Effects of lanthanides on structural and dielectric properties of NdNbO$_4$-LnNbO$_4$ ceramics

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ABSTRACT

Recently, lanthanide niobates have attracted significant attentions in multi-functional materials. Herein a series of fergusonite structure-related (1-x)NdNbO$_4$-xLnNbO$_4$ (Ln = Yb, Er, Ho, Dy, Gd and Ce; $0.02 \leq x \leq 0.08$) ceramics were prepared via conventional solid-state reaction method and the microwave dielectric properties were systematically discussed. The X-ray diffraction, Raman spectra were employed to investigate the crystal structure. Obtained results indicate that the ceramic samples present single monoclinic phase belong to the space group of $I2/a$. Microwave dielectric behaviors shown that the permittivity (ε_r) and the quality factor ($Q \times f$) were influenced by the relative density, and the temperature coefficients of resonant frequency (τ_f) value kept the same variation tendency with the Nb-site bond valence. Furthermore, Far-IR and bond energy study evidenced the Ln-O oscillations dominated the main dielectric polarization and system stability. Good microwave dielectric properties, with $\varepsilon_r \sim 20.88$, $Q \times f \sim 66,510$ GHz (at 8.60 GHz) and $\tau_f \sim -36.59$ ppm/°C, were obtained in 0.94NdNbO$_4$–0.06YbNbO$_4$ ceramics when sintered at 1250 °C for 4 h. The (Nd$_{0.94}$Yb$_{0.06}$)NbO$_4$ might be potential candidate for the applications of modern microwave devices.

1. Introduction

Due to the fast development of the wireless industry, the demands for a wide range of low loss, high relative permittivity and near zero temperature coefficient of resonant frequency ceramics are becoming an indispensable problem for our society [1,2]. Microwave dielectric materials with high performance and good structure-property were always attracted considerable attentions [3,4]. Therefore, the desires for exploiting high performance microwave dielectric ceramics devices are in the process.

Recently, ABO$_4$ compounds have raised many researches' interests due to its structure-proper flexibility with different A- and B-site elements, and exhibits good microwave dielectric properties when applied in microwave circuit areas [5–7]. Among of these series of compounds, the lanthanide niobates (ReNbO$_4$), with similar structural properties, have shown excellent advantages on the application of multifunctional materials.

The microwave dielectric properties of ReNbO$_4$ ceramics were firstly reported by Kim et al. [8]. According to the research of Kim et al., the NdNbO$_4$ ceramics present suitable microwave dielectric properties with $\varepsilon_r = .6$, $Q \times f = 33,000$ GHz and $\tau_f = -24$ ppm/°C. Then,

numbers works on enhancing the microwave dielectric properties of NdNbO$_4$ ceramics were carried out [9–16]. For example, Zhang et al. [9,10] firstly improved the $Q \times f$ values of NdNbO$_4$ ceramics through the method of introducing the additives. The NdNbO$_4$–2.0 wt% CaF$_2$ ceramics and NdNbO$_4$–0.6 wt% CaTiO$_3$ ceramics show high $Q \times f$ value of 75000 GHz and 70,000 GHz, respectively. In order to meet the demands of LTCC technology, CuO additions were used to lower the sintering temperature of NdNbO$_4$ ceramics. The NdNbO$_4$ ceramics doped with 0.2 wt% CuO could be well densified below 1000 °C [11]. However, the phase compositions of the ceramics samples were changed and always introduced some unexpected impurities through this approach. Therefore, ionic solid solution would be a promising method to improve the microwave dielectric properties as well as maintain the pristine phase. Example, using tantalum to form a solid solution of LaNb$_{1-x}$Ta$_x$O$_4$, which can be as a promising electrolyte materials [12]. Recent works by Helena et al. showed that the lanthanides have vital effects on the phase transformation and structural properties of LnNbO$_4$ film [13]. For the microwave dielectric ceramics, Zhou et al. reveled the effects of lanthanides on the microwave dielectric properties of ABO$_4$ typed ceramics [14–17], which inspires us lanthanides may be also helpful to improve the microwave dielectric

properties of NdNbO$_4$ ceramics. In our past works, we studied the effects of part of trivalent ions (Y^{3+}, La^{3+}, Sm^{3+}) on the microwave dielectric properties of NdNbO$_4$ ceramic, and introduced the complex chemical bond theory to investigate the intrinsic factors of microwave dielectric properties [18–20]. However, to our best knowledge, there are so far no research articles which cover the effects of other lanthanides (like Yb, Er, Ho, Dy, Gd and Ce) on the structural and dielectric properties of NdNbO$_4$ ceramics. Raman and Far-IR technologies arised as promising approaches to study some structural and dielectric properties of the microwave dielectric ceramics [21,22]. In fact, due to the difficult existed in the fitting process, there were few works reported the vibrational spectroscopy of the NdNbO$_4$ ceramics. All the above attempts would further stimulate us to have a deeply investigation on the NdNbO$_4$ ceramics.

Here, we are inspired to use the lanthanide (Yb, Er, Ho, Dy, Gd and Ce) to induce the monoclinic fergusonite solid solution. Moreover, the influence of different trivalent ions substitution on the phase evolution, crystal structure and microwave dielectric properties of the as-prepare ceramics were discussed. An available method based on the Rietveld refinement of X-ray techniques was used to analyze the crystal structure.

2. Results and discussion

0.94NdNbO$_4$–0.06LnNbO$_4$ (Ln = Yb, Er, Ho, Dy, Gd and Ce) ceramics were synthesized by high-purity oxide powders (See Supporting Information). The XRD patterns of the 0.94NdNbO$_4$–0.06LnNbO$_4$ ceramics sintered at 1250 °C for 4 h are shown in Fig. 1(a). All the peaks of the sintered samples (except Ln = Er) are indexed as the monoclinic fergusonite phase (PDF no. 32-0680), no secondary phase is detected.
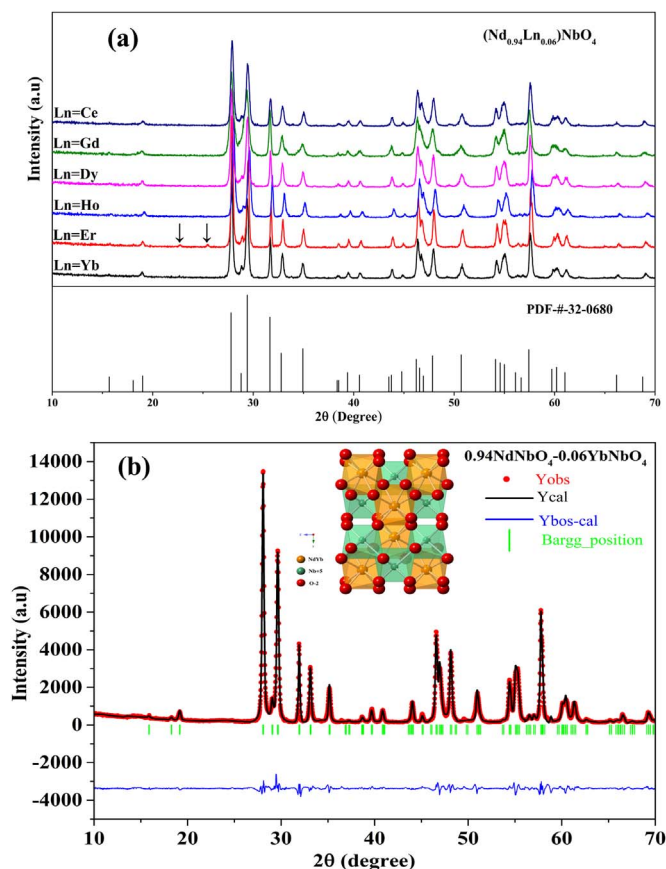

Fig. 1. The XRD patterns of 0.94NdNbO$_4$–0.06LnNbO$_4$ (Ln = Yb, Er, Ho, Dy, Gd and Ce) ceramics sintered at 1250 °C (a), and structural refinement patterns of the 0.94NdNbO$_4$–0.06YbNbO$_4$ ceramic (b).

Table 1
Refined atomic fractional coordinates and atomic occupations from XRD data in 0.94NdNbO$_4$–0.06YbNbO$_4$ ceramics.

Ele.	Wyck.site	x	y	z	Occ.
Nd	4e	0.25000	0.12079	0.00000	0.47
Yb	4e	0.25000	0.12079	0.00000	0.03
Nb	4e	0.25000	0.64552	0.00000	0.50
O1	8f	0.06600	0.70900	0.17400	1.00
O2	8f	0.92600	0.47230	0.24000	1.00

The X-ray diffraction pattern of the 0.94NdNbO$_4$–0.06ErNbO$_4$ sample is a little different from that of other sintered samples, little impurities at 2θ = 23° and 26° were found. To evaluate the intrinsic phase transitions occurred in 0.94NdNbO$_4$–0.06LnNbO$_4$ system, the Rietveld refinement based on the XRD data was performed using the Full-prof program. Fig. 1(b) shows the obtained structural refinement schematic of 0.94NdNbO$_4$–0.06YbNbO$_4$ ceramics. The refined lattice parameters in 0.94NdNbO$_4$–0.06YbNbO$_4$ ceramics are a = 5.444 Å, b = 11.252 Å, c = 5.140 Å, β = 94.42° and V = 313.88 Å^3, the discrepancy factors are R_p = 7.95% and R_{wp} = 11.07%. Table 1 listed the atomic fractional coordinates and atomic occupations of 0.94NdNbO$_4$–0.06YbNbO$_4$ ceramics. From comparisons of the refined results in our past works of (Nd$_{1-x}$Y$_x$)NbO$_4$ ceramics [18], we found that the atomic fractional coordinates of the O1 site in this paper is different with the previous reports, which maybe influence the structural properties of the NdNbO$_4$ ceramics.

To study cell parameters change tendency occurred in 0.94NdNbO$_4$–0.06LnNbO$_4$ (Ln = Yb, Er, Ho, Dy, Gd and Ce) ceramics. Fig. 2 presents the cell parameters of a, b, c, and V, also included the Nd-site and Nb-site bond length with different ionic radius based on refined results. As seen from Fig. 2(a), as ionic radius increases from Yb^{3+} to Ce^{3+}, both of a and b values show a linearly increasing trend, a stable variation found in the c value, and this phenomenon would cause a liner increase in the cell volume. From the crystal structure shown in Fig. 1(b), two NdO8 and NbO6 polyhedron structure were observed in a, b, and c axis, when a linear increase occurred in cell parameters, which would result in a structural change on polyhedron structure. From Fig. 2(b), when A-site ion is occupied by from Yb^{3+} to Ce^{3+} ions, both of Nd-site bond length and Nb-site bond length exhibit a linear increase trend. The variation exhibited in Nb-site bond length seems to be more intense than the Nd-site bond length, this indicates that the fergusonite solid solution of (1-x)NdNbO$_4$-xLnNbO$_4$ is mainly influenced by NbO6 octahedral structure. In additional, the shortest and longest Nb-site bond length in this paper are about 1.55 Å and 2.58 Å, respectively, which are very different with previous reports (1.73 Å and 2.30 Å) [18]. We think the obtained results in this paper is mainly caused by the change of fractional coordinates in the O1 site.

Raman spectroscopy technology was a powerful tool for identifying the crystalline phases or lattice strains of the most of inorganic materials. Based on the Raman rules, the Raman peaks depend on the intrinsic chemical bond of the crystal. Using the phonon modes presented by Dias et al. [23], the irreducible representations of NdNbO$_4$ are described as following:

$$\Gamma = 8A_g + 10B_g + 8A_u + 10B_u$$

where 'g' for Raman active modes and 'u' for IR active modes. Thus, we can obtain 18 gerade Raman modes and 15 IR ungerade modes (A$_u$ + 2B$_u$ belong to acoustic modes). To study the complexity of the spectra, the experimental Raman data were fitted using Gaussian method, which is a little different from Dias's work. Fig. 3 shows the measured and calculated spectrum of 0.94NdNbO$_4$–0.06LnNbO$_4$ ceramics. Fifteen bands were obtained in this paper, and their wavenumbers are presented in Table S1. We can observe that all wavenumbers at 94–288 cm^{-1} (assignment to Re units) and 634–803 cm^{-1} (assignment to NbO$_4$ units) present an increasing tendency and an decreasing