DR DI ZHOU (Orcid ID : 0000-0001-7411-4658)

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Modification of $NdNbO_4$ Microwave Dielectric Ceramic by Bi Substitutions

Li-Xia Pang[a] and Di Zhou[*b]

[a]Micro-optoelectronic Systems Laboratories, Xi'an Technological University, Xi'an 710032, Shaanxi, China

[b]Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education & International Center for Dielectric Research, School of Electronic and Information Engineering, Xi'an Jiaotong University, Xi'an 710049, Shaanxi, China

ABSTRACT

In the present work, Bi^{3+} was used to substitute for Nd^{3+} in the $NdNbO_4$ ceramic and pure fergusonite solid solution was formed within 20 mol. % substitutions. Microwave dielectric permittivity of the $(Nd_{1-x}Bi_x)NbO_4$ ($x \leq 0.2$) ceramics increased linearly with x value due to the larger ionic polarizability of Bi^{3+} than Nd^{3+}. Excellent microwave dielectric properties

[*]Corresponding author E-mail address: zhoudi1220@gmail.com (Di Zhou)

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with a permittivity (ε_r) ~ 22.5, a Qf (Q = quality factor, f = resonant frequency) ~ 50,000 GHz, and a TCF ~ – 9 ppm/°C were obtained in the $(Nd_{0.9}Bi_{0.1})NbO_4$ ceramic. This method might work in other fergusonite-type rare-earth ortho-niobates.

KEYWORDS

Microwave dielectric ceramics; $NdNbO_4$; fergusonite

1. INTRODUCTION

Microwave dielectric ceramics have been widely used in dielectric resonators (DR), dielectric filters, dielectric substrates for antenna, multi-layer 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.

$NdNbO_4$ 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 $NdNbO_4$ ceramics by introduction of Ln and Zn^{2+} ions into A site and Sb^{5+}/Ta^{5+} ions into B site.[13-16] Although the Qf values were kind of improved, its TCF value is still large negative. Even addition of $CaTiO_3$ ceramic with large positive TCF value did not adjust its TCF to near zero.[17] In the studies of $Bi_2Mo_2O_9$ and $BiNbO_4$ 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_2O_3 (> 99%, Fisher Scientific), Bi_2O_3, (> 99%, Sigma-Aldrich) and Nb_2O_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_2O_3 powders were calcined at 1200 ^oC for 4 h before weighing. Powders were mixed and ball-milled for 24 h using isopropanol. The powder mixture was then dried and calcined at 1000 ^oC for 4 h. The calcined powders were re-milled for 24 h and pressed into cylinders (12 mm in diameter and 4 ~ 5 mm in height) at 50 MPa. Samples were sintered 2 h at 1080 ^oC ~ 1280 ^oC in air. X-ray diffraction (XRD) was performed using with CuKα radiation (Bruker D2 Phaser) form 10-65 ^{o} 2θ at a step size of 0.02 ^{o}. As-fired surfaces were observed by using a scanning electron microscopy (SEM; Quanta 250, FEI). Dielectric properties at microwave frequency were measured with the $TE_{01\delta}$ 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 (τ_f) was calculated with the following formula:

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

where f_{85} and f_{25} are the $TE_{01\delta}$ resonant frequencies at 85 °C and 25 °C, respectively.

3. RESULTS AND DISCUSSIONS

Fig. 1 shows the XRD patterns of the $(Nd_{1-x}Bi_x)NbO_4$ ($x \leq 0.2$) ceramics (schematic of crystal structure in inset) and the cell parameters as a function of x value. Pure $NdNbO_4$ was well denified at about 1250 °C and crystallized in a fergusonite structure, which is similar to the literatures' reports [12]. As the substitutions of Bi for Nd in $NdNbO_4$ increased from 0 to 0.2, the sintering temperature decreased from 1250 °C to about 1150 °C. As seen from Fig. 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 $NdNbO_4$ 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^{3+} (1.109 Å).[20] As shown in Fig. 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^3 at x = 0 to 318.21 Å^3 at x = 0.2.

SEM images of the $(Nd_{1-x}Bi_x)NbO_4$ ($x \leq 0.2$) ceramics sintered at their optimal temperatures are presented in Fig. 2. Dense microstructure with clear grain boundaries were well revealed from SEM images. For all the $(Nd_{1-x}Bi_x)NbO_4$ ($x \leq 0.2$) 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 $(Nd_{1-x}Bi_x)NbO_4$ ($x \leq 0.2$) ceramics as a function of x value are shown in Fig. 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^{3+} (6.12 $Å^3$) than Nd^{3+} (5.01 $Å^3$) as reported by Shannon.[21] 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 $(Nd_{1-x}Bi_x)NbO_4$ ($x \leq 0.2$) ceramics can be achieved in a narrow sintering temperature range (< 40 °C). It is quite interesting to note that the TCF values of the $(Nd_{1-x}Bi_x)NbO_4$ ($x \leq 0.2$) ceramic shifted linearly from − 39 at x = 0 to + 27 ppm/°C at x = 0.2. Near-zero TCF values − 9 and + 15 ppm/°C 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:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \sum_{j=1}^{n} \frac{\omega_{pj}^2}{\omega_{oj}^2 - \omega^2 - j\gamma_j\omega} \qquad (2)$$

where $\varepsilon^*(\omega)$ is complex dielectric function, ε_∞ is the optical-frequency dielectric constant, γ_j, ω_{oj} and ω_{pj} 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:

$$R(\omega)=\left|\frac{1-\sqrt{\varepsilon^{*}(\omega)}}{1+\sqrt{\varepsilon^{*}(\omega)}}\right|^{2} \quad (3)$$

Fig. 4 presents the measured and fitted infrared reflectivity spectra, using equations (2) and (3) above, of the $(Nd_{0.85}Bi_{15})NbO_4$ ceramic (solid lines for fitting values) and the complex dielectric spectra. It can be seen that the measured real and imaginary parts of permittivity are quite similar to the extrapolated values from far infrared region using the fitted data, which means that main dielectric polarizations at microwave region are contributed by the photon oscillations at infrared frequency. However, this result also indicates that there is no much space for increase of Qf values by improving the ceramic processing. Anyway, the infrared reflectivity spectra fitting further helped confirm the high performance of $(Nd_{0.85}Bi_{15})NbO_4$ ceramic.

4. CONCLUSIONS

In summary, the fergusonite structured solid solution was obtained in the $(Nd_{1-x}Bi_x)NbO_4$ ceramics within $x \leq 0.2$. Cell volume increased with the Bi contents due to its larger ionic radius than Nd3+. Microwave permittivity values were found to increase linearly with Bi contents due to its larger ionic polarizability than Nd3+. The TCF values were successfully adjusted from negative to positive value with increase in Bi content. High performance of microwave dielectric properties with ε_r ~ 22.5, Qf ~ 50,000 GHz, TCF ~ − 9 ppm/^{o}C and ε_r ~ 24.8, Qf ~ 41,900 GHz, TCF ~ +15 ppm/^{o}C were obtained in the $(Nd_{0.9}Bi_{0.1})NbO_4$ and $(Nd_{0.85}Bi_{0.15})NbO_4$ ceramics sintered at 1150 ^{o}C and they might be promising candidates for modern microwave devices.

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ORCID

Di Zhou http://orcid.org/ 0000-0001-7411-4658.

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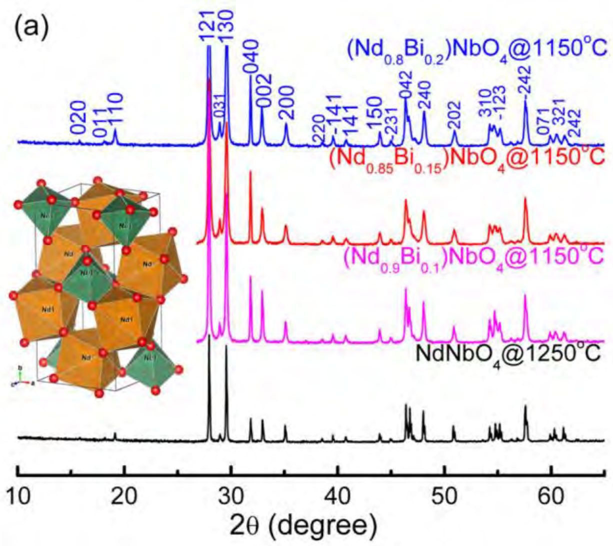
Figure Captions

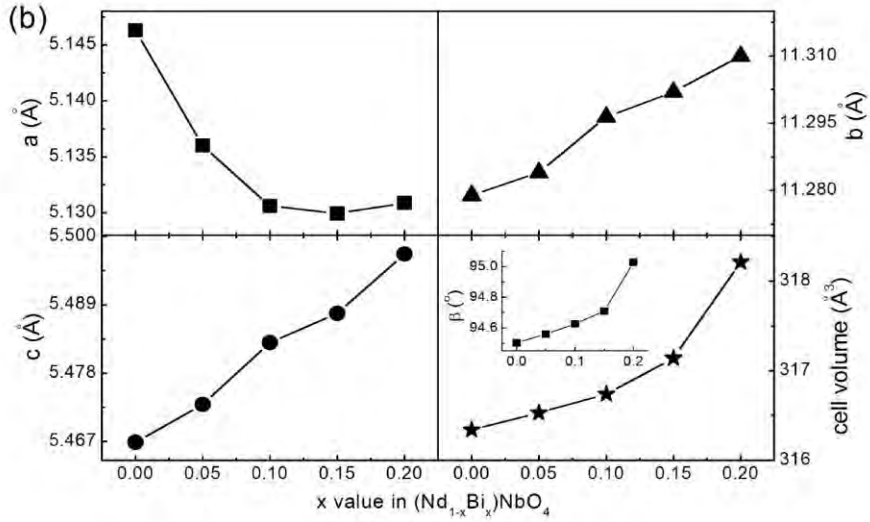
Figure 1. XRD patterns of the $(Nd_{1-x}Bi_x)NbO_4$ ($x \leq 0.2$) ceramics (a) and the cell parameters as a function of x value (b)

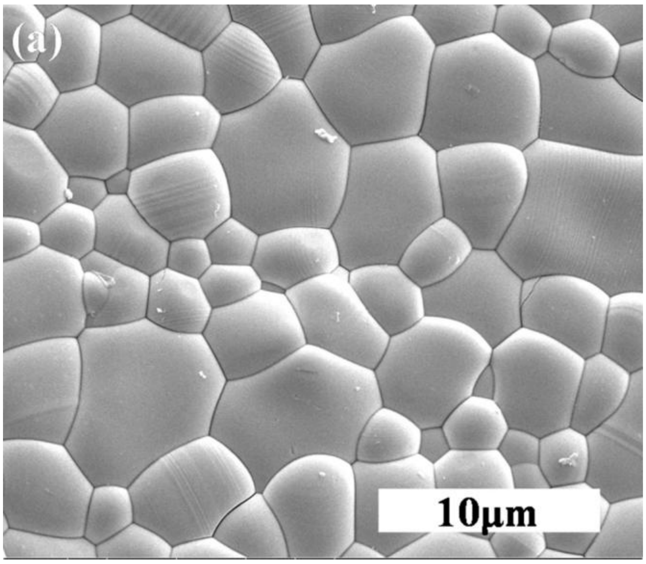
Figure 2. SEM images of the $(Nd_{1-x}Bi_x)NbO_4$ ceramics sintered at their optimal temperatures for x = 0 (a), x = 0.1 (b), x = 0.15 (c) and x = 0.2 (d)

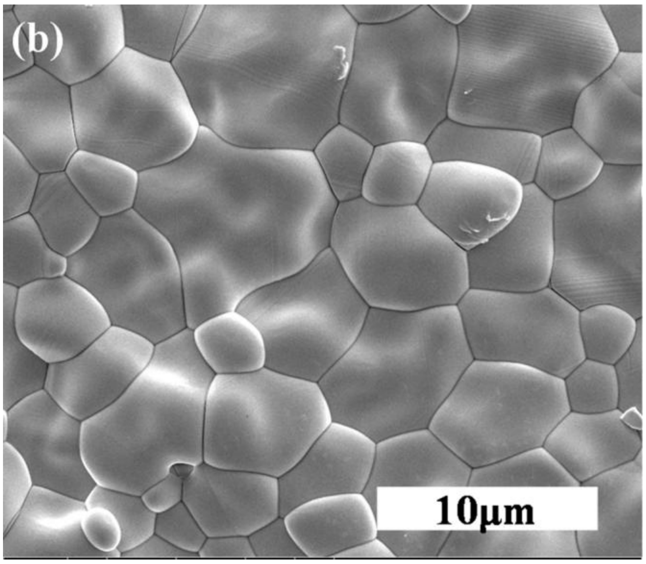
Figure 3. Microwave dielectric properties (permittivity, Qf and TCF values) of the $(Nd_{1-x}Bi_x)NbO_4$ ($x \leq 0.2$) ceramics as a function of x value

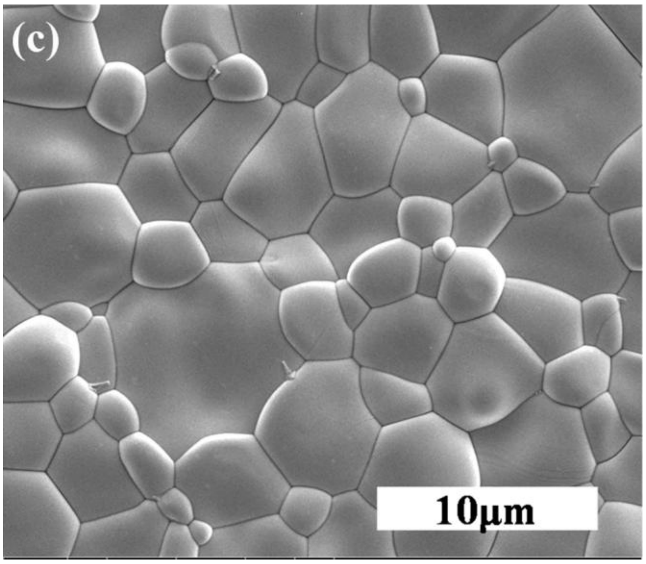
Figure 4. Measured and calculated infrared reflectivity spectra of the $(Nd_{0.85}Bi_{15})NbO_4$ ceramic (solid lines for fitting values) and the complex dielectric spectra

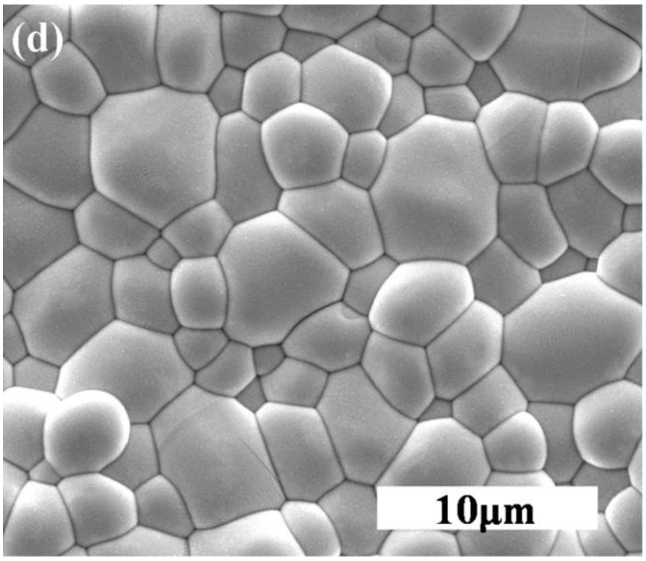

(a)
(Nd0.8Bi0.2)NbO4@1150°C
(Nd0.85Bi0.15)NbO4@1150°C
(Nd0.9Bi0.1)NbO4@1150°C
NdNbO4@1250°C
121
130
040
002
200
020
011
110
031
220
-141
141
150
231
042
240
202
310
-123
242
071
321
242
10
20
30
40
50
60
2θ (degree)

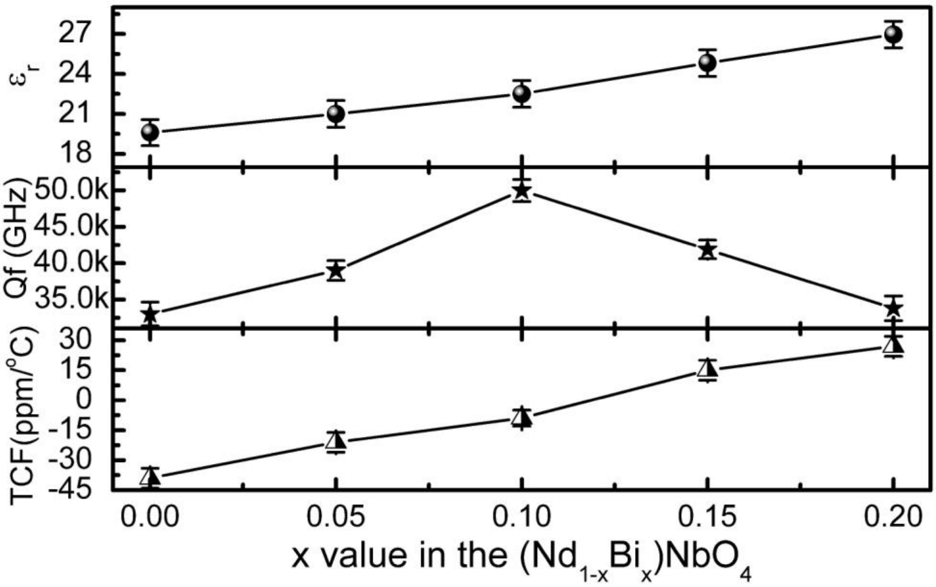

(b)
a (Å)
5.145
5.140
5.135
5.130
b (Å)
11.310
11.295
11.280
c (Å)
5.500
5.489
5.478
5.467
cell volume (Å³)
318
317
316
β (°)
95.0
94.8
94.6
0.0
0.1
0.2
0.00
0.05
0.10
0.15
0.20
x value in (Nd1-xBix)NbO4


(a)
10μm

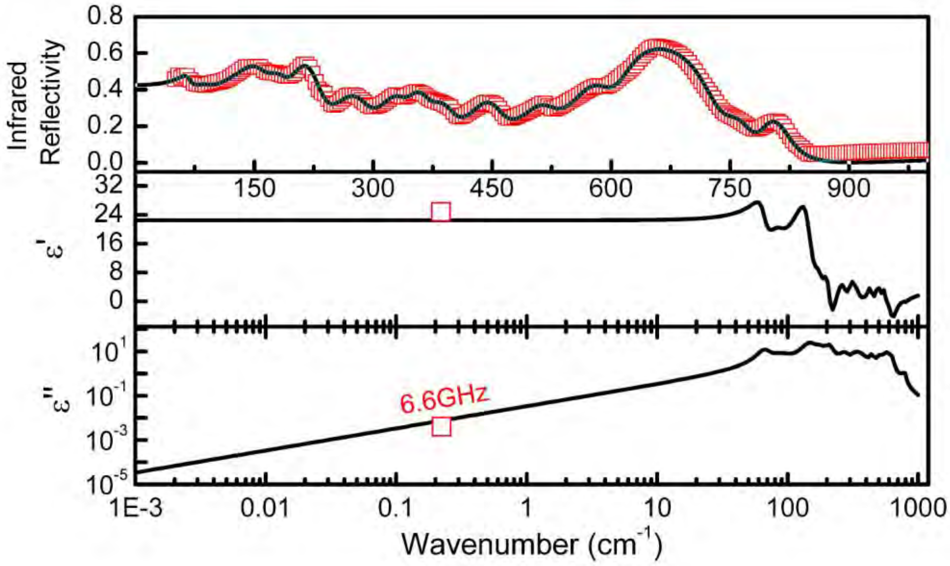

(b)
10μm


(c)
10μm


(d)
10μm



27
24
21
18
εr
50.0k
45.0k
40.0k
35.0k
Qf (GHz)
30
15
0
-15
-30
-45
TCF(ppm/°C)
0.00
0.05
0.10
0.15
0.20
x value in the (Nd1-xBix)NbO4



Infrared Reflectivity
0.8
0.6
0.4
0.2
0.0
150
300
450
600
750
900
ε'
32
24
16
8
0
ε''
10^1
10^-1
10^-3
10^-5
6.6GHz
1E-3
0.01
0.1
1
10
100
1000
Wavenumber (cm^-1)