Modification of NdNbO₄ microwave dielectric ceramic by Bi substitutions

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Abstract
In the present work, Bi³⁺ was used to substitute for Nd³⁺ in the NdNbO₄ ceramic and pure fergusonite solid solution was formed within 20 mol. % substitutions. Microwave dielectric permittivity of the (Nd₁₋ₓBix)NbO₄ (x ≤ 0.2) ceramics increased linearly with x value due to the larger ionic polarizability of Bi³⁺ than Nd³⁺. Excellent microwave dielectric properties with a permittivity (εᵣ) ~22.5, a Qf (Q = quality factor, f = resonant frequency) ~50 000 GHz, and a TCF ~−9 ppm/°C were obtained in the (Nd₀.9Bi₀.1)NbO₄ ceramic. This method might work in other fergusonite-type rare-earth ortho-niobates.

KEYWORDS
fergusonite, microwave dielectric ceramics, NdNbO₄

1 | INTRODUCTION

Microwave dielectric ceramics have been widely used in dielectric resonators (DR), dielectric filters, dielectric substrates for antenna, multilayer co-fired capacitors (MLCC) in modern electronic systems.¹⁻⁵ Microwave permittivity, Qf value (Q = 1/dielectric loss, f = resonant frequency), and TCF value (temperature coefficient of resonant frequency) are the three key physical parameters for microwave dielectric ceramics. In the past half-century, a series of high-performance microwave dielectric ceramics have been explored due to the fast development of communication technology, such as 3G/4G.¹⁻⁸ Facing the challenge from 5G technology, microwave dielectric ceramics are required to possess higher Qf values than before.

NdNbO₄ material belongs to a fergusonite-type rare-earth ortho-niobates family, which was reported to follow a reversible ferroelastic phase transition to scheelite structure at high temperatures.⁹⁻¹¹ In 2006, its microwave dielectric properties were first reported by Kim et al.¹² with a permittivity ~19.6, a Qf ~33 000 GHz and a TCF ~−24 ppm/°C and a sintering temperature about 1250°C. Subsequently, a number of efforts were made to modify the microwave dielectric properties of NdNbO₄ ceramics by introduction of Ln and Zn²⁺ ions into A site and Sb⁵⁺/Ta⁵⁺ ions into B site.¹³⁻¹⁶ Although the Qf values were kind of improved, its TCF value is still large negative. Even the addition of CaTiO₃ ceramic with large positive TCF value did not adjust its TCF to near zero.¹⁷ In the studies of Bi₂Mo₂O₉ and BiNbO₄ ceramics,¹⁸,¹⁹ it was found that Ln...
substitutions for Bi$^{3+}$ ion is effective to decrease their TCF values. Hence, these results inspire us to use Bi$^{3+}$ ion to substitute for Nd$^{3+}$ in NdNbO$_4$ ceramic to modify its TCF values. In the present work, microwave dielectric properties of the (Nd$_{1-x}$Bi$_x$)NbO$_4$ ($x \leq 0.2$) ceramics were studied in detail.

2 | EXPERIMENTAL

Reagent-grade Nd$_2$O$_3$ (>99%, Fisher Scientific), Bi$_2$O$_3$, (>99%, Sigma-Aldrich), and Nb$_2$O$_5$ (>99%, Fisher Scientific) were weighed according to the stoichiometric formulation (Nd$_{1-x}$Bi$_x$)NbO$_4$ ($x = 0.05$, 0.10, 0.15 and 0.20). Nd$_2$O$_3$ powders were calcined at 1200°C for 4 hours before weighing. Powders were mixed and ball-milled for 24 hours using isopropanol. The powder mixture was then dried and calcined at 1000°C for 4 hours. The calcined powders were re-milled for 24 hours and pressed into cylinders (12 mm in diameter and 4.5 mm in height) at 50 MPa. Samples were sintered for 2 hours at 1080-1280°C in air. X-ray diffraction (XRD) was performed using with CuK$\alpha$ radiation (Bruker D2 Phaser) form 10°-65° 2θ at a step size of 0.02°. As-fired surfaces were observed by a scanning electron microscopy (SEM; Quanta 250, FEI). Dielectric properties at microwave frequency were measured with the TE$_{015}$ dielectric resonator method with a network analyzer (8720ES, Agilent, Palo Alto, CA) and a home-made heating system. The temperature coefficient of resonant frequency TCF ($\tau_f$) was calculated with the following formula:

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

where $f_{85}$ and $f_{25}$ are the TE$_{015}$ resonant frequencies at 85 and 25°C, respectively.

![FIGURE 1 XRD patterns of the (Nd$_{1-x}$Bi$_x$)NbO$_4$ (x $\leq$ 0.2) ceramics (A) and the cell parameters as a function of x value (B) [Color figure can be viewed at wileyonlinelibrary.com]]
3 | RESULTS AND DISCUSSIONS

Figure 1 shows the XRD patterns of the (Nd<sub>1-x</sub>Bi<sub>x</sub>)NbO<sub>4</sub> (x ≤ 0.2) ceramics (schematic of crystal structure in inset) and the cell parameters as a function of x value. Pure NdNbO<sub>4</sub> was well-defined at about 1250°C and crystallized in a fergusonite structure, which is similar to the literatures’ reports. As the substitutions of Bi for Nd in NdNbO<sub>4</sub> increased from 0 to 0.2, the sintering temperature decreased from 1250°C to about 1150°C. As seen from Figure 1A, as x value increased from 0 to 0.2, all the patterns can be indexed as a single fergusonite structure without any traces of secondary phases, which means that the solid solubility of Bi in NdNbO<sub>4</sub> is larger than 20%. In the fergusonite structure, A and B site ions are 8-coordinated and 6-coordinated, respectively. Bi ion has a ionic radius 1.17 Å, which is a little larger than that of Nd<sup>3+</sup> (1.109 Å). As shown in Figure 1B, both the cell parameters b and c increased almost linearly with the increase of Bi contents along with the increase of β angle while cell parameter a decreased, which resulted in the increase of cell volume from 316.34 Å<sup>3</sup> at x = 0 to 318.21 Å<sup>3</sup> at x = 0.2.

Scanning electron microscopy images of the (Nd<sub>1-x</sub>Bi<sub>x</sub>)NbO<sub>4</sub> (x ≤ 0.2) ceramics sintered at their optimal temperatures are presented in Figure 2. Dense microstructure with clear grain boundaries were well revealed from SEM images. For all the (Nd<sub>1-x</sub>Bi<sub>x</sub>)NbO<sub>4</sub> (x ≤ 0.2) ceramics, the grains sizes lied between 3-8 μm and Bi substitutions did not bring much influence.

Microwave dielectric properties (permittivity, Qf, and TCF values) of the (Nd<sub>1-x</sub>Bi<sub>x</sub>)NbO<sub>4</sub> (x ≤ 0.2) ceramics as a function of x value are shown in Figure 3. It is seen that microwave permittivity increased linearly from 19.6 at x = 0 to 26.95 at x = 0.2 and this can be attributed to the larger ionic polarizability of Bi<sup>3+</sup> (6.12 Å<sup>3</sup>) than Nd<sup>3+</sup> (5.01 Å<sup>3</sup>) as reported by Shannon. The Qf values increased from 33 000 GHz at x = 0 to about 50 000 GHz at x = 0.10 and then decreased with further increase of Bi contents. Qf values at microwave region were influenced...
by many factors, such as gain boundary, pores and etc., which are highly related with the sintering process. Here we did not present the relation between Qf and sintering temperature. The optimal Qf values of the (Nd$_{1-x}$Bi$_x$ NbO$_4$ (x ≤ 0.2) ceramics can be achieved in a narrow sintering temperature range (<40°C). It is quite interesting to note that the TCF values of the (Nd$_{1-x}$Bi$_x$ NbO$_4$ (x ≤ 0.2) ceramic shifted linearly from −39 at x = 0 to +27 ppm/K at x = 0.2. Near-zero TCF values −9 and +15 ppm/K were obtained in x = 0.10 and x = 0.15 samples, which indicates that the TCF values can be precisely adjusted from negative to positive by modifying Bi contents. At the moment it is hard to say what is the intrinsic reason for adjusting TCF value and it will be studied in the future.

Infrared reflectivity spectra are usually used to study the intrinsic microwave dielectric properties with the following harmonic oscillator model:

$$\varepsilon'(\omega) = \varepsilon_\infty + \sum_{j=1}^{n} \frac{a^2_{j\omega}}{\omega^2_{j\omega} - \omega^2 - i\gamma_j\omega}$$

(2)

where $\varepsilon'(\omega)$ is the complex dielectric function, $\varepsilon_\infty$ is the optical-frequency dielectric constant, $\gamma_j$, $\omega_{j\omega}$, and $a_{j\omega}$ are the damping factor, the transverse frequency, and plasma frequency of the $j$th Lorentz oscillator, respectively. According to Maxwell relation, the complex reflectivity R($\omega$) and complex permittivity have the following relation:

$$R(\omega) = \frac{1 - \sqrt{\varepsilon'(\omega)}}{1 + \sqrt{\varepsilon'(\omega)}}$$

(3)

Figure 4 presents the measured and fitted infrared reflectivity spectra, using Equations (2) and (3) above, of the (Nd$_{0.85}$Bi$_{1.5}$)NbO$_4$ ceramic (solid lines for fitting values) and the complex dielectric spectra.

### 4 | CONCLUSIONS

In summary, the fergusonite structured solid solution was obtained in the (Nd$_{1-x}$Bi$_x$)NbO$_4$ ceramics within x ≤ 0.2. Cell volume increased with the Bi contents due to its larger ionic radius than Nd$^{3+}$. Microwave permittivity values were found to increase linearly with Bi contents due to its larger ionic polarizability than Nd$^{3+}$. The TCF values were successfully adjusted from negative to positive value with increase in Bi content. High performance of microwave dielectric properties with $\varepsilon_r$ ~ 22.5, Qf ~50 000 GHz, TCF ~ −9 ppm/K and $\varepsilon_r$ ~24.8, Qf ~41 900 GHz, TCF ~ +15 ppm/K were obtained in the (Nd$_{0.9}$Bi$_{0.1}$)NbO$_4$ and (Nd$_{0.85}$Bi$_{1.15}$)NbO$_4$ ceramics sintered at 1150°C and they might be promising candidates for modern microwave devices.

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