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Correlation of crystal structure and microwave dielectric properties of $Zn_{1-x}Ni_xZrNb_2O_8$ ($0 \leq x \leq 0.1$) ceramics

J.X. Bi, C.F. Xing, Y.H. Zhang, C.H. Yang, H.T. Wu*

School of Materials Science and Engineering, University of Jinan, Jinan, 250022, China

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ABSTRACT

Wolframite-structured $Zn_{1-x}Ni_xZrNb_2O_8$ ($0 \leq x \leq 0.1$) ceramics were synthesized by the conventional solid-state method. The effects of Ni^{2+} substitution on sintering characteristic, crystal structure, and microwave dielectric properties of $ZnZrNb_2O_8$ samples were systematically studied. The relationship among bond ionicity, lattice energy, thermal expansion coefficient and microwave dielectric properties was also investigated by the complex chemical bond theory. The dielectric constant of $Zn_{1-x}Ni_xZrNb_2O_8$ ceramics sintered at 1150 °C slightly decreases from 28.06 to 26.35 with the increasing Ni^{2+} content, which can be explained by the variation of bond ionicity and polarizability. Raman scattering spectra also reveal that the increase in Ni^{2+} content leads to the shift in all the vibration modes and the variation of ionicity in Nb–O bond. The $Q{\cdot}f$ values increases from about 40,000 to 60,000 GHz with the increasing Ni^{2+} content, which can be explained by the variation of lattice energy. As for τ_f value, it is shifted to positive direction, which can be explained in term of the variation in Nb-site bond energy. In addition, the thermal expansion coefficient plays little effect on the temperature stability of ceramics. Typically, the $Zn_{0.96}Ni_{0.04}ZrNb_2O_8$ samples sintered at 1150 °C exhibit excellent properties with $\varepsilon_r = 27.10$, $Q{\cdot}f = 62{,}700$ GHz and $\tau_f = -14.72$ ppm/°C.

1. Introduction

Microwave dielectric ceramic is a kind of material operating in millimeter wave frequency range, which has received great attention due to the explosive growth of mobile communication applications such as Internet of Things (IoT), Direct-broadcast satellite television (DBS TV), software radio and GPS, etc. In order to promote the industrial development in passive components, scientists are searching for novel materials with small size, low cost, facile use, and high performance [1,2]. Thus, the microwave dielectric ceramics should meet the following basic characteristics: an appropriate dielectric constant (ε_r), a high quality factor ($Q{\cdot}f$) and a near zero temperature coefficient of resonant frequency (τ_f) [3,4].

Recently, the wolframite-structured $ZnZrNb_2O_8$ ceramics have attracted extensive attention due to their excellent combination of dielectric properties. More specifically, Liao et al. firstly reported that $ZnZrNb_2O_8$ ceramics possessed microwave dielectric properties of $\varepsilon_r = 30$, $Q{\cdot}f = 61{,}000$ GHz and $\tau_f = -52$ ppm/°C [5]. Thereafter, the crystal structure and cell parameters of $ZnZrNb_2O_8$ system, which possessed a space group of p2/c, were analyzed by Murthy et al. [6]. Ionic substitution is an effective method to investigate structure-property relationship as well as to adjust dielectric performances. Some typical wolframite-structured compounds such as $Mg_{0.9}Ca_{0.1}ZrTa_2O_8$ [7], $ZnTi_{0.6}Sn_{0.4}Nb_2O_8$ [8], $CoTi_{0.4}Zr_{0.6}Nb_2O_8$ [9] and $0.63MgZrNb_2O_8$-$0.37TiO_2$ [10] were reported recently for their suitable properties. As for $ZnZrNb_2O_8$ ceramics, Li et al. initially determined the possibility of substituting different A and B-site cations to achieve excellent microwave properties, while the difference between intrinsic and extrinsic factors was not completely elucidated in their reports [11,12]. In our previous works, $Zn_{1-x}A_xZrNb_2O_8$ (A = Mn, Co, Mg) ceramics were prepared to improve the dielectric properties and to lower the sintering temperature of the matrix [13–15]. For example, a near zero τ_f value of −5.61 ppm/°C could be obtained by $Zn_{0.9}Mn_{0.1}ZrNb_2O_8$ samples sintered at 1200 °C [13], and the $Zn_{0.94}Co_{0.06}ZrNb_2O_8$ ceramics possessed suitable properties of $\varepsilon_r = 27.05$, $Q{\cdot}f = 56{,}300$ GHz and $\tau_f = -10.56$ ppm/°C [14]. In addition, the bond ionicity, lattice energy, bond energy and thermal expansion coefficient (TEC), which could be derived from

* Corresponding author.
E-mail address: mse_wuht@ujn.edu.cn (H.T. Wu).

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crystallographic data and generalized P-V-L theory, were also used to correlate the crystal structure with the microwave dielectric behavior. However, to the best of our knowledge, there are few researches talking about the Ni^{2+} substituted $ZnZrNb_2O_8$ ceramics. The radius of Ni^{2+} (0.69 Å) is similar to that of Zn^{2+} (0.74 Å) and the difference between two radii is less than 15%. Therefore, effort is directed toward substituting Zn^{2+} with Ni^{2+} to improve the microwave dielectric properties of $ZnZrNb_2O_8$. What's more, a comprehensive investigation on the structure-property relationship can be also executed in $Zn_{1-x}Ni_xZrNb_2O_8$ ceramics.

In this work, a series of wolframite-structured $Zn_{1-x}Ni_xZrNb_2O_8$ ceramics were prepared by the conventional solid-state method. The microwave dielectric properties of samples were characterized by both classic indicators (bond valence and octahedra distortion) and novel indicators (bond ionicity, lattice energy and coefficient of thermal expansion). Raman scattering spectra of the $Zn_{1-x}Ni_xZrNb_2O_8$ ceramics were also investigated to obtain the correlation among lattice vibration modes, crystal structure and microwave dielectric properties. Finally, the relationship among microwave dielectric properties, crystal structure and intrinsic factors was systematically investigated.

2. Experimental procedures

The samples were prepared by the conventional solid-state method with oxide powders (analytical-grade ZnO, NiO, ZrO_2 and Nb_2O_5; Aladdin Shanghai Biochemical Technology Co., Ltd. Shanghai, China). The raw materials were mixed according to the formula of $Zn_{1-x}Ni_xZrNb_2O_8$ ($0 \le x \le 0.1$) 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 alumina crucibles. The obtained powders were reground for 24 h, dried and mixed with 8 wt% polyvinyl alcohol as binders. The granulated powders were pressed into cylinders of 10 mm diameter and 6 mm height at a pressure of 200 MPa. The resultant cylinders were preheated at 500 °C for 4 h to expel the binders 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 ($\lambda = 0.1542$ nm) at 40 kV and 40 mA settings. The cell parameters of $Zn_{1-x}Ni_xZrNb_2O_8$ were refined by Fullprof software. The reliability of the refinement result was determined by the pattern R factor (R_p) and weighted pattern R factor (R_{wp}). Based on XRD analysis, the microstructure of the sintered samples was characterized by a scanning electron microscope (Model JEOL JEM-2010, FEI Co., Japan). Raman scattering spectra of the samples were excited with the 532 nm light source of a high resolution Raman spectrometer (LobRAM HR Evolution, HORIB AJobin Yvon S.A.S.), with the frequency in 50–1000 cm^{-1} range. The apparent density of the sintered pellets was measured using the Archimedes method (Mettler ToledoXS64), and the relative density of the sample was obtained from the crystal structure and atomic weight [16]. 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 [17]. Unloaded quality factors were measured using TE01d mode by the cavity method [18]. All measurements were finished at room temperature and in the frequency of 5–11 GHz. Temperature coefficients of resonant frequency were measured in the temperature range of 25–85 °C.

3. Results and discussion

3.1. Sintering characteristics

The apparent densities of $Zn_{1-x}Ni_xZrNb_2O_8$ ($0 \le x \le 0.1$) ceramics as a function of sintering temperature are given in Fig. 1. With the temperature increasing from 1050 °C to 1250 °C, the apparent densities of all the samples increase steadily, reaching about 5.2 g/cm^3 at 1150 °C. Thereafter, there are no significant changes in these values, implying the ceramics can densify above 1150 °C. Theoretical densities and relative densities of the ceramics are calculated as Eqs. (1) and (2).

$$\rho_{th} = \frac{nM}{NV} \tag{1}$$

$$\rho_{re} = \frac{\rho_{ap}}{\rho_{th}} \times 100\% \tag{2}$$

where n is the number of molecular in unit cell (n = 1 in this work), M is the theoretical molecular weight, V is the refined unit cell volume and N is Avogadro's number. The inset of Fig. 1 illustrates the variation of relative densities in $Zn_{1-x}Ni_xZrNb_2O_8$ ceramics sintered at 1150 °C. These values vary slightly from 92.15% to 95.52%, which indicate that the substitution of Ni^{2+} doesn't affect the sintering characteristics of the matrix. The surface micrographs of $Zn_{1-x}Ni_xZrNb_2O_8$ ($0 \le x \le 0.1$) ceramics sintered at 1150 °C are illustrated in Fig. 2(a–f). Homogeneous microstructures with almost no pores are revealed in all compositions, which indicate that the dense microstructure can be obtained at 1150 °C. In addition, the grain sizes of the matrix are lower than 4 μm, while that of Ni^{2+} substituted samples are in the range of 1–5 μm, implying the ionic substitution plays a certain role in affecting the grain growth of the matrix.

3.2. Rietveld refinement and crystal structure analysis

The XRD patterns of $Zn_{1-x}Ni_xZrNb_2O_8$ ($0 \le x \le 0.1$) ceramics sintered at 1150 °C are shown in Fig. 3. It is observed that all the samples possess the wolframite structure with a space group of p2/c, and the results match well with JCPDS file of No. 48-0324. There are no obvious changes in the intensity of diffraction peaks, implying that the substitution of Ni^{2+} doesn't influence the

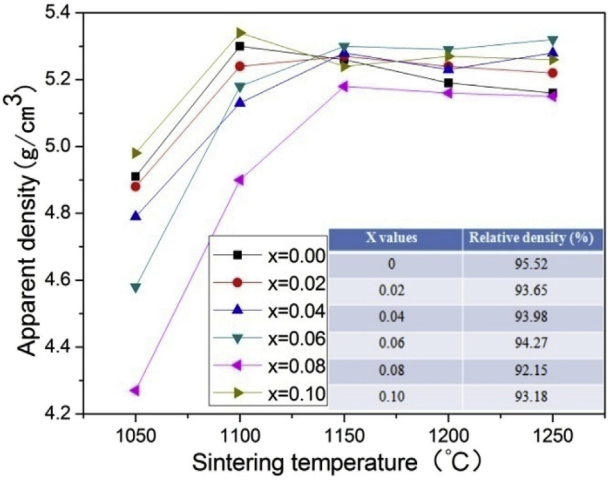

Fig. 1. Apparent density of $Zn_{1-x}Ni_xZrNb_2O_8$ ceramics as a function of sintering temperature and relative density of ceramics sintered at 1150 °C.