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Microwave dielectric properties of the novel low temperature fired $Ni_{0.5}Ti_{0.5}NbO_4 + xwt\%BiVO_4$ ($2.5 \le x \le 10$) ceramics

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ABSTRACT

The low temperature fired $Ni_{0.5}Ti_{0.5}NbO_4 + xwt\%BiVO_4$ ($2.5 \le x \le 10$) ceramics were prepared through the solid state synthesis methods, effects of various contents of $BiVO_4$ on different phases, microstructures and microwave dielectric properties for $Ni_{0.5}Ti_{0.5}NbO_4$ were researched systematically. The sintering temperatures of $Ni_{0.5}Ti_{0.5}NbO_4$ ceramics can be effectively decreased from 1100 °C to 900 °C by adding 10 wt% $BiVO_4$ ceramics, and the sintering relative density over 96% could be prepared at 900 °C, meanwhile the temperature coefficient of the resonant frequency were decreased as the $BiVO_4$ additions increased. Typically, preferred dielectric properties of $Ni_{0.5}Ti_{0.5}NbO_4$ + 10 wt%$BiVO_4$ composites with $\varepsilon_r = 56.7$, $Q \times f = 7062$ GHz, $\tau_f = +55.59$ ppm/°C were obtained when they were sintered at 900 °C.

1. Introduction

Nowadays, microwave dielectric materials show the significance in designing the microwave device, such as resonators, antennas and filters [1–4]. The requirements for dielectric materials application in communication systems are as follows: low dielectric loss ($Q \times f$ values > 5000), great dielectric constant (ε_r > 10) and a near-zero temperature of the resonant frequency [5].

Niobate dielectric materials have attracted so many attentions of researchers as their excellent properties; meanwhile, a serial of niobate materials could generate a wide permittivity ranges, and also high $Q \times f$ values are obtained at the same time. The highly dielectric constant is benefit to device miniaturization, and $Ni_{0.5}Ti_{0.5}NbO_4$ [6] ceramics possess relatively higher dielectric constant among the $A^{2+}Nb_2O_6$ and $A^{2+}TiNb_2O_8$ compounds. Finally it shows the dielectric properties: $\varepsilon_r = 56.8$, $Q \times f = 21{,}100$ GHz, $\tau_f = +79.1$ ppm/°C when sintered at 1100 °C, thus, it could be a good candidate to fabricate resonators, and it is the major phase of the composite in this work.

Low temperature co-fired ceramic technology is an effective method to fabricate the microwave device. Which need the sintering temperature of ceramic must be lower than 950 °C. $BiVO_4$ used as sintering aids to lower the sintering temperature of other ceramics have been studied by many researchers [7]. Wee [8] have studied the low-fired $ZnNb_2O_6$ ceramics with $BiVO_4$ addition, and $ZnNb_2O_6$ ceramics present excellent microwave dielectric properties of $\varepsilon_r = 26$, $Q \times f = 55{,}000$ GHz, $\tau_f = -57$ ppm/°C with 5% $BiVO_4$ addition, and the sintering temperature decrease form 1200 °C to 950 °C. In view of this point, novel low temperature fired $Ni_{0.5}Ti_{0.5}NbO_4 + xwt\%BiVO_4$ ($2.5 \le x \le 10$) ceramics were prepared in this work.

2. Material and methods

$Ni_{0.5}Ti_{0.5}NbO_4$ and $BiVO_4$ ceramic powders were prepared independently using the solid-state reaction method with the precursors: NiO (98%), Bi_2O_3 (99%), TiO_2 (99.9%), Nb_2O_5 (99.5%) V_2O_5 (99%). Raw materials were mixed in a ball mill with ZrO_2 balls for 10 h using water as the liquid medium. Thereafter the $Ni_{0.5}Ti_{0.5}NbO_4$ powders were pre-sintered at 1040 °C for 10 h and $BiVO_4$ powders were pre-sintered at 550 °C for 3 h. The two kinds of powers were then mixed as the ratio of $Ni_{0.5}Ti_{0.5}NbO_4 + xwt\%BiVO_4$ (2. 5 < x < 10). Then the powders were re-milled for further 10 h to obtain fine powders, and were pressed into pellet disks with 5% PVA. Then, the disks were sintered at 860–920 °C for 6 h, and furnace-cooled to room temperature. The phase formation was examined by an X-ray diffract-meter (XRD, DX-2700, Haoyuan co.) with Cu Kα radiation. The microstructures and EDX were measured by a scanning electron microscope (JSM-6490, JEOL, Japan). The microstructure and elemental analysis of the sintered specimens were examined from polished surfaces by a scanning electron microscopy (SEM, JSM-6490LV, Japan). The bulk density was measured by the Archimedes method. The ε_r values and $Q \times f$ values were determined by the Hakki-Coleman dielectric resonator

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method using an HP83752A network analyzer. The τ_f value was measured by using the equation:where f_{25} and f_{85} are the resonant frequencies at 25 °C and 85 °C respectively.

3. Results and discussion

The XRD patterns of the $Ni_{0.5}Ti_{0.5}NbO_4$+xwt%$BiVO_4$ composites are shown in Fig. 1. As we can see that the $BiVO_4$ added to $Ni_{0.5}Ti_{0.5}NbO_4$ ceramics sintered at low temperatures contained three phases: $Ni_{0.5}Ti_{0.5}NbO_4$ (JCPDS #52-1875), $BiVO_4$ (JCPDS #75-2481) and a small amount of $NiNb_2O_6$ (JCPDS #15-0159) phase. Obviously, the intensity of diffraction peaks of $BiVO_4$ phase was strengthened gradually with the increasing $BiVO_4$ phase addition. The right pattern of the Fig. 1 shows the (1 1 0) plane diffraction peaks of $Ni_{0.5}Ti_{0.5}NbO_4$ phase which was shifted to lower angle, this phenomenon maybe ascribed to Bi^{3+} ion whose radius is 105 Å which is bigger than all the positive ions of $Ni_{0.5}Ti_{0.5}NbO_4$ phase [9].

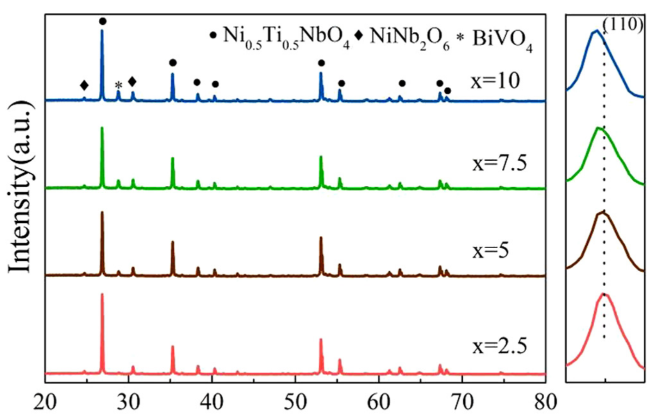

Fig. 1. XRD patterns of the $Ni_{0.5}Ti_{0.5}NbO_4$ + xwt%$BiVO_4$ composites with different x value changes sintered at 900 °C.

Fig. 2 illustrates SEM micrographs of $Ni_{0.5}Ti_{0.5}NbO_4$ + xwt% $BiVO_4$ composites sintered at 900 °C. The results indicated that grain size of $Ni_{0.5}Ti_{0.5}NbO_4$ + xwt%$BiVO_4$ composites were enlarged as the $BiVO_4$ proportion increased, meanwhile, fewer porous and highly dense microstructures could be obtained with the $BiVO_4$ additions. For further study of the influence on sintering properties, we measured the relative density of $Ni_{0.5}Ti_{0.5}NbO_4$+xwt% $BiVO_4$ which are shown in Fig. 3(a), the relative density was notably increased as $BiVO_4$ proportion increased, and the relative density was higher than 96% when the addition of $BiVO_4$ was beyond 7.5 wt%, particularly, the samples with 10 wt% $BiVO_4$ possess a relative density of 96.9%. So that, the addition of $BiVO_4$ can effective decrease the sintering temperatures of $Ni_{0.5}Ti_{0.5}NbO_4$ ceramics.

Microwave dielectric constants of $Ni_{0.5}Ti_{0.5}NbO_4$ with $BiVO_4$ addition are shown in Fig. 3(b), the dielectric constant increased as the $BiVO_4$ proportion increased. This phenomenon may be caused by two factors, one is that more $BiVO_4$ additions have improved the sintering process, and formed high density ceramics, which will influence the dielectric constant [10], the other one is that dielectric constant of $BiVO_4$ ceramic is 68 is higher than $Ni_{0.5}Ti_{0.5}NbO_4$ ceramic, so that the $BiVO_4$ added to $Ni_{0.5}Ti_{0.5}NbO_4$ would increase the dielectric constant and $Ni_{0.5}Ti_{0.5}NbO_4$ + 10 wt%$BiVO_4$ composites sintered at 900 °C obtained a dielectric constants of 56.7.

The room temperature $Q \times f$ values of $Ni_{0.5}Ti_{0.5}NbO_4$ + xwt% $BiVO_4$ composites sintered at different temperatures are presented in Fig. 3(c). As we can see, $Q \times f$ values of all the samples sintered at low temperatures were smaller than pure $Ni_{0.5}Ti_{0.5}NbO_4$ ceramic sintered at 1100 °C, this phenomenon may be attributed to the addition of $BiVO_4$ since $BiVO_4$ ceramics have a lower $Q \times f$ values. Generally speaking, the $Q \times f$ values are decided by intrinsic factors and extrinsic factors, the extrinsic factors contain: packing fraction, the second phase and porosity [11]. As is analyzed in Fig. 2 and Fig. 3(a), relative densities of the composites changed a lot with $BiVO_4$ addition at low sintering temperature, therefore, the $BiVO_4$ addition would influence the $Q \times f$ values, and the $Q \times f$ values increased as the $BiVO_4$ proportion increased, this tendency was coincided with the tendency of relative densities. the samples with

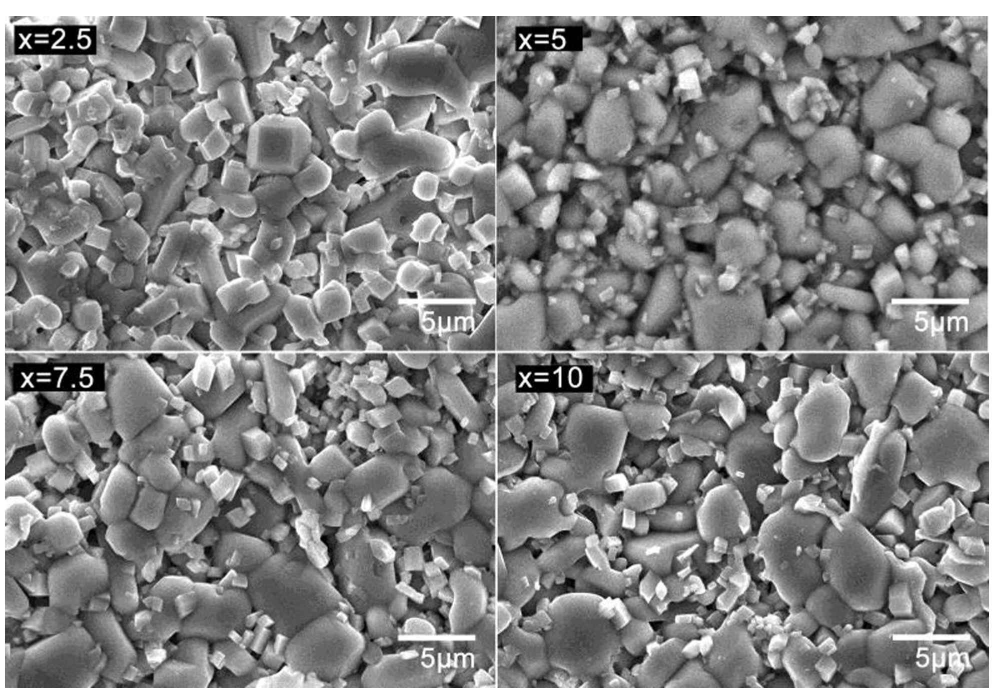

Fig. 2. SEM micrographs of the fracture morphologies of the $Ni_{0.5}Ti_{0.5}NbO_4$ + xwt%$BiVO_4$ composites with different x value changes sintered at 900 °C.