Microwave dielectric properties of the novel low temperature fired Ni$_{0.5}$Ti$_{0.5}$NbO$_4$ + xwt%BiVO$_4$ (2.5 ≤ x ≤ 10) ceramics

Xin Huang *, Huaiwu Zhang *, Yuanming Lai, Gang Wang, Jie Li

State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, China

**Abstract**

The low temperature fired Ni$_{0.5}$Ti$_{0.5}$NbO$_4$ + xwt%BiVO$_4$ (2.5 ≤ x ≤ 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 $e_r = 56.7$, $Q_f = 7062$ 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 ($Q_f$ values > 5000), great dielectric constant ($e_r > 10$) 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 $Q_f$ 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$_2$O$_6$ and A$_2$+TiNb$_2$O$_8$ compounds. Finally it shows the dielectric properties: $e_r = 56.8$, $Q_f = 21,100$ 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$_2$O$_6$ ceramics with BiVO$_4$ addition, and ZnNb$_2$O$_6$ ceramics present excellent microwave dielectric properties of $e_r = 26$, $Q_f = 55,000$ 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 ≤ x ≤ 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$_2$O$_3$ (99%), TiO$_2$ (99.9%), Nb$_2$O$_5$ (99.5%) V$_2$O$_5$ (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 powders 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 K$_\alpha$ 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 $e_r$ values and $Q_f$ values were determined by the Hakki-Coleman dielectric resonator

---

*Corresponding authors.

E-mail addresses: 201511030133@std.uestc.edu.cn (X. Huang), hwzhang@uestc.edu.cn (H. Zhang).
method using an HP83752A network analyzer. The \( f_1 \) 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\(_2\)O\(_6\) (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. 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 \( Q \times f \) values increased as the BiVO\(_4\) proportion increased, this tendency was coincided with the tendency of relative densities. The samples with