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The Correlations Among Bond Ionicity, Lattice Energy and Microwave Dielectric Properties of $(\text{Nd}_{1-x}\text{La}_x)\text{NbO}_4$ Ceramic

Ping Zhang*, Yonggui Zhao, Lingxia Li

School of Electronic and Information Engineering, Tianjin University, Tianjin 300072, China

Abstract

$(\text{Nd}_{1-x}\text{La}_x)\text{NbO}_4$ ceramics were prepared via a conventional solid-state reaction route and the correlations between bond ionicity, lattice energy, phase stability and microwave dielectric properties were investigated. The diffraction patterns showed that the $(\text{Nd}_{1-x}\text{La}_x)\text{NbO}_4$ ceramics performed the monoclinic fergusonite structure. The chemical bond ionicity, bond covalency and lattice energy were calculated using the empirical method. The phase structure stability varied with the lattice energy which was resulted by the substitution content of La^{3+} ions. With the increasing of La^{3+} ion contents, the decrease of Nd/La-O bond ionicity was observed, which could be contributed to the electric polarization. The ϵ_r had a close relationship with the Nd/La-O bond covalency. The increase of the $Q \times f$ values and τ_f values could attribute to the change of the lattice energy. The microwave dielectric properties of $(\text{Nd}_{1-x}\text{La}_x)\text{NbO}_4$ ceramics with monoclinic fergusonite structure were strongly dependent on the chemical bond ionicity, bond covalency and lattice energy.

Keywords: Bond ionicity; Lattice energy; Phase stability; Microwave dielectric properties

1. Introduction

Chemical bond ionicity and lattice potential are important in considering the stability of new inorganic materials [1-3]. Zhang *et al* [4-5] reported that the chemical bond ionicity of complex crystals

*Corresponding author. Tel. : +86 13702194791

Email address: zptai@163.com (P. Zhang)

could be evaluated by generalized P-V-L dielectric theory. And the lattice energy could be obtained according to the chemical bond ionicity. The lattice energy played an important role in diverse thermodynamic analysis of the existence and stability of ionic crystals, which was one of the most important quantities in elucidating the structure, character, and behavior of solids [6-9]. However, there were few reports about evaluation on microwave dielectric properties using the chemical bond ionicity and lattice energy.

Recently, *Kim et al.* [10] reported that NdNbO₄ ceramics possessed ϵ_r of 19.6, $Q \times f$ of 33, 000 GHz and τ_f of -24 ppm/°C sintered at 1250 °C. However, the three parameters were not excellent to apply in microwave devices. In our previous work, we investigated the microwave dielectric properties of NdNbO₄ ceramics doping with CaF₂. NdNbO₄ ceramics with 2.0 wt.% CaF₂ sintered at 1225°C for 4 h showed excellent microwave dielectric properties, $Q \times f \sim 75, 000$ GHz and $\tau_f \sim -19$ ppm/ °C[11]. And we discovered that the microwave properties of NdNbO₄ ceramics could be optimized using bivalent ions substituted to Nd³⁺ ionic owing to the formation of solid solutions, the phase composition would be changed when Nd³⁺ ionic was substituted by other bivalent ions (Sr²⁺, Ca²⁺, Mn²⁺, Co²⁺)[12,13]. In our recent work, we investigated the correlation of crystal structure and microwave dielectric properties Nd_{1.02}(Nb_{1-x}Ta_x)_{0.988}O₄ ceramics[14], and discovered that the NdNbO₄ system possessed the oxygen octahedron structure which had non-negligible influence on the microwave dielectric properties. However, few works were reported about the relationships among crystalline structure, phase stability, bond ionicity, lattice energy and microwave dielectric properties of (Nd_{1-x}La_x)NbO₄ ceramics.

In this paper, for the first time, quantitative calculation was made in bond ionicity of the (Nd_{1-x}La_x)NbO₄ (0 ≤ x ≤ 0.08) ceramics using the generalized P-V-L dielectric theory based on the crystalline structure refinement. The lattice energy was calculated by the chemical bond method and

unit-cell method. Phase stability was strongly dependent on the variation of the lattice energy. The microwave dielectric properties of $(\text{Nd}_{1-x}\text{La}_x)\text{NbO}_4$ ceramics had a close relationship with the bond ionicity and the lattice energy.

2. Experimental procedure and Theory

2.1 Experimental Section

$(\text{Nd}_{1-x}\text{La}_x)\text{NbO}_4$ microwave dielectric ceramics were prepared by using a conventional solid-state reaction route from the raw powders Nd_2O_3 (99.99%), Nb_2O_5 (99.99%) and La_2O_3 (99.99%). The raw materials were mixed according to the formula of $(\text{Nd}_{1-x}\text{La}_x)\text{NbO}_4$ ($x=0.0, 0.02, 0.04, 0.06, 0.08$). The mixed powders were milled for 10 h with distilled water in a nylon container with ZrO_2 balls. All the slurries were dried and pre-sintered at 900 °C for 4 h. The pre-sintered powders were re-milled for 10 h. After drying and sieving, the powders were pressed into pellets with 10 mm diameter and 5 mm thickness. Then these pellets were sintered at temperatures of 1275 °C for 4 h.

The crystalline phases of the sintered samples were identified by X-ray diffraction (XRD, Rigaku D/max 2550 PC, Tokyo, Japan) with $\text{Cu K}\alpha$ radiation generated at 40 kV and 40 mA. The microwave dielectric properties were measured in the frequency range of 8-12 GHz using a HP8720ES network analyzer. The dielectric constant and the quality factor were measured by the Hakki-Coleman method [15-16]. The temperature coefficients of resonant frequency (τ_f) were measured in the temperature range from 25 °C to 85 °C and calculated by noting the change in resonant frequency (Δf)

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \quad (1)$$

where f_1 was resonant frequency at T_1 and f_2 was the resonant frequency at T_2 .

2.2 Theory Development

As we all know, we can deal with many binary crystals especially of the $A^N B^{8-N}$ by using the PV theory [6,7,17]. Then Levine *et al.* [18, 19] successfully deal with complex crystals such as ABC_2 , ABC_3 and ABC_4 and more complex crystals. However an explicit expression is not given for decomposing the complex multiband crystals into the sum of binary crystals. After considering these ideas in chemical bond representation, Zhang *et al.* [4, 5] succeed in generalizing P-V-L theory for multiband systems and given an explicit expression about how to decompose the complex crystals into binary crystals. Suppose that A denotes cations and B anions, any multiband complex crystal could be written as:

$$A_{a_1}^1 A_{a_2}^2 \dots A_{a_i}^i \dots B_{b_1}^1 B_{b_2}^2 \dots B_{b_j}^j$$

where A^i and B^j represent the different elements or the different sites of a given element of cations and anions, respectively, and a_i , b_j represent the number of the corresponding elements.

Thus, any complex crystals could be decomposed into the sum of binary crystals with the crystallographic data by the following formula:

$$A_{a_1}^1 A_{a_2}^2 \dots A_{a_i}^i \dots B_{b_1}^1 B_{b_2}^2 \dots B_{b_j}^j = \sum_{ij} A_{m_i}^i B_{n_j}^j \quad (2)$$

$$m_i = \frac{N(B^i - A^i)a_i}{N_{CAi}} \quad (3)$$

$$n_j = \frac{N(B^j - A^j)b_j}{N_{CBj}} \quad (4)$$

where N_{CAi} and N_{CBj} represent the nearest total coordination numbers of the A^i and B^j ions in the crystal; $N(B^i - A^i)$ represents the nearest coordination number contributed by the A^i ion; and $N(A^i - B^j)$ represents the nearest coordination contributed by the B^j ion. After decomposing the complex crystal into the sum of different kinds of binary crystals, the P-V-L theory can be directly applied to the calculation of the chemical bond parameters in complex crystals.

According to the generalized P-V-L theory, the bond ionicity f_i^μ and bond covalency f_c^μ of an individual bond μ can be defined as follows:

$$f_i^\mu = \frac{(C^\mu)^2}{(E_g^\mu)^2} \quad (5)$$

$$f_c^\mu = \frac{(E_h^\mu)^2}{(E_g^\mu)^2} \quad (6)$$

where E_g^μ is the average energy gap for the type bond μ , which is composed of homopolar E_h^μ and heteropolar C^μ parts as follows:

$$(E_g^\mu)^2 = (E_h^\mu)^2 + (C^\mu)^2 \quad (7)$$

where

$$(E_h^\mu)^2 = \frac{39.74}{(d^\mu)^{2.48}} \quad (8)$$

For any binary crystal A_mB_n type compounds, the heteropolar C^μ parts can be calculated as following:

$$C^\mu = 14.4b^\mu \exp(-k_s^\mu r_o^\mu) \left[\left(\frac{(Z_A^\mu)^*}{r_o^\mu} - (n/m) \frac{(Z_B^\mu)^*}{r_o^\mu} \right) \right] \text{ (if } n > m) \quad (9)$$

$$C^\mu = 14.4b^\mu \exp(-k_s^\mu r_o^\mu) \left[\left((m/n) \frac{(Z_A^\mu)^*}{r_o^\mu} - \frac{(Z_B^\mu)^*}{r_o^\mu} \right) \right] \text{ (if } n < m) \quad (10)$$

where b^μ is a correction factor that is proportional to the square of the average coordination number N_c^μ , $(Z_A^\mu)^*$ is the effective number of valence electrons on the cation A and $(Z_B^\mu)^*$ is the effective number of valence electrons on the anion B.

The correction factor b^μ is defined as:

$$b^\mu = \beta(N_c^\mu)^2 \quad (11)$$

$$N_c^\mu = \frac{m}{m+n} N_{cA}^\mu + \frac{n}{m+n} N_{cB}^\mu \quad (12)$$

β is 0.089[20], N_{CA}^{μ} is the coordination number of μ type of bond for cation A, and N_{CB}^{μ} is the coordination number of bond for anion B.

$\exp(-k_s^{\mu} r_o^{\mu})$ is the Thomas-Fermi screening factor,

$$k_s^{\mu} = \left(\frac{4k_F^{\mu}}{\pi a_B} \right)^{1/2} \quad (13)$$

$$k_F^{\mu} = \left[3\pi^2 (N_e^{\mu})^* \right]^{1/3} \quad (14)$$

$$r_o^{\mu} = d^{\mu} / 2 \quad (15)$$

where a_B is the Bohr radius and has the value 0.5292 Å and r_o^{μ} is the average radius of A and B in angstroms. $(N_e^{\mu})^*$ is the number of μ valence electrons of bond per cubic centimeter.

$$(N_e^{\mu})^* = \frac{(n_e^{\mu})^*}{v_b^{\mu}} \quad (16)$$

$$(n_e^{\mu})^* = \frac{(Z_A^{\mu})^*}{(N_{CA}^{\mu})^*} + \frac{(Z_B^{\mu})^*}{(N_{CB}^{\mu})^*} \quad (17)$$

where $(n_e^{\mu})^*$ is the number of the effective valence electrons per μ bond, v_b^{μ} is the bond volume.

$$v_b^{\mu} = \frac{(d^{\mu})^3}{\sum_v (d^v)^3 N_b^v} \quad (18)$$

N_b^v is the number of bonds per cubic centimeter, which can be obtained from the crystal structural data.

The best-known calculation methods about lattice energy for binary solids can be divided in two fields, which were the chemical bond method and the unit-cell volume method.

2.2.1 Chemical Bond Method

On the basis of generalized P-V-L theory, Zhang *et al.* reported that the lattice energy can be obtained by the chemical bond ionicity [4,5,7]. And the lattice energy U_{cal} of any complex crystal can be written as:

$$U_{cal} = \sum_{\mu} U_b^{\mu} \quad (19)$$

$$U_b^{\mu} = U_{bc}^{\mu} + U_{bi}^{\mu} \quad (20)$$

$$U_{bc}^{\mu} = 2100m \frac{(Z_+^{\mu})^{1.64}}{(d^{\mu})^{0.75}} f_C^{\mu} \quad (21)$$

$$U_{bi}^{\mu} = 1270 \frac{(m+n)Z_+^{\mu}Z_-^{\mu}}{d^{\mu}} \left(1 - \frac{0.4}{d^{\mu}}\right) f_i^{\mu} \quad (22)$$

where U_{bc}^{μ} was the covalent part and U_{bi}^{μ} was the ionic part of μ bond. Z_+^{μ} and Z_-^{μ} were the valence states of cation and anion which constituted bond μ .

2.2.2 Unit-Cell Volume Method

Jenkins et al.[21,22] proposed a sample method about lattice energy which can be calculated using the unit-cell volume, the formula could be written as follows:

$$U = AI(2I/V_m)^{1/3} \quad (23)$$

$$2I = \sum_i n_i Z_i^2 \quad (24)$$

$$V_m = V_{cell} / Z \quad (25)$$

where A ($=121.39 \text{ kJ mol}^{-1} \text{ nm}$) was the term $1/2N_A M e^2 / 4\pi\epsilon_0$, N_A (mol^{-1}) was Avogadro's number, M was the Madelung constant of the rock salt (sodium chloride)-type lattice ($=1.74756$) on which the simplifications of the Kapustinskii equation were based, e/C was the charge on the electron and $4\pi\epsilon_0 / C^2$ ($\text{J}^{-1}\text{m}^{-1}$) was the vacuum permittivity. And I was the ionic strength, V_m was the volume per formula unit.

3. Results and discussion

3.1 Multiphase refinement and Structure analysis

The X-ray diffraction patterns of $(\text{Nd}_{1-x}\text{La}_x)\text{NbO}_4$ ceramics are given in Fig. 1. To reduce noise, all data have been smoothed by Adaptive smoothing method and deducted background using Powder X.

All parameters including background, zero-point, scale factors for all phases, half-width, asymmetry parameters, unit-cell parameters, atomic positional coordinates, temperature factors were refined step-by-step for avoiding correlations. A pure single-phase NdNbO₄ (ICDD #32-0680) without any secondary phase is observed in the range of $x=0-0.06$ from the diffraction patterns, which is belong to the monoclinic fergusonite structure with the space group I2/a (no. 15). The lattice parameters from Rietveld refinement are calculated as $a=5.146 \text{ \AA}$, $b=11.294 \text{ \AA}$, $c=5.451 \text{ \AA}$, and $V_{cell}=317.25 \text{ \AA}^3$. With the increasing of substitution content, the LaNb₅O₁₄ peaks (indexed as LaNb₅O₁₄, ICDD #42-0386) can be detected when $x=0.08$. In the following study, we will carefully discuss the relationship between phase stability and lattice energy for the formation of the second phase.

The parts of refinement crystal structure data are shown in Table. 1. The results shows that the unit-cell volume decreased with the increasing La³⁺ ion contents up to $x=0.06$ and then increased slightly with a further increase of La³⁺ ion content. It is also noted that the peak position slightly shifted to higher degree with the increasing in substitution from the illustration of Fig. 1, which indicating the decrease of cell volume[11].

Fig.2 shows a schematic representation of an NdNbO₄ supercell (1×1×1). In the supercell, there contains four NdNbO₄ molecules per primitive cell and we can see that there contains an oxygen octahedron in the NdNbO₄ supercell, and with the Nb ion at the center of the oxygen octahedron. Due to the special structure, the change of the oxygen octahedron can affect the microwave dielectric properties. In this paper, with the different amounts of substitution of La³⁺ ions, the atomic interactions of NdNbO₄ are changed, which could result in bond length of the oxygen octahedron. And the bond length of oxygen octahedron has close connection to the B-site lattice energy, which plays an important role in considering the NdNbO₄ system.

3.2 Bond Ionicity Calculation of $(Nd_{1-x}La_x)NbO_4$ System

According to the crystallographic data and the complex chemical bond theory, the complex crystals $NdNbO_4$ can be decomposed into the sum of binary crystals as follows:

$$\begin{aligned} NdNbO_4 &= NdNbO(1)_2 O(2)_2 \\ &= Nd_{1/2}O(1) + Nd_{1/2}O(2)_{4/3} + Nb_{2/3}O(1) + Nb_{1/3}O(2)_{2/3} \end{aligned}$$

Fig.3 shows the coordination number and charge distribution of ions in the $NdNbO_4$ system. The effective valence electron numbers of cations in the above bond are $Z_{Nd}=3$ and $Z_{Nb}=5$, but the effective valence electron numbers of O^{2-} anions in each type bond are different. They are $Z_O=13/2$ in $Nd_{1/2}-O(1)$ bond, $Z_O=55/8$ in $Nd_{1/2}-O(2)_{4/3}$ bond, $Z_O=14/3$ in $Nb_{2/3}-O(1)$ bond and $Z_O=11/2$ in the $Nb_{1/3}-O(2)_{2/3}$ bond. The difference in O^{2-} anions are owing to charge balance for each sub-formula.

Table.2 shows the calculated results of bond ionicity for $(Nd_{1-x}La_x)NbO_4$ ($0 \leq x \leq 0.08$) ceramics. According to the results, although both of the average ionicity of the Nd/La-O bond and the Nb-O bond decrease with the increasing the amounts of La^{3+} ions, we discover that the Nd/La-O bond has higher bond ionicity. It is suggested that the substitution of La^{3+} ions has more effect on the A-site ionicity. We have also calculated the bond covalency of $Nd/La-O(1)^2$ ($f_{e\text{Nd/La-O}(1)^2(A)}$) which keeps the same change with the substitution of La^{3+} ions. The calculations of bond ionicity and the bond covalency indicates that the $f_{e\text{Nd/La-O}(1)^2(A)}$ is dominant in microwave dielectric properties of $(Nd_{1-x}La_x)NbO_4$ ceramics.

3.3 Lattice Energy and Phase Stability

The lattice energies are calculated by chemical bond ionicity and unit-cell volume for $(Nd_{1-x}La_x)NbO_4$ ($0 \leq x \leq 0.08$) ceramics shown in Table.3 and Table.4, respectively. The concept of the lattice energy is defined as the heat of dissociation that one mole of solid into its structural components, which can be applied to evaluate the phase stability of a crystal structure [23]. As shown in Table.3 and

Table.4. The total of lattice energy for $(\text{Nd}_{1-x}\text{La}_x)\text{NbO}_4$ ($0 \leq x \leq 0.06$) ceramics were increasing with the increasing of La^{3+} ion content. The calculations of lattice energy have some difference between chemical bond method and unit-cell volume method, which is because of the different calculational model. Although the unit-cell volume method is sample and contains few parameters, it can't reflect the detailed information about the internal crystalline structure. Hence, the chemical bond method is vital to realize the details of the internal crystalline structure and the phase transformation. Then we calculated the average lattice energy of Nd/La-O bond ($AU_{\text{Nd/La-O}}$) and Nb-O bond ($AU_{\text{Nb-O}}$) illustrated in Table.3. The $AU_{\text{Nb-O}}$ is higher than the $AU_{\text{Nd/La-O}}$, which is due to the special oxygen octahedron structure (we have investigated the structure of oxygen octahedron in the parts of **Structure analysis**). Combining with the analysis of the lattice energies in Fig.1 and Table.4 , the $AU_{\text{Nb-O}}$ has minimum value when the second phase was formed when $x=0.08$. It is suggested that the phase change of the NdNbO_4 ceramics could be predicted by the $AU_{\text{Nb-O}}$.

3.4 Microwave Dielectric Properties

The microwave dielectric properties of $(\text{Nd}_{1-x}\text{La}_x)\text{NbO}_4$ ($0 \leq x \leq 0.08$) ceramics are illustrated in Table.5. The microwave dielectric properties of these compounds are varied regularly with Nd^{3+} ionic substitution for La^{3+} ionic. Coordination with the chemical bond ionicity and the lattice energy in the compounds, the $f_{c \text{ Nd/La-O}(1)2(\text{\AA})}$ and the $AU_{\text{Nb-O}}$ play an important role in $(\text{Nd}_{1-x}\text{La}_x)\text{NbO}_4$ system with monoclinic fergusonite structure.

According to the P-V-L theory studied by *Kolmykov et al*[24], the relationship between dielectric constant and bond ionicity was founded as follows:

$$\varepsilon_r = \frac{n^2 - 1}{1 - f_i} + 1 \quad (26)$$

where n was the refractive index. It was indicated that the dielectric constant increased with the increasing of the bond ionicity. However, in this paper, the relationship between dielectric constant and the bond ionicity are different to the Eq.(26), which could be attributed to the special crystal structure of NdNbO_4 system (oxygen octahedron structure). Therefore, in accordance with Eq. (26), we have made a guess, and the dielectric constant and the bond covalency could be defined by Eq.(27):

$$\varepsilon_r = \frac{n^2 - 1}{1 - f_c} + 1 \quad (27)$$

Fig.4 shows the variation of the dielectric constant and the $f_{c \text{ Nd/La-O}(1)2}$ as a function of the x values of $(\text{Nd}_{1-x}\text{La}_x)\text{NbO}_4$ ceramics. The dielectric constant keeps the same change with the $\text{Nd/La-O}(1)^2$ bond covalency ($f_{c \text{ Nd/La-O}(1)2}$). This results are suggested that the $f_{c \text{ Nd/La-O}(1)2}$ has the main influence on the dielectric constant in the $(\text{Nd}_{1-x}\text{La}_x)\text{NbO}_4$ ceramics.

The $Q \times f$ values and the lattice energies of $(\text{Nd}_{1-x}\text{La}_x)\text{NbO}_4$ ($0 \leq x \leq 0.08$) ceramics are shown in Fig.5. The influence of the $Q \times f$ values at microwave frequencies included the intrinsic and extrinsic part. The extrinsic factor, such as defect concentration, impurities, grain size, and porosity, is not under consideration in this article owing to the well-densified samples. The intrinsic factor on $Q \times f$ values is minimum loss related with lattice anharmonicity [25-26]. In this study, the trend of $Q \times f$ values shows no obvious relationship with the bond ionicity, but the $Q \times f$ values are strongly dependent on the lattice energy. As shown in Fig.5, the $Q \times f$ values increased with the lattice energy increasing. In accordance with the results in Table.4, the Nb-O type of bond lattice energy makes a big contribution to the total of the lattice energy. The variations of the $Q \times f$ values are suggested that the Nb-O type of bond lattice energy plays a non-negligible role in NdNbO_4 system. It is indicated that the lattice energy could be under consideration as an intrinsic factor in investigation of the $Q \times f$ values.

The temperature coefficient of resonant frequency τ_f is the relations between resonant frequency and the temperature, and it reveals the stability of the system. Fig.6 shows the τ_f values and the B-site lattice energy of $(\text{Nd}_{1-x}\text{La}_x)\text{NbO}_4$ ($0 \leq x \leq 0.08$) ceramics as a function of the x values. The τ_f values shift to the zero with the increasing of the B-site lattice energy, indicating that the system tend to stable. Higher lattice energy correlates with higher bond strength. Therefore, the restoring force which resulted in the tilting on oxygen octahedron, increased with the increase of B-site lattice energy, and the τ_f towards to zero.

4. Conclusions

The $(\text{Nd}_{1-x}\text{La}_x)\text{NbO}_4$ ($0 \leq x \leq 0.08$) ceramics were prepared by conventional oxide mixed method. The single phase with monoclinic fergusonite structure was obtained in region of $0 \leq x \leq 0.06$. With a further increase of substitution La^{3+} ion, the second phase could be detected. In the $(\text{Nd}_{1-x}\text{La}_x)\text{NbO}_4$ ceramics, the lattice energy increased when Nd^{3+} ion was substituted by La^{3+} ion, which indicated that the stability of crystal structure was enhanced, and the phase change could be predicted by the variation of the lattice energy. For the first time, the chemical bond ionicity of $(\text{Nd}_{1-x}\text{La}_x)\text{NbO}_4$ ($0 \leq x \leq 0.08$) ceramics was calculated by the generalized P-V-L theory and evaluated the microwave dielectric properties. In the $(\text{Nd}_{1-x}\text{La}_x)\text{NbO}_4$ ($0 \leq x \leq 0.08$) ceramics, the dielectric constant ϵ_r was strongly dependent on $f_{c\text{Nd/La-O}(1)2}$. The $Q \times f$ values had a same variation trend with the lattice energy which was considered as an intrinsic factor. The τ_f of the specimens had a close relationship with the Nb-O type of bond lattice energy.

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Figure Captions

Fig.1 The X-ray diffraction patterns of $(\text{Nd}_{1-x}\text{La}_x)\text{NbO}_4$ ($0 \leq x \leq 0.08$) ceramics.

Fig.2 The crystal structure patterns ($1 \times 1 \times 1$) supercell of monoclinic fergusonite structured NdNbO_4 .

Fig.3 The coordination number and charge distribution of ions in NdNbO_4 ceramics.

Fig.4 The ϵ_r values and the $\text{Nd/La-O}(1)^2$ bond covalency of $(\text{Nd}_{1-x}\text{La}_x)\text{NbO}_4$ ($0 \leq x \leq 0.08$) ceramics.

Fig.5 The $Q \times f$ values and the lattice energy of $(\text{Nd}_{1-x}\text{La}_x)\text{NbO}_4$ ($0 \leq x \leq 0.08$) ceramics.

Fig.6 The τ_f values and the average of B-site lattice energy of $(\text{Nd}_{1-x}\text{La}_x)\text{NbO}_4$ ($0 \leq x \leq 0.08$) ceramics.

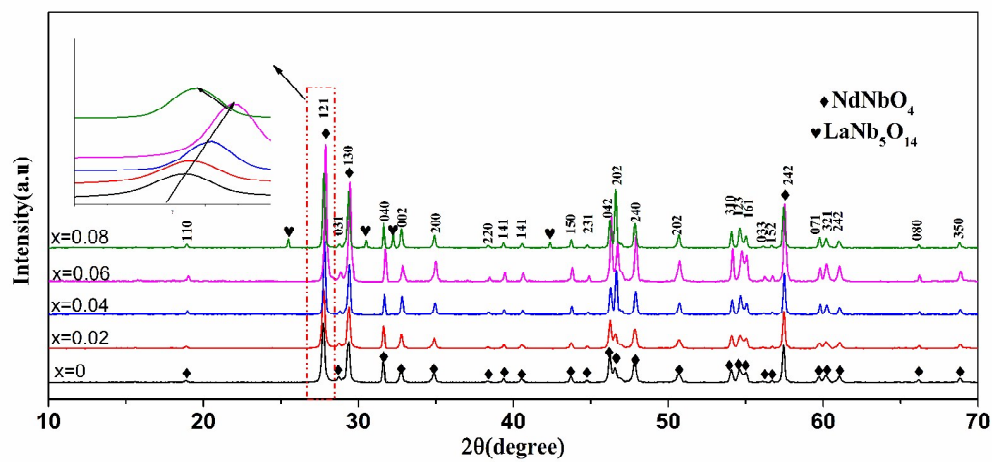


Fig.1

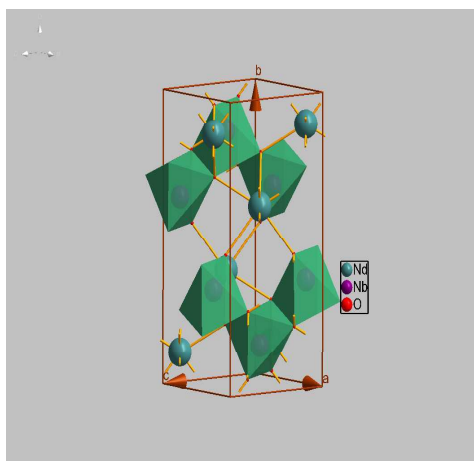


Fig.2

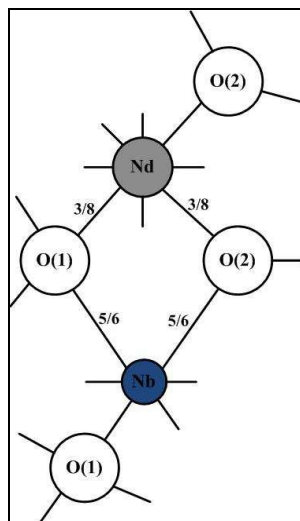


Fig.3

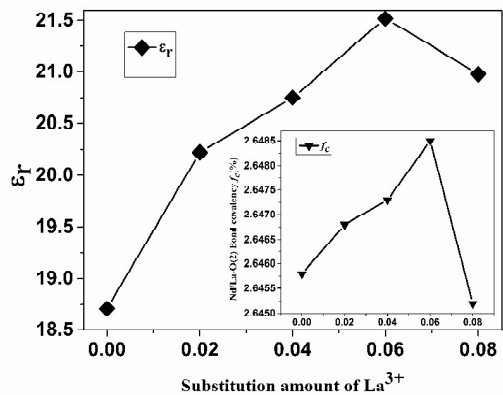


Fig.4

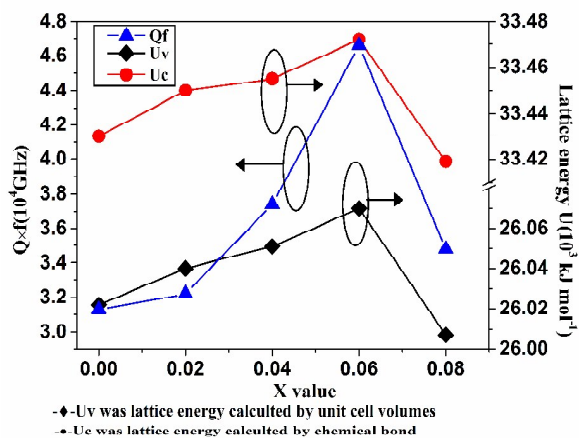


Fig.5

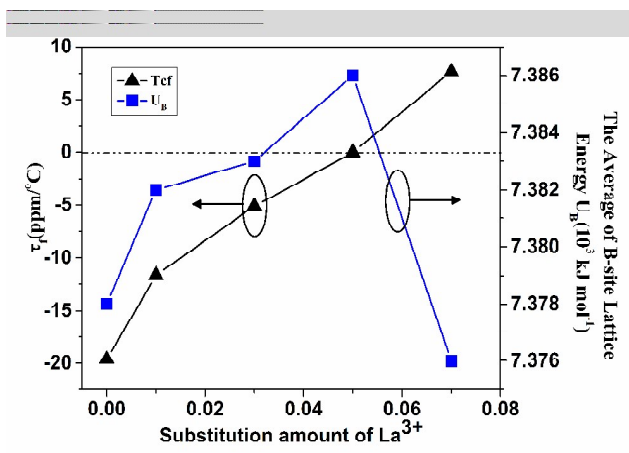


Fig.6

Table.1 Crystallographic data from Rietveld refinement for $(\text{Nd}_{1-x}\text{La}_x)\text{NbO}_4$ ($0 \leq x \leq 0.08$) ceramics

x value	x=0	x=0.02	x=0.04	x=0.06	x=0.8
<i>a</i>	5.150	5.147	5.146	5.138	5.154
<i>b</i>	11.294	11.283	11.277	11.272	11.306
<i>c</i>	5.471	5.468	5.465	5.464	5.470
$V_{\text{cell}}(\text{\AA}^3)$	317.25	316.56	316.17	315.48	317.77
β	94.47	94.52	94.48	94.50	94.47
R_p	0.0769	0.0859	0.0909	0.1021	0.0787
R_{wp}	0.1194	0.1256	0.1020	0.1145	0.1367
$\text{Nd/La-O}(1)^1(\text{\AA}) \times 2$	2.4352	2.4344	2.4328	2.4314	2.4362
$\text{Nd/La-O}(1)^2(\text{\AA}) \times 2$	2.4809	2.4784	2.4777	2.4758	2.4828
$\text{Nd/La-O}(2)^1(\text{\AA}) \times 2$	2.3674	2.3649	2.3648	2.3622	2.3696
$\text{Nd/La-O}(2)^2(\text{\AA}) \times 2$	2.4844	2.4928	2.4913	2.4902	2.4959
$\text{Nb-O}(1)^1(\text{\AA}) \times 2$	1.9126	1.9120	1.9108	1.9094	1.9135
$\text{Nb-O}(1)^2(\text{\AA}) \times 2$	2.4857	2.4832	2.4826	2.4809	2.4870
$\text{Nb-O}(2)(\text{\AA}) \times 2$	1.8794	1.8775	1.8770	1.8759	1.8802

Table.2 Bond ionicity for $(\text{Nd}_{1-x}\text{La}_x)\text{NbO}_4$ ($0 \leq x \leq 0.08$) ceramics

Bond type	Bond Ionicity f_i (%)				
	x=0	x=0.02	x=0.04	x=0.06	x=0.08
$\text{Nd/La-O}(1)^1$	97.3292	97.3291	97.3280	97.3270	97.3293
$\text{Nd/La-O}(1)^2$	97.3542	97.3532	97.3527	97.3515	97.3548
$\text{Nd/La-O}(2)^1$	96.7617	96.7607	96.7604	96.7586	96.7625

$Nd/La-O(2)^2$	96.8289	96.8286	96.8277	96.8269	96.8291
$Nb-O(1)^1$	44.8442	44.8410	44.8270	44.8107	44.8502
$Nb-O(1)^2$	49.1511	49.1418	49.1371	49.1265	49.1537
$Nb-O(2)$	73.8284	73.8168	73.8119	73.8024	73.8316
$AI_{(Nd/La-O)}$	97.0685	97.0679	97.0672	97.0660	97.0683
$AI_{(Nb-O)}$	55.9412	55.9332	55.9253	55.9132	55.9452
$f_c Nd/La-O(1)2 (\text{\AA})$	2.6458	2.6468	2.6473	2.6485	2.6452

*The AI was the average of the bond ionicity and f_c was the bond covalency of Nd/La-O(1)².

Table.3 Lattice energy calculated by chemical bond ionicity for (Nd_{1-x}La_x)NbO₄ (0≤x≤0.08)

ceramics

Bond type	Lattice Energy U_c (kJ/mol)				
	x=0	x=0.02	x=0.04	x=0.06	x=0.08
$Nd/La-O(1)$	2950	2951	2953	2954	2950
$Nd/La-O(1)^2$	2907	2909	2909	2911	2905
$Nd/La-O(2)^1$	2777	2779	2779	2782	2775
$Nd/La-O(2)^2$	2663	2665	2666	2667	2662
$Nb-O(1)^1$	8700	8702	8704	8707	8697
$Nb-O(1)^2$	7487	7493	7493	7497	7485
$Nb-O(2)$	5946	5951	5951	5954	5945
$AU_{Nd/La-O}$	3766	3768	3769	3771	3764
AU_{Nb-O}	7378	7382	7383	7386	7376
Total	33430	33450	33455	33472	33419

<i>Phase composition</i>	single	Single	single	single	second
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*The AU was the average of the Lattice Energy.

Table.4 Lattice energy calculated by unit cell volumes for $(\text{Nd}_{1-x}\text{La}_x)\text{NbO}_4$ ($0 \leq x \leq 0.08$) ceramics

x value	$V_{\text{cell}}(\text{\AA}^3)$	A(kJ mol ⁻¹ nm)	I	Z	Uv(kJ mol ⁻¹)	Phase composition
0	317.25	121.39	25	4	26022	single
0.02	316.56	121.39	25	4	26040	single
0.04	316.17	121.39	25	4	26051	single
0.06	315.48	121.39	25	4	26070	single
0.08	317.77	121.39	25	4	26007	second

Table.5 The microwave dielectric properties of $(\text{Nd}_{1-x}\text{La}_x)\text{NbO}_4$ ($0 \leq x \leq 0.08$) ceramics

x value	Dielectric constant	Q×f (GHz)	$\tau_f(\text{ppm}/^\circ\text{C})$
0	18.71	31300	-19.65
0.02	20.22	32200	-11.65
0.04	20.75	37400	-5.11
0.06	21.52	46600	0
0.08	20.98	34800	7.67