ARTICLE IN PRESS

Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Effects of structural characteristics on microwave dielectric properties of low-loss $(Zn_{1\text{-}x}Ni_x)ZrNbTaO_8$ ceramics

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A R T I C L E I N F O

Keywords:
Ceramic matrix composites
Dielectric loss
Microwaves
Structure
Sintering
Complex chemical bond theory

A B S T R A C T

Low-loss $(Zn_{1\text{-}x}Ni_x)ZrNbTaO_8$ ($0.02 \le x \le 0.10$) ceramics possessing single wolframite structure are initiatively synthesized by solid-state route. Based on the results of Rietveld refinement, complex chemical bond theory is used to establish the correlation between structural characteristics and microwave performance in this ceramic system. A small amount of Ni^{2+} ($x = 0.06$) in A-site with the fixed substitution of Ta^{5+} in B-site can effectually raise the $Q \times f$ value of $ZnZrNb_2O_8$ ceramic, embodying a dense microstructure and high lattice energy. The dielectric constant and τ_f are mainly affected by bond ionicity and the average octahedral distortion. The $(Zn_{0.94}Ni_{0.06})ZrNbTaO_8$ ceramic sample sintered at 1150 °C for 3 h exhibits an outstanding combination of microwave dielectric properties: $\varepsilon_r = 27.88$, $Q \times f = 128{,}951$ GHz, $\tau_f = -39.9$ ppm/°C. Thus, it is considered to be a candidate material for the communication device applications at high frequency.

1. Introduction

Owing to the ever-growing frequency of communication applications such as 5 G and satellite navigation systems, low-loss microwave dielectric ceramics are becoming increasingly important. Corresponding to the low loss, high $Q \times f$ value that signifying the enhancement of frequency selectivity in 5 G applications is necessary. Moreover, ceramics with high $Q \times f$ value always present a relatively lower dielectric constant and impede the miniaturization of devices for 5 G requirements. On the contrary, due to the vibration in crystal, high dielectric constant will lead to a relatively lower $Q \times f$ value. Consequently, the research on the ceramics with the optimum combination of high $Q \times f$ value and medium dielectric constant is ongoing [1–3].

Recently, as a member of rutile-like structural compounds, new wolframite-structured $ZnZrNb_2O_8$ ceramic with high $Q \times f$ value (~ 61,000 GHz) and appropriate dielectric constant (~ 30) has received much more interests and made it very promising for microwave applications [4–11]. However, considering the demands of ever-higher frequency in communication applications, the $Q \times f$ value of $ZnZrNb_2O_8$ ceramic should be further enhanced to ensure the high-precision of microwave devices, and such research is certainly needed. In general, crystal structure is the key factor to determine the microwave dielectric properties of ceramics. Considering that the crystal of monoclinic wolframite structural $ZnZrNb_2O_8$ has two different cation positions [5], Zn^{2+}/Zr^{4+} in A-site and Nb^{5+} in B-site are deemed to be hexa-coordinated with oxygen ions and respectively occupy the Wyckoff positions of 2*f* and 2*e*. Afterwards, oxygen ions can be classified in two kinds, O(1) and O(2), holding the 4*g* positions. And, O(1) is respectively connected to one cation in B-site with short bond and two cations in A-site with relatively longer bonds, whereas O(2) is bonded with the rest cations. Previously, conventional ion substitution in A-site by Ni^{2+} or B-site by Ta^{5+} for improving $Q \times f$ value was somewhat effective [6,7]. And, for further optimization, co-doping occurred in A-site and B-site simultaneously may be feasible.

In this work, we modify the $ZnZrNb_2O_8$ ceramic by Ni^{2+} and a fixation content of Ta^{5+} using solid state reaction method, obtaining a single wolframite phase. In the formative $(Zn_{1\text{-}x}Ni_x)ZrNbTaO_8$ ($0.02 \le x \le 0.10$) ceramics, based on the variations of Ni^{2+} content, crystal structure and microwave characteristics are systematically investigated. The influence factors of microwave dielectric properties in $(Zn_{1\text{-}x}Ni_x)ZrNbTaO_8$ ceramics, including bond ionicity, lattice energy and octahedral distortion, are comprehensively discussed.

2. Experimental procedure

The $(Zn_{1\text{-}x}Ni_x)ZrNbTaO_8$ ($0.02 \le x \le 0.10$) ceramics are synthesized through solid state reaction method. The raw materials are high-purified oxide powders (99.9%) of ZnO, NiO, ZrO_2, Nb_2O_5 and Ta_2O_5. The start materials are proportionately ball milled after pretreatment, and the medium is ethanol. Through desiccation, the particles are calcined at 900 °C, and then pressed into cylinders with a size of 10 mm

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https://doi.org/10.1016/j.ceramint.2018.04.030
Received 9 March 2018; Received in revised form 31 March 2018; Accepted 4 April 2018
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Please cite this article as: Luo, W., Ceramics International (2018), https://doi.org/10.1016/j.ceramint.2018.04.030

and 5 mm for diameter and thickness, respectively. The green bodies are sintered at a range of 1130–1200 °C for 3 h, and the heating speed is controlled as 10 °C/min.

The phase compositions of samples are indexed by an X-ray diffractometer (Rigaku, D/MAX-2500, Tokyo, Japan) using Cu-Kα radiation with a scanning speed of 4°/min. The microstructures are analyzed using a scanning electron microscopy (SEM, PHILIPS XL30 ESEM, Netherlands). Rietveld refinement is used to analyze the structural variation of Ni^{2+} substitution and the $ZnZrNb_2O_8$ reported by Ramarao is the starting model [5].

The microwave dielectric properties of $(Zn_{1\text{-}x}Ni_x)ZrNbTaO_8$ ceramics are measured on a network analyzer (8720ES, Agilent, Santa Clara, CA). Herein, dielectric constants are measured using Hakki-Coleman method under TE_{011} resonant mode [10]. Unloaded quality factors are measured by the cavity method under $TE_{01\sigma}$ mode [11]. The τ_f is calculated by Eq. (1):

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \tag{1}$$

where f_1 and f_2 are the $TE_{01\delta}$ resonant frequency of the $(Zn_{1\text{-}x}Ni_x)ZrNbTaO_8$ ceramics at 25 °C and 85 °C, respectively.

3. Results and discussion

Fig. 1 illustrated the X-ray diffraction patterns of the $(Zn_{1\text{-}x}Ni_x)ZrNbTaO_8$ ceramics sintered at 1150 °C for 3 h. All these compositions formed in a solid solution with monoclinic wolframite structure (indexed as $ZnZrNb_2O_8$, JCPDS #48-0324), occupying the space group *P*2/c (C_{2h}^{4}). With the content of Ni^{2+} increased, pure wolframite phases were visibly found with no generation of secondary phase. It could be seen that ions co-doping had no effects on the phase compositions, combining the illustration in Fig. 1, Ni^{2+} and Ta^{5+} could completely dissolve in this structure with Ni^{2+} in A-site and Ta^{5+} in B-site, respectively. In order to clarify the effects of Ni^{2+} ionic substitution for Zn^{2+} ionic on the structural variation of $(Zn_{1\text{-}x}Ni_x)ZrNbTaO_8$ ceramics, relevant parameters including scale factors, background, zero point, unit-cell parameters, half-width, temperature factors atomic, positional coordinates, asymmetry parameters were refined step-by-step independently using FullProf Suite software. The refinement patterns of $(Zn_{1\text{-}x}Ni_x)ZrNbTaO_8$ ceramics were shown in Fig. 2, and the results were presented in Table 1. With the increasing of Ni^{2+} content, lattice parameters and cell volumes slightly decreased as a result of the Ni^{2+} (0.69 Å, CN = 6) with smaller coordination radius replaced the Zn^{2+} (0.74 Å, CN = 6) in A-site [12]. However, as the content of Ni^{2+} reaching to 0.06 mol, the lattice parameters began to increase that might be determined by the change of microstructures.

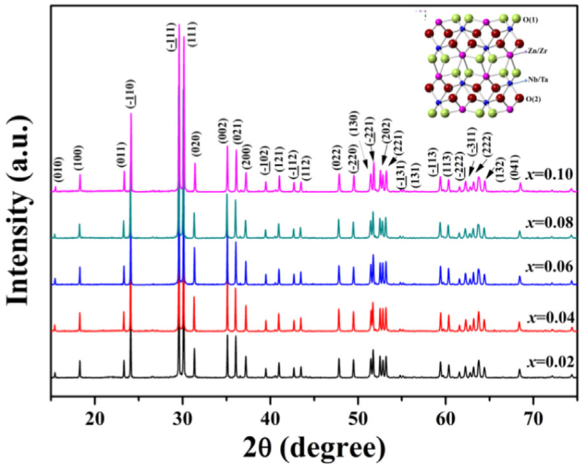

Fig. 1. XRD patterns for $(Zn_{1\text{-}x}Ni_x)ZrNbTaO_8$ sintered at 1150 °C for 3 h, where *x* = 0.02, 0.04, 0.06, 0.08, 0.10.

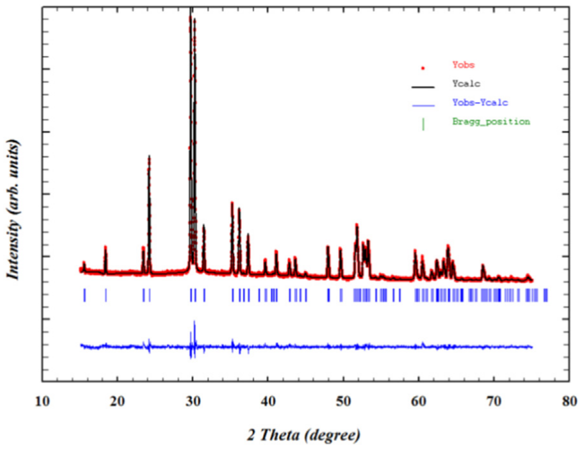

Fig. 2. The profile fits for the Rietveld refinement of $(Zn_{0.94}Ni_{0.06})ZrNbTaO_8$ ceramic.

Fig. 3 demonstrated the SEM micrographs of $(Zn_{1\text{-}x}Ni_x)ZrNbTaO_8$ specimens sintered 1150 °C for 3 h. In the SEM images, for all the compositions of $(Zn_{1\text{-}x}Ni_x)ZrNbTaO_8$ ceramics, compact grain structures were obtained with no pores and no impurities, which was in accordance with the XRD patterns. As the content of Ni^{2+} increased, very small grains in 1–3 μm were firstly observed at $x = 0.02$, then, the grain size obviously increased with ever more substitution of Ni^{2+} until x = 0.06. Thus, during the process of crystal growth, a certain amount co-introduction of Ni^{2+} and Ta^{5+} had not yet destroyed the crystallization of the former wolframite structure, to some extent, could promote the densification of $(Zn_{1\text{-}x}Ni_x)ZrNbTaO_8$ ceramics.

Table 2 illustrated the relative densities and microwave dielectric properties of the $(Zn_{1\text{-}x}Ni_x)ZrNbTaO_8$ ceramics sintered at 1150 °C for 3 h. As the content of Ni^{2+} varied from 0.02 to 0.10, with high relative densities (≥95%) in all samples, the dielectric constant of the samples firstly decreased and then increased. Meanwhile, there was an opposite tendency for $Q \times f$ value, and the τ_f kept a trend of moving positively. From these results, the specimens of $(Zn_{0.94}Ni_{0.06})ZrNbTaO_8$ showed a good combination of microwave performance as a high $Q \times f$ value of 128,951 GHz, appropriate ε_r of 27.88 and a τ_f value of −39.9 ppm/°C.

Fig. 4 illustrated the variation of theoretical polarizability and dielectric constant in $(Zn_{1\text{-}x}Ni_x)ZrNbTaO_8$ ceramics at 1150 °C. In general, the decisive factors that affected the dielectric constant could be boiled down to the polarizabilities, relative density , the tilting and distortion of the oxygen octahedron in crystal [13–16]. Herein, owing to the high relative density (≥ 95%) obtained from the XRD analysis, it was not the absolute factor that determined the dielectric constant. Actually, it was mainly depended on the dielectric polarizabilities and the characteristics of structure. Based on the additive rule, the theoretical dielectric polarizability (α_D) of $(Zn_{1\text{-}x}Ni_x)ZrNbTaO_8$ ceramics was evaluated using Eq. (2) [17]:

$$\begin{aligned}\alpha_D &= \alpha(Zn_{1-x}Ni_xZrNbTaO_8)\\ &= (1-x)\alpha(Zn^{2+}) + x\alpha(Ni^{2+}) + \alpha(Zr^{4+})\\ &\quad + \alpha(Nb^{5+}) + \alpha(Ta^{5+}) + 8\alpha(O^{2-})\end{aligned} \tag{2}$$

Therefrom, with the *x* value increased from 0.02 to 0.06, the dielectric constant decreased from 28.97 to 27.88 linearly, which could be ascribed to the lower polarization of Ni^{2+} ions (1.23 $Å^3$). Reasonably, polarization was proved as one important factor that in relation to the dielectric constant.

However, with the *x* value increased further, the dielectric constant slightly increased which were not in good agreement with α_D. This result might be connected with the microstructural changes of $(Zn_{1\text{-}x}Ni_x)ZrNbTaO_8$ ceramics. Moreover, in consideration of the bond ionicity, dielectric constant could be calculated as followed [18]:

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