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Correlation of crystal structure and microwave dielectric characteristics of temperature stable $Zn_{1-x}Mn_xZrNb_2O_8$ (0.02≤x≤0.1) ceramics

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ABSTRACT

Wolframite-structured $Zn_{1-x}Mn_xZrNb_2O_8$ (x=0.02, 0.04, 0.06, 0.08, 0.10) ceramics were synthesized by the conventional solid-state method. The effects of Mn^{2+} substitution on the crystal structure, crystal chemistry and microwave dielectric properties of $ZnZrNb_2O_8$ were investigated. Bond ionicity, lattice energy and thermal expansion of the ceramics were calculated by the complex chemical bond theory, which were used to investigate the correlation between intrinsic factors and microwave dielectric properties. The ε_r values were dependent on the electronic oxide polarizabilities of $Zn_{1-x}Mn_xZrNb_2O_8$ ceramics. The $Q{\cdot}f$ values decreased from 51,300 to 44,900 GHz, which could be explained in terms of packing fraction and lattice energy. The τ_f values were shifted to positive direction with the increase of Mn^{2+} contents, which indicated that the distortion of the [BO6] octahedral was closely related to τ_f values. In addition, thermal expansion coefficient also affected the temperature stability of ceramics. Typically, an excellent microwave dielectric property was obtained in the $Zn_{0.9}Mn_{0.1}ZrNb_2O_8$ with a ε_r of 29.43, an appropriate $Q{\cdot}f$ of 44,900 GHz and a near zero τ_f of −5.61 ppm/°C.

1. Introduction

Microwave dielectric materials have attracted increasing attention for their potential applications in mobile and satellite communications. For these high frequency wireless communication applications, the microwave dielectric materials should possess high dielectric constant, high quality factor, and near-zero temperature coefficient of resonant frequency, which are desirable for minimization of the microwave circuit component, maximum signal intensity and adaptation to environmental temperature changes. The microwave dielectric ceramics are good candidates and nowadays many of them have been reported for their excellent microwave dielectric properties [1–4]. Recently, great attentions have been paid on wolframite-structured $ZnZrNb_2O_8$ ceramics for their high quality factors and appropriate dielectric constants [5–10]. For instance, Liao et al. firstly reported $ZnZrNb_2O_8$ ceramics exhibited microwave dielectric properties of ε_r=30, $Q{\cdot}f$=61,000 GHz and τ_f=−52 ppm/°C [5]. Murthy et al. reported the crystal cell parameters of $ZnZrNb_2O_8$ were a=4.81110 Å, b=5.67996 Å, c=5.07655 Å with the β angle of 91.73° [6]. However, the large negative τ_f values limited its further practical applications. Ionic substitution is one of the effective ways to investigate crystal structure and improve microwave dielectric properties of matrix compounds. Li et al. reported the effect of ions substitutions on microwave dielectric properties of $ZnZrNb_2O_8$ ceramics. In their reports, the $Zn_{0.95}Ni_{0.05}ZrNb_2O_8$ ceramics sintered at 1280 °C possessed excellent microwave dielectric properties with ε_r=29.02, $Q{\cdot}f$=83,558 GHz and τ_f=−52.6 ppm/°C. In addition, the τ_f values were also shifted to −40.05 ppm/°C by substituting 5% Mn^{2+} for Zn^{2+} at A-site [7,8]. The radius of Mn^{2+}(0.83 Å) is higher than that of Zn^{2+}(0.74 Å) and the difference between the two radii is less than 15%. Therefore, effort is directed toward substituting Mn^{2+} for Zn^{2+} to improve the τ_f values of $ZnZrNb_2O_8$.

Intrinsic parameters such as bond ionicity, lattice energy and coefficient of thermal expansion could be obtained by the complex chemical bond theory, which were used to investigate basic properties of complex crystals [9,10]. Zhang et al. built a close relationship between complex chemical bond theory and microwave dielectric properties in $ZnZr(Nb_{1-x}Ta/Sb_x)_2O_8$. In their report, the variation of dielectric constant and quality factors were explained in terms of Nb-O bond ionicity and Nb-site lattice energy [9]. In our previous works, the ε_r and $Q{\cdot}f$ values of $AZrNb_2O_8$ were linearly correlated with the Nb-site bond ionicity and lattice energy, which showed the same result with Zhang's report. The crystal structure changed with the variation of A site ions, which also indirectly affected the Nb-O octahedral [10]. It was reported that the Nb-O octahedral played a predominate role in affecting the phase stability of ABO_4 compounds. Some reports also investigated the relationship between B-site octahedral and microwave dielectric properties [11,12]. However, the effects of slight A-site cation substitutions on the crystal structure, crystal chemistry and microwave dielectric properties of $ZnZrNb_2O_8$ were not reported. In this work, the

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effects of Mn^{2+} substitutions on the packing fraction, bond valence and octahedral distortion were studied based on Rietveld refinement. Complex chemical bond theory was performed on all the compositions to investigate the variation of bond ionicity, lattice energy and thermal expansion coefficient. Furthermore, the structure-property relationship of the $Zn_{1-x}Mn_xZrNb_2O_8$ ceramics was systematically investigated based on all the above methods of characterization.

2. Experimental procedure

The samples were prepared by the conventional solid-state method from oxide powders (analytical-grade ZnO, MnO, ZrO_2 and Nb_2O_5; Aladdin Shanghai Biochemical Technology Co., Ltd. Shanghai, China). The raw materials were mixed according to the formula of $Zn_{1-x}Mn_xZrNb_2O_8$ (x=0.02, 0.04, 0.06, 0.08 and 0.1) and milled with ZrO_2 balls in ethanol for 24 h. The wet powders were dried and calcined at 1050 °C for 4 h in the alumina crucibles. The obtained powders were reground for 24 h, dried and mixed with 8 wt% polyvinyl alcohol as a binder. The granulated powders were pressed into cylinders of 10 mm diameter and about 6 mm height at a pressure of 200 MPa. The resultant cylinders were preheated at 500 °C for 4 h to expel the binder and sintered at 1050–1250 °C for 4 h in air at a heating rate of 5 °C/min.

Phase analysis of samples was conducted with the help of a Rigaku diffractometer (Model D/MAX-B, Rigaku Co., Japan) using Ni filtered CuKα radiation (λ=0.1542 nm) at 40 kV and 40 mA settings. The cell parameters of $Zn_{1-x}Mn_xZrNb_2O_8$ were refined via Jade 6.5 software. The microstructure of the sintered samples was characterized by a scanning electron microscopy (Model JEOL JEM-2010, FEI Co., Japan). The apparent densities of the sintered samples were measured using the Archimedes method (Mettler ToledoXS64), and the relative density of the sample was obtained from the crystal structure and atomic weight [13]. A network analyzer (N5234A, Agilent Co., America) was used for the measurement of microwave dielectric properties. Dielectric constants were measured using Hakki-Coleman post-resonator method by exciting the TE011 resonant mode of dielectric resonator by using an electric probe as suggested by Hakki and Coleman [14]. Unloaded quality factors were measured using TE01d mode by the cavity method [15]. All measurements were operated at room temperature and in the frequency of 6–11 GHz. Temperature coefficients of resonant frequency were measured in the temperature range of 25–85 °C.

3. Results and discussion

The apparent densities of $Zn_{1-x}Mn_xZrNb_2O_8$ (x=0.02, 0.04, 0.06, 0.08, 0.10) as a function of sintering temperatures were given in Fig. 1. The values of all the samples gradually increased with the sintering temperatures increasing from 1050 to 1200 °C. Samples sintered at 1200 °C showed the highest densities compared to the samples sintered at 1150 °C and 1250 °C. The relative densities of the ceramics sintered at 1200 °C were shown in the inside of Fig. 1. All the samples possessed more than 95% of their theoretical density, which indicated the dense samples could be obtained at 1200 °C. SEM micrograph of $Zn_{0.94}Mn_{0.06}ZrNb_2O_8$ ceramics sintered at 1200 °C was also illustrated in inside of Fig. 1. It was easily found that no pores existed in the sample, which also indicated nearly dense microstructure of $Zn_{1-x}Mn_xZrNb_2O_8$ could be obtained at 1200 °C. What's more, the trapped porosity developed by exaggerated grain growth caused the reduction in apparent density at elevated temperatures.

The XRD patterns of $Zn_{1-x}Mn_xZrNb_2O_8$ (0≤x≤0.1) ceramics sintered at 1200 °C were shown in Fig. 2. All the samples showed a wolframite-structured phase with the space group of p2/c, which matched well with JCPDS file No. 48-0324. With the Mn^{2+} content increasing, the XRD patterns were shifted to lower angle. Secondary phases of ZrO_2 could be observed around 27° when x value was more than 0.06, but its smaller diffraction peaks proved the fewer contents. Rietveld refinement was performed on all the $Zn_{1-x}Mn_xZrNb_2O_8$ ceramics sintered at 1200 °C, and the refinement parameters were listed in Table 1. Substitution of higher ionic radius elements Mn^{2+}(0.83 Å) in place of lower radius elements Zn^{2+}(0.74 Å) increased the unit cell volume from 138.19 to 139.23 Å^3, which caused the reflections to be shifted toward lower angle. Based on the atomic coordinate information, the schematic crystal structure of wolframite-structured $Zn_{1-x}Mn_xZrNb_2O_8$ ceramics was shown in the inside of Fig. 2. The crystallographic data of all the samples was illustrated in Table 2. It could be observed that oxygen O1 was connected to one A-site (A=Zn, Mn, Zr) cation with a short terminal bond and two B-site (B=Nb) cations with longer bonds. On the other hand, oxygen O2 connected two A-site cations and one B-site cation. Thus, it could be considered that the substitution of Mn^{2+} for Zn^{2+} would enlarge or compress both the Zn/ZrO_6 and NbO_6 octahedra.

The octahedra distortion of $Zn_{1-x}Mn_xZrNb_2O_8$ was calculated using the bond length from Rietveld refinement and defined as Eq. (1) [16].

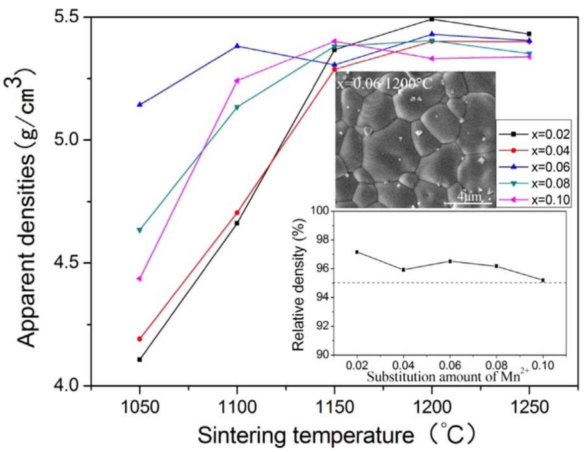

Fig. 1. Apparent densities of $Zn_{1-x}Mn_xZrNb_2O_8$ ceramics as a function of sintering temperature, relative densities of ceramics sintered at 1200 °C and SEM micrographs of $Zn_{0.94}Mn_{0.06}ZrNb_2O_8$ sintered at 1200 °C.

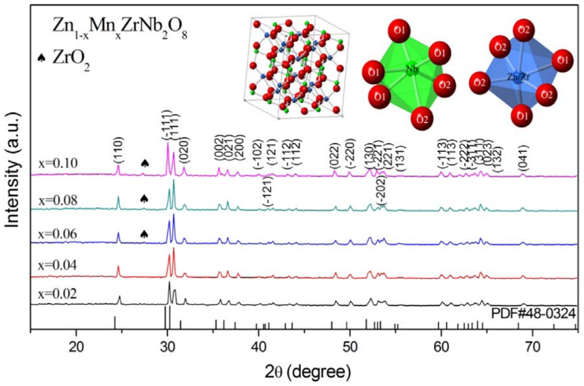

Fig. 2. The XRD patterns for the $Zn_{1-x}Mn_xZrNb_2O_8$ ceramics sintered at 1200 °C, schematic representation of wolframite structured $Zn_{1-x}Mn_xZrNb_2O_8$ (2×2×2) supercell and corresponding octahedron.

Table 1
The refinement parameters of $Zn_{1-x}Mn_xZrNb_2O_8$ ceramics sintered at 1200 °C.

$Zn_{1-x}Mn_xZrNb_2O_8$	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)	R
X=0.02	4.7867	5.6713	5.0920	91.3679	138.19	0.1973
X=0.04	4.7916	5.6846	5.0909	91.2480	138.64	0.1906
X=0.06	4.7969	5.6784	5.0929	91.3510	138.69	0.1810
X=0.08	4.8024	5.6884	5.0849	91.3282	138.87	0.1912
X=0.10	4.8079	5.6939	5.0873	91.2867	139.23	0.2049