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Crystal structure and microwave dielectric properties of $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ ceramics

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Abstract

The crystal structure and microwave dielectric properties of $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ ($x = 0.00$, 0.05, 0.10, 0.15) ceramics sintered at temperatures ranging from 1100 °C to 1140 °C for 6 h were investigated. A single phase with ixiolite structure was obtained. With the increase of Sn content, the dielectric constant decreased attributed to the decrease of dielectric polarizability. The Qf value decreased with the decrease of packing fraction and grain size. The temperature coefficient of resonant frequency (τ_f) increased due to the increase of the bond valence of $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ ceramics. The excellent microwave dielectric properties of $\varepsilon = 35.05$, Qf = 49,100 GHz, $\tau_f = -27.6 \times 10^{-6}$/°C were obtained for $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ ($x = 0.05$) specimens sintered at 1120 °C for 6 h.

Keywords: A. Sintering; D. Niobates; Crystal structure; Microwave dielectric properties

1. Introduction

During the past couple of decades, microwave dielectric ceramics are increasingly used for resonators, filters, duplexers and antenna in systems for wireless communications. The advantages of microwave dielectric ceramics that have high Qf value with moderate dielectric constant characteristics and good thermal stability at high frequencies are utilized [1,2].

$ZnTiNb_2O_8$ has high Qf value (42,500 GHz), high dielectric constant (34.3), low sintering temperature (1120 °C) [3]. However, its temperature coefficient of resonator frequency is too large (-52×10^{-6}/°C) for the practical application at microwave frequencies. It has been reported that temperature coefficient of resonator frequency (τ_f) increased with the increase of bond valence which can increase the bonding strength between oxygen and cation. The bond valence could be calculated from the Eq. (1) [4,5]:

$$v_{ij} = \exp\left(\frac{R_{ij} - d_{ij}}{b'}\right) \quad (1)$$

where R_{ij} is the bond valence parameter, d_{ij} the bond length between atoms i and j, and b' is commonly taken to be a universal constant equal to 0.37 Å. When the bond length d_{ij} is invariable, the bond valence v_{ij} increases with the increase of bond valence parameter R_{ij}. Thus τ_f can be improved by increasing the bond valence parameter. In the $ZnTiNb_2O_8$ system, the bond valence parameter of Nb ($R_{Nb-O} = 1.911$ Å) is larger than R_{Ti-O} (1.815 Å) and R_{Zn-O} (1.704 Å). When the Nb content was increased, the bond valence parameter would increase. Therefore, the $Zn_{0.9}Ti_{0.8}Nb_{2.2}O_8$ ceramic was studied. To further increase the bond valence parameter, Sn having relatively larger bond valence parameter ($R_{Sn-O} = 1.905$ Å) was chosen to be added to the $Zn_{0.9}Ti_{0.8}Nb_{2.2}O_8$ ceramic.

In the present work, the microwave dielectric properties of $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ ceramics were investigated. The correlation of crystal structure and microwave dielectric properties of $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ ceramics was discussed through the crystal structure Rietveld refinement [6].

2. Experimental procedure

The $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ ($x = 0.00$, 0.05, 0.10, 0.15) ceramics were prepared by the conventional solid-state solution, using high-purity ZnO (99.9%), Nb_2O_5 (99.9%), TiO_2 (99.9%), and SnO_2 (99.9%) powders as the raw materials.

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The weighed raw materials were mixed, by ball milling with zirconia media, in deionized water for 6 h. The dried powders were pressed into disks of 10 mm in diameter and 4–5 mm in height after being calcined at 900 °C for 3 h. The disks were sintered at temperatures ranging from 1100 °C to 1140 °C in air for 6 h.

The microstructures were observed using a scanning electron microscope (Phillips, XL30, Antilles, Netherlands), and the phase constitution of the specimens was investigated using X-ray diffraction (Rigaku, D/MAX-2500, Tokyo, Japan) in the 2θ range of 10° to 70°. Structure analyses were carried out by the Rietveld refinement. The bond valence of $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ ceramics was calculated from the bond valence parameters of all cation and the distance between cation and oxygen [5]. The packing fraction was obtained by the summation of the volume of packed ions over the volume of a primitive unit cell, which could be calculated from Eq. (2) [7]:

$$\text{Packing fraction}\,(\%) = \frac{\text{volume of the atoms in the cell}}{\text{volume of primitive unit cell}} = \frac{\text{volume of the atoms in the cell}}{\text{volume of unit cell}} \times Z \quad (2)$$

where Z is the number of formula units per unit cell.

The microwave dielectric properties of the specimens were measured in the frequency range of 6–9 GHz using a network analyzer (Agilent, 8720ES, Santa Clara, CA). The dielectric constant was measured by the Hakki-Coleman method, as modified by Courtney [8], and the unloaded Q values were measured by the cavity method [9]. The temperature coefficient of resonant frequency was determined from the resonant frequencies at the temperature of 25 °C and 85 °C. The measurement errors of dielectric constant, temperature coefficient of resonant frequency and Qf value were $<0.5\% \times \varepsilon_r$, 0.5×10^{-6}/°C, and $5\% \times$ Qf respectively.

3. Results and discussion

3.1. Crystal structure analyses

The X-ray powder diffraction patterns of the $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ ceramics sintered at 1120 °C for 6 h are given in Fig. 1. A single phase with ixiolite structure (index as $ZnTiNb_2O_8$ JCPDS #48-0323) was obtained. Rietveld refinement [6] was used to analyze the crystal structure of $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ ceramics. The lattice parameters of the sintered specimens were determined as shown in Table 1, and bond valence, packing fraction were calculated.

As could be seen from Table 1, the lattice parameters increased with the increase of Sn content. And with the increase of Sn content, the atomic interactions of $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ ceramics would be changed, which resulted in the changes of the bond valence of $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ ceramics. Table 2 shows the bond valence of $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ (x = 0.00, 0.05, 0.10, 0.15) ceramics calculated using Eq. (1) and following Eq. (3) [4]:

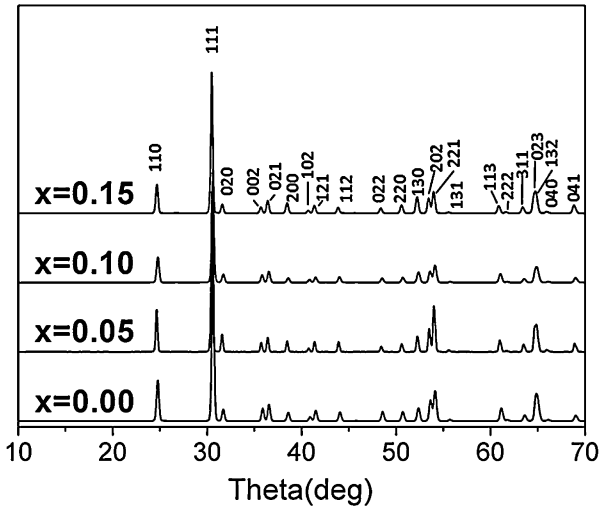

Fig. 1. XRD patterns of $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ ceramics at 1120 °C.

$$V_i = \sum_j v_{ij} \quad (3)$$

Table 1
Lattice parameters of $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ (x = 0.00, 0.05, 0.10, 0.15) ceramics.

Value of x (mol)	a (Å)	b (Å)	c (Å)
0.00	4.6704	5.6537	5.0148
0.05	4.6755	5.6571	5.0159
0.10	4.6773	5.6587	5.0239
0.15	4.6849	5.6685	5.0354

Table 2
Bond valence of $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ (x = 0.00, 0.05, 0.10, 0.15) ceramics.

x (mol)	$d_{(\text{cation-O})}$ (Å)	$R_{(\text{cation-O})}$	$v_{(\text{cation-O})}$	$V_{(\text{cation-O})}$
0.00	1.9514	1.8435	0.7471	3.6518
	2.0192		0.6220	
	1.9514		0.7471	
	2.0192		0.6220	
	2.1335		0.4567	
	2.1335		0.4567	
0.05	1.9134	1.8447	0.8305	3.7212
	2.0414		0.5876	
	1.9134		0.8305	
	2.0414		0.5876	
	2.1464		0.4425	
	2.1464		0.4425	
0.10	1.9244	1.8458	0.8087	3.7766
	2.0213		0.6224	
	1.9244		0.8087	
	2.0213		0.6224	
	2.1354		0.4572	
	2.1354		0.4572	
0.15	1.8593	1.8470	0.9673	3.8383
	2.0409		0.5921	
	1.8593		0.9673	
	2.0409		0.5921	
	2.2253		0.3597	
	2.2253		0.3597	

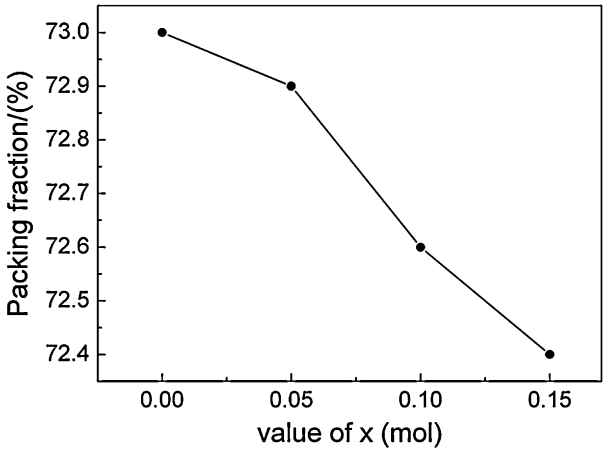

Fig. 2. Packing fraction of $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ ceramics at 1120 °C.

The bond valence parameters followed the values in the previous report [10]. With the increase of Sn content, the bond valence of $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ ceramics increased.

Fig. 2 shows the packing fraction of $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ ceramics at 1120 °C calculated by the Eq (2). Kim et al. reported that Qf value decreases with the decrease of packing fraction [7].

3.2. Scanning electron microscopy (SEM)

Fig. 3 shows the SEM micrographs of $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ ($x = 0.00, 0.05, 0.10, 0.15$) specimens sintered at 1120 °C. In general, all specimens were densified and the pore was hardly seen indicating that the $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ ceramics had good sintering properties at 1120 °C. Fig. 3 illustrated that the grain size decreased with the increase of Sn content.

3.3. Microwave dielectric properties

Fig. 4 shows the dielectric constant and dielectric polarizability of $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ ceramics. The dielectric constant is strongly dependent on the dielectric polarizability. Shannon [11] suggested that molecular polarizabilities of complex compounds can be estimated by summing the polarizabilities of constituent ions. The corresponding equation for the studied ceramics could be defined as follows Eq. (4):

$$\alpha(Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8) = 0.9\alpha(Zn^{2+}) + (0.8-x)\alpha(Ti^{4+}) + x\alpha(Sn^{4+}) + 2.2\alpha(Nb^{5+}) + 8\alpha(O^{2-}) \quad (4)$$

where α is polarizability. With the aid of estimated polarizability and the Clausius-Mosotti relation shown in Eq. (5), the dielectric constant can be calculated.

$$\varepsilon_r = \frac{3V_m + 8\pi\alpha_D}{3V_m - 4\pi\alpha_D} \quad (5)$$

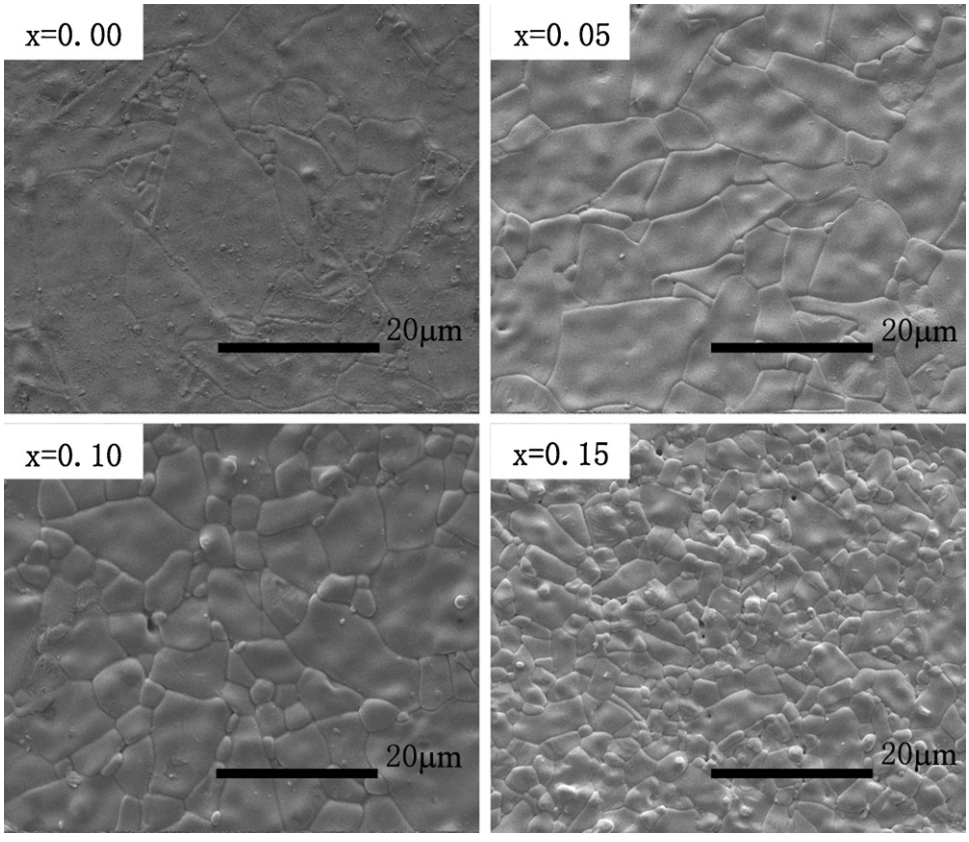

Fig. 3. SEM micrographs of $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ specimens sintered at 1120 °C for 6 h.

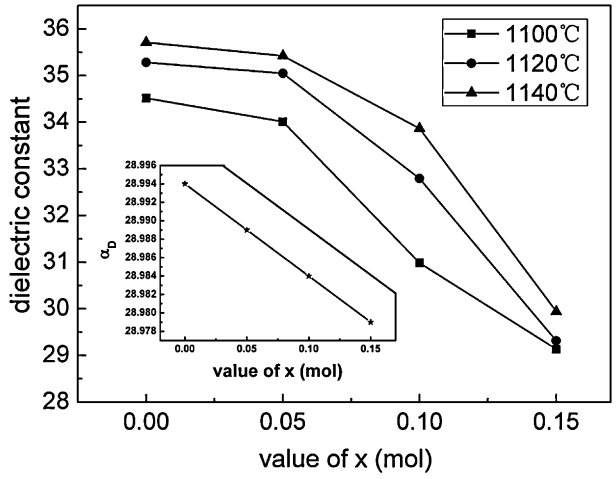

Fig. 4. Dielectric constant and dielectric polarizability of $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ ceramics.

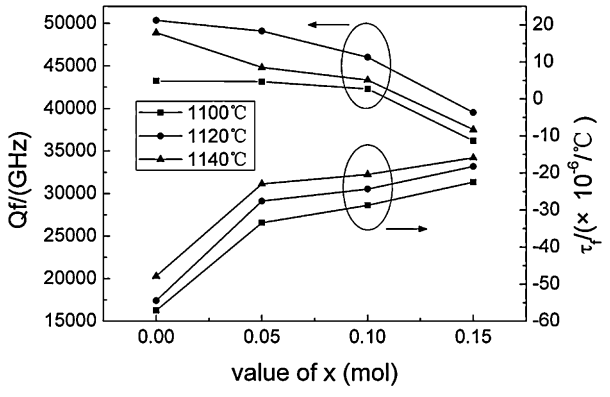

Fig. 5. Qf value and τ_f of $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ ceramics.

where V_m is molar volume, α_D is the sum of ionic polarizabilities of individual ions and can be calculated from the Eq. (4). As shown in Fig. 4, with the increase of Sn content, the decreasing trend of dielectric constant was in accordance with the decreasing trend of dielectric polarizability. Therefore, the dielectric constant of $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ ceramics decreased due to the decrease of dielectric polarizability.

The Qf value and τ_f of $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ ceramics are given in Fig. 5. It has been reported that Qf depended on the extrinsic factors such as density, impurity, secondary phase and grain size, and intrinsic ones representing the minimum loss related with lattice anharmonicity that can be expected for a particular composition and crystal structure of the materials [12]. As to the extrinsic factors, with the decrease of grain size, the Qf value decreased due to the increase of grain boundaries where defects, impurities, and large inner stress are usually concentrated. Therefore, with the increase of Sn content, the Qf value decreased with the decrease of grain size. As to the intrinsic factors, the decreasing trend of Qf value was in consistent with the decreasing trend of packing fraction as shown in Fig. 2. For these reasons, the Qf value of $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ ceramics decreased with the increase of Sn content.

It is reported that the temperature coefficient of permittivity (τ_ε) increases with the increase of the temperature dependence of the macroscopic polarizability at constant volume [13]. And τ_f is related to τ_ε and the linear thermal expansion coefficient α_L by Eq. (6):

$$\tau_f = -\left(\frac{\tau_\varepsilon}{2} + \alpha_L\right) \quad (6)$$

In the $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ ceramics, the increase of τ_f is mainly attributed to the increase of the bond valence. When the bond valence increased, the bonding strength between oxygen and cation was become stronger, and the dilution of the average ionic polarizability was decreased leading to the decrease of τ_ε. This would lead to the τ_f of $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ ceramics moving toward positive direction.

4. Conclusions

The crystal structure and microwave dielectric properties of $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ ceramics were investigated. With the increase of Sn content, the dielectric constant decreased due to the decrease of dielectric polarizability. The Qf value decreased with the decrease of the packing fraction and grain size. In the $ZnTiNb_2O_8$ system, the temperature coefficient of resonant frequency was improved from -52×10^{-6}/°C to -27.6×10^{-6}/°C by adding Sn. It was due to the τ_f of the specimens moving toward positive direction with the increase of the bond valence of $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ ceramics. Typically values of $\varepsilon = 35.05$, Qf = 49,100 GHz, $\tau_f = -27.6 \times 10^{-6}$/°C were obtained for $Zn_{0.9}Ti_{0.8-x}Sn_xNb_{2.2}O_8$ ($x = 0.05$) specimens sintered at 1120 °C for 6 h.

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