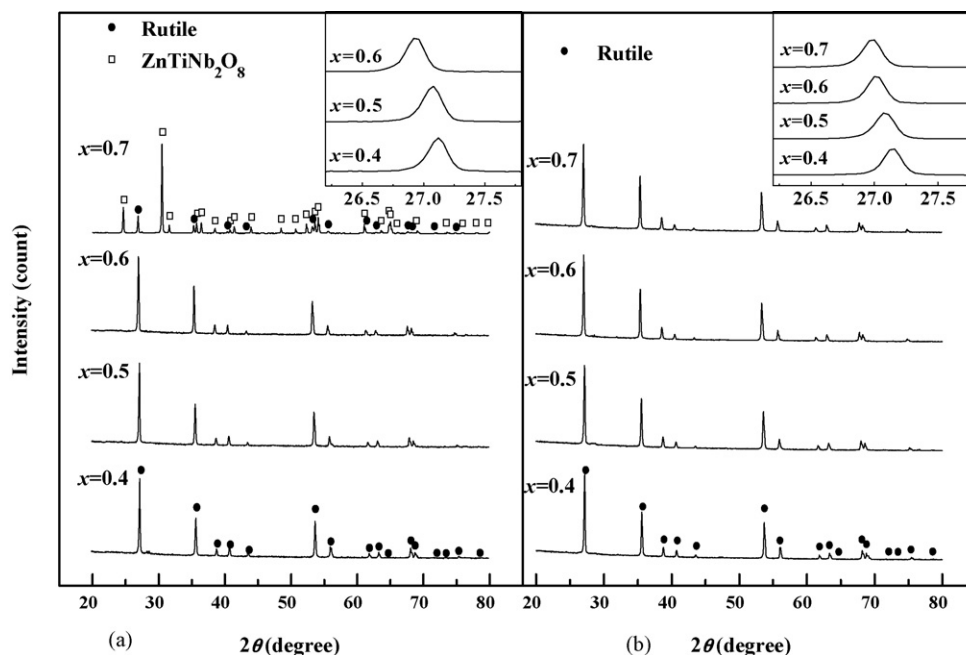


Fig. 1. X-ray diffraction patterns of $(\text{Zn}_{1/3}\text{B}_{2/3}^{5+})_x\text{Ti}_{1-x}\text{O}_2$ ($0.4 \leq x \leq 0.7$) sintered specimens: (a) $\text{B}^{5+} = \text{Nb}$ and (b) $\text{B}^{5+} = \text{Ta}$.

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