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Effect of Co^{2+} substitution on crystal structure and microwave dielectric properties of $MgZrNb_2O_8$ ceramics

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ABSTRACT

Dense $Mg_{1-x}Co_xZrNb_2O_8$ ($0 \le x \le 0.10$) ceramics samples were prepared through solid-state reaction method. The influence of Co^{2+} substitution on phase composition, crystal structure and microwave dielectric properties were investigated systematically. Dielectric polarizability, packing fraction and bond valence were calculated respectively to investigate the correction with dielectric constant, quality factor and temperature coefficient of resonant frequency. Especially, optimal microwave dielectric properties with $\varepsilon_r = 25.18$, $Q \times f = 70709$ GHz, $\tau_f = -46.09$ ppm/°C were obtained for the sample of $Mg_{0.98}Co_{0.02}ZrNb_2O_8$ sintered at 1260 °C for 4 h.

1. Introduction

With the development of microwave communication technology, microwave dielectric materials have attracted much attention for their potential applications. The microwave dielectric materials should have high dielectric constant, high quality factor and near-zero temperature coefficient of resonant frequency in order to facilitate miniaturization, to increase frequency selectivity and guarantee high-temperature stability [1,2].

Lots of work has been done on $MgZrNb_2O_8$ due to the excellent microwave dielectric properties. Ramarao et al. [3] first prepared $MgZrNb_2O_8$ ceramics through solid-state reaction, and the microwave dielectric properties of samples sintered at 1500 °C were $\varepsilon_r = 9.60$, $Q \times f = 58500$ GHz, $\tau_f = -31.5$ ppm/°C. $MgZrNb_2O_8$ ceramics were also synthesized by Pan et al. [4] through reaction sintering method, the microwave dielectric properties of ceramics samples sintered at 1250 °C were $\varepsilon_r = 26.54$, $Q \times f = 57477$ GHz, $\tau_f = -17.69$ ppm/°C (1-x) $MgZrNb_2O_8$ − x TiO_2 ceramics were prepared to explore the relationship between the structure and properties [5]. Four different phase regions were observed by changing the content of TiO_2 and near-zero temperature coefficient of resonant frequency (−2.5 ppm/°C) was obtained when x = 0.37. The substitution effects of Ca^{2+} for Mg^{2+} in $MgZrTa_2O_8$ ceramic were studied by Lin et al. [6] and $Mg_{0.9}Ca_{0.1}ZrTa_2O_8$ showed the optimum microwave dielectric properties. Niu et al. [7] reported the dielectric properties of $Zn_{1-x}Mg_xZrNb_2O_8$ ceramics and the $Q \times f$ value increased from 46800 GHz to 53400 GHz when x increased from 0 to 0.1. In our previous work, the B-site ion substitution of $MgZr_{1-x}Sn_xNb_2O_8$ ceramics was studied, the quality factor rose first and reached the maximum value at x = 0.15 then showed a downward trend [8], and $MgZr_{0.85}Sn_{0.15}Nb_2O_8$ sintered at 1260 °C with microwave dielectric properties $\varepsilon_r = 24.91$, $Q \times f = 94014.2$ GHz, $\tau_f = -43.93$ ppm/°C were obtained. We also reported that the substitution of Ta^{5+} for Nb^{5+} in $MgZrNb_2O_8$ ceramics could greatly improve the quality factor and the $Q \times f$ value of $MgZr(Nb_{0.9}Ta_{0.1})_2O_8$ is 88440 GHz, which is much higher than that of $MgZrNb_2O_8$ ceramics [9].

In this study, $Mg_{1-x}Co_xZrNb_2O_8$ ($0 \le x \le 0.10$) ceramics were synthesized and Rietveld refinement was performed to investigate the influence of Co^{2+} ion substitution on crystal structure. Moreover, the correlations among dielectric polarizability, packing fraction, bond valence and microwave dielectric properties were discussed systematically.

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2. Experimental procedures

$Mg_{1-x}Co_xZrNb_2O_8$ ($0 \le x \le 0.10$) ceramics were synthesized through traditional solid-state reaction method with analytically pure MgO, $CoCO_3$, ZrO_2 and Nb_2O_5 powders as starting materials. The raw materials were weighted according to the stoichiometric ratio of $Mg_{1-x}Co_xZrNb_2O_8$ (x = 0, 0.02, 0.04, 0.06, 0.08 and 0.10) and then placed in a nylon container with distilled water as dispersant and ball milled for 6 h. After dried and calcined at 1100 °C for 2 h, the obtained powders were ball milled again for another 6 h. After dried, the powders were mixed with 6 wt% paraffin and pressed into cylinders with 10 mm in diameter and 5 mm in height under the pressure of 10 MPa. Finally, the samples were sintered at 1220 °C–1280 °C for 4 h in air.

The crystalline phases of the ceramics specimen were identified by X-ray diffraction (XRD, Rigaku D/max 2550 PC, Japan) with Cu Kα radiation. The microstructure of the ceramics surfaces were observed by scanning electron microscopy (SEM, ZEISS MERLIN Compact, Germany). The microwave dielectric properties were measured in the frequency range of 7–12 GHz with network analyzer (N5234A, Agilent Co, USA). The temperature coefficient of resonant frequency (τ_f) was measured from 25 °C to 85 °C and calculated by the following formula:

$$\tau_f = \frac{f_{85} - f_{25}}{f_{25}(85-25)} \times 10^6 \quad (1)$$

where f_{85} and f_{25} represented the resonant frequencies at 85 °C and 25 °C, respectively.

3. Results and discussion

The apparent densities of $Mg_{1-x}Co_xZrNb_2O_8$ ($0 \le x \le 0.10$) ceramics at different sintering temperature are shown in Fig. 1(a). When the sintering temperature rose from 1220 °C to 1260 °C, the apparent densities showed an upward trend, especially when x = 0.02 or 0.04. However, when the sintering temperature reached up to 1280 °C, the apparent densities decreased slightly. Samples sintered at 1260 °C appeared the highest densities. Thus, 1260 °C could be considered as the optimum sintering temperature. Fig. 1(b) shows the relative densities of samples with different substitution amount sintered at 1260 °C, the relative densities were all greater than 95%.

Fig. 2 shows the XRD patterns of $Mg_{1-x}Co_xZrNb_2O_8$ ($0 \le x \le 0.10$) ceramics sintered at 1260 °C. All the patterns were indexed as monoclinic wolframite structure with *P*2/*c* space group and no second phase was found. When x increased from 0 to 0.02, the main diffraction peak shifted to the right, which could be attributed to the distortion of crystal structure induced by Co^{2+}. When x increased from 0.02 to 0.10, the main diffraction peak slightly shifted to the left, indicating the fact that the unit cell volume became larger. Fig. 3 shows the SEM images of $Mg_{1-x}Co_xZrNb_2O_8$ ($0 \le x \le 0.10$) ceramics sintered at 1260 °C, from which we can see that all the samples were well-densified. The grain size had no significant change with the increase of Co^{2+} substitution amount.

Rietveld refinement was performed using the software Fullprof to analyze the effect of Co^{2+} substitution on crystal structure. Parameters including instrumental, profile, background, atoms were refined to improve the reliability of results. The refinement result of $Mg_{0.98}Co_{0.02}ZrNb_2O_8$ is given in Fig. 4 as an example. The Rietveld discrepancy factors R_p and R_{wp} of all the samples are less than 15, which means refinement results are acceptable. The detailed refinement results of all the samples are shown in Table 1, from

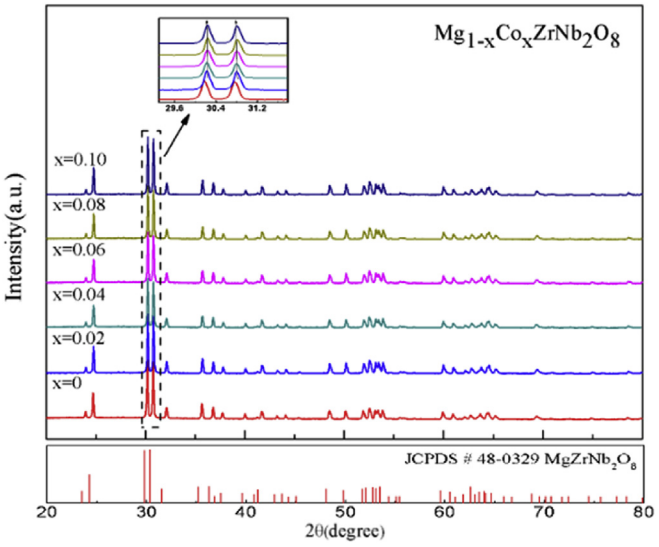
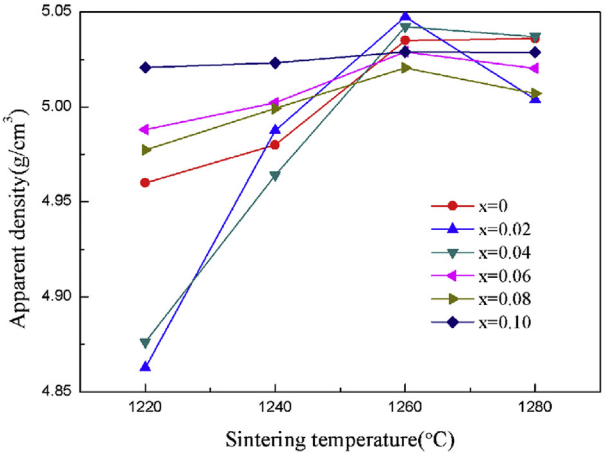
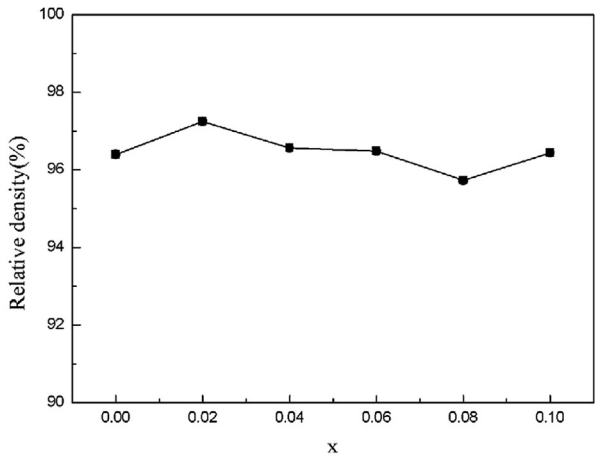


Fig. 2. The XRD patterns of $Mg_{1-x}Co_xZrNb_2O_8$ ceramics sintered at 1260 °C.



(a) The apparent densities at different sintering temperature



(b) The relative densities of the samples sintered at 1260 °C

Fig. 1. The density of $Mg_{1-x}Co_xZrNb_2O_8$ ceramics.