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Relationship between bond ionicity, lattice energy, coefficient of thermal expansion and microwave dielectric properties of $\text{Nd}(\text{Nb}_{1-x}\text{Sb}_x)\text{O}_4$ ceramics

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Abstract

The crystalline structure refinement, chemical bond ionicity, lattice energy and coefficient of thermal expansion were carried out for $\text{Nd}(\text{Nb}_{1-x}\text{Sb}_x)\text{O}_4$ ceramics with monoclinic fergusonite structure to investigate the correlations between the crystalline structure, phase stability, bond ionicity, lattice energy, coefficient of thermal expansion, and microwave dielectric properties. The bond ionicity, lattice energy, and coefficient of thermal expansion of $\text{Nd}(\text{Nb}_{1-x}\text{Sb}_x)\text{O}_4$ ceramics were calculated using a semiempirical method based on the complex bond theory. The phase structure stability varied with the lattice energy which was resulted by the substitution constant of Sb^{5+} . With the increasing of Sb^{5+} constant, the decrease of Nb/Sb-O bond ionicity was observed, which could be contributed to the electric polarization. The ϵ_r had a close relationship with the Nb/Sb-O bond ionicity. The increase of the $Q \times f$ and $|\tau_f|$ values could attribute to the lattice energy and the coefficient of thermal expansion. The microwave dielectric properties of $\text{Nd}(\text{Nb}_{1-x}\text{Sb}_x)\text{O}_4$ ceramics with monoclinic fergusonite structure were strongly dependent on the chemical bond ionicity, lattice energy and coefficient of thermal expansion.

Keywords: Bond ionicity; Lattice energy; Coefficient of thermal expansion; Phase stability; Microwave dielectric properties;

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1. Introduction

It was well known that the concepts of chemical bond ionicity were very important for explaining many basic properties in diverse area [1-3]. The chemical bond ionicity could be evaluated by P-V-L theory, which was generalized to application for complex crystals by Zhang *et al* [4-5]. We could obtain the lattice energy using the chemical bond ionicity. The lattice energy and the coefficient of thermal expansion played an important role in diverse thermodynamic analysis of the existence and stability of ionic crystals. It 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, lattice energy and coefficient of thermal expansion.

Recently, Kim *et al.* [10] had reported that NdNbO₄ 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, these three parameters were not excellent to apply in microwave devices. In our previous work, we had 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]. Recently, 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, coefficient of thermal expansion and microwave dielectric properties of $\text{Nd}(\text{Nb}_{1-x}\text{Sb}_x)\text{O}_4$ ceramics.

In this paper, for the first time, quantitative calculation was made in bond ionicity of the $\text{Nd}(\text{Nb}_{1-x}\text{Sb}_x)\text{O}_4$ ($0 \leq x \leq 0.10$) ceramics using the generalized P-V-L dielectric theory based on the crystalline structure refinement. The lattice energy was calculated according to the bond ionicity, and the coefficient of thermal expansion had a close relationship with the lattice energy. Phase stability was investigated according to the variation of the lattice energy. The microwave dielectric properties of $\text{Nd}(\text{Nb}_{1-x}\text{Sb}_x)\text{O}_4$ ceramics were really dependent on bond ionicity, lattice energy and coefficient of thermal expansion.

2. Experimental procedure and Theory

2.1 Experimental Section

$\text{Nd}(\text{Nb}_{1-x}\text{Sb}_x)\text{O}_4$ microwave dielectric ceramics were prepared using a conventional solid-state reaction method. The starting materials were the oxides of the respective elements (Nd_2O_3 (99.99%), Nb_2O_5 (99.99%) and Sb_2O_5 (99.99%)) and were wet mixed in distilled water. After it was mixed and ground for 10 h, the slurry was dried and calcined at 1000 °C for 4 h. The calcined 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 1250 °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

2.2.1 Complex chemical bond theory

As we all know, we could deal with many binary crystals especially of the $A^N B^{8-N}$ by using the PV theory [6, 7, and 17]. Then Levine *et al.* [18, 19] successfully dealt with complex crystals such as ABC_2 , ABC_3 and ABC_4 and more complex crystals. However an explicit expression was not given for decomposing the complex multibond crystals into the sum of binary crystals. After considering these ideas in chemical bond representation, Zhang *et al.* [4, 5] succeeded in generalizing P-V-L theory for multibond systems and given an explicit expression about how to decompose the complex crystals into binary crystals. Suppose A denotes cations and B anions, any multibond 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 $N(A^i-B^i)$ represents the nearest coordination contributed by the B^i 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 was the average energy gap for the type bond μ , which was 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:

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

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

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

The correction factor b^μ was 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 was 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.

2.2.2 Lattice energy of a complex crystal

On the basis of generalized P-V-L theory, Zhang et al. reported that the lattice energy can be obtained by the chemical bond [4, 5, and 7]. And the lattice energy U_{cal} of a 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 .

2.2.3 Coefficient of thermal expansion

Based on the lattice energy, the coefficient of thermal expansion α of a complex crystal can be written as:

$$\alpha = \sum_{\mu} F_{mn}^{\mu} \alpha_{mn}^{\mu} \quad (23)$$

where F_{mn}^{μ} is the proportion of μ bond in the total bonds of a supercell.

For any binary crystal A_mB_n type compounds, the coefficient of thermal expansion α_{mn}^{μ} can be calculated as following:

$$\alpha_{mn}^{\mu} = -3.1685 + 0.8376\gamma_{mn} \quad (24)$$

$$\gamma_{mn} = \frac{kZ_A^\mu N_{CA}^\mu}{U_b^\mu \Delta_A} \beta_{mn} \quad (25)$$

$$\beta_{mn} = \frac{m(m+n)}{2n} \quad (26)$$

where k is the Boltzmann constant, Z_A^μ the valence states of cation, N_{CA}^μ is the coordination number of μ type of bond for cation A , and Δ_A is a correction factor ($\Delta_{Nd} = 1.74$, $\Delta_{Nb} = 1.56$).

3. Results and discussion

3.1 Multiphase refinement and Structure analysis

The X-ray diffraction patterns of $\text{Nd}(\text{Nb}_{1-x}\text{Sb}_x)\text{O}_4$ ($0 \leq x \leq 0.10$) ceramics are shown in Fig. 1. To reduce noise, all data have been smoothed by Adaptive smoothing method and had 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 are refined step-by-step for avoiding correlations. A pure single-phase NdNbO_4 (ICDD #32-0680) without any secondary phase is observed in the range of $x=0-0.08$ from the diffraction patterns and it was belong to the monoclinic fergusonite structure with the space group $I2/a$ (no. 15). The lattice parameters from Rietveld refinement are calculated as $a=5.451 \text{ \AA}$, $b=11.294 \text{ \AA}$, $c=5.150 \text{ \AA}$, $\beta=94.47^\circ$ and $V_{unit} = 317.25 \text{ \AA}^3$. With the substitution Sb^{5+} constant increased, the $\text{Nd}_2\text{Sb}_5\text{O}_{10.5}$ peaks (indexed as $\text{Nd}_2\text{Sb}_5\text{O}_{10.5}$, ICDD #34-0942) can be detected when $x=0.10$. The formation of $\text{Nd}_2\text{Sb}_5\text{O}_{10.5}$ phase could attribute to the reaction of the Nd^{3+} with the unsubstituted Sb^{5+} . In the following study, we will carefully discuss the relationship between phase stability and the 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 Sb^{5+} ion constant up to $x=0.08$ and then increased slightly with further increase of Sb^{5+} ion constant. The substitution of

Sb^{5+} (ionic radius, abbr. $r=0.60$ Å, coordination numbers, abbr. CN = 6) ion is smaller than the Nb^{5+} (ionic radius, abbr. $r=0.64$ Å, coordination numbers, abbr. CN = 6) ion. Therefore, the substitution of Nb^{5+} ion by Sb^{5+} would decrease the volume of the unit cell.

A schematic representation of an NdNbO_4 supercell ($1 \times 1 \times 1$) is shown in Fig.2. In the supercell, there contains four NdNbO_4 molecules per primitive cell and we can see that the NdNbO_4 consists of an oxygen octahedron, 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 increase of substitution Sb^{5+} ions, the atomic interactions of NdNbO_4 will be changed, which could result in bond length of the oxygen octahedron. And the bond length of oxygen octahedron has a close connection to the bond ionicity, lattice energy and the coefficient of thermal expansion, which plays an important role in considering the NdNbO_4 system. That is to say, the difference of substitution Sb^{5+} ion has vital effect on the microwave dielectric properties for the NdNbO_4 system.

3.2 Bond Ionicity Calculation of $\text{Nd}(\text{Nb}_{1-x}\text{Sb}_x)\text{O}_4$ 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:

$$\begin{aligned} \text{NdNbO}_4 &= \text{NdNbO}(1)_2 \text{O}(2)_2 \\ &= \text{Nd}_{1/2}\text{O}(1) + \text{Nd}_{1/2}\text{O}(2)_{4/3} + \text{Nb}_{2/3}\text{O}(1) + \text{Nb}_{1/3}\text{O}(2)_{2/3} \end{aligned}$$

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 $Z_{\text{Nd}}=3$ and $Z_{\text{Nb}}=5$, but the effective valence electron numbers of O^{2-} anions in each type bond are different. They are $Z_{\text{O}}=13/2$ in $\text{Nd}_{1/2}\text{O}(1)$ bond, $Z_{\text{O}}=55/8$ in $\text{Nd}_{1/2}\text{O}(2)_{4/3}$ bond, $Z_{\text{O}}=14/3$ in $\text{Nb}_{2/3}\text{O}(1)$ bond and $Z_{\text{O}}=11/2$ in the $\text{Nb}_{1/3}\text{O}(2)_{2/3}$ bond. The difference in O^{2-} anions are owing to charge balance for each sub-formula.

The calculated results of bond ionicity for $\text{Nd}(\text{Nb}_{1-x}\text{Sb}_x)\text{O}_4$ ($0 \leq x \leq 0.10$) ceramics are shown in Table.2. According to the calculated results, although both of the average ionicity of Nd-O bond ($A f_{i(\text{Nd-O})}$) and the Nb/Sb-O bond ($A f_{i(\text{Nb/Sb-O})}$) decreased with increasing the constant of Sb^{5+} ions, the variation of the average bond ionicity for the Nd-O bond ($\Delta A f_{i(\text{Nd-O})}$) is not obvious. According to the calculated results shown in Table.2, we can find that $\Delta A f_{i(\text{Nd-O})} = 0.0026$ and $\Delta A f_{i(\text{Nb/Sb-O})}(\%) = 0.0567$. It is clarified that the substitution of Sb^{5+} has more effect on the B-site bond ionicity, and the bond ionicity of Nb/Sb-O type has dominant effect on the microwave dielectric properties of $\text{Nd}(\text{Nb}_{1-x}\text{Sb}_x)\text{O}_4$ ceramics.

3.3 Lattice Energy and Phase Stability

The lattice energies are calculated by chemical bond method of the $\text{Nd}(\text{Nb}_{1-x}\text{Sb}_x)\text{O}_4$ ($0 \leq x \leq 0.10$) ceramics shown in Table.3. 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 [21-23]. From the calculated results in Table.3, the total lattice energy of $\text{Nd}(\text{Nb}_{1-x}\text{Sb}_x)\text{O}_4$ ($0 \leq x \leq 0.08$) ceramics increased with the Sb^{5+} ion constant increasing, and the $U_{\text{Nd-O}}$ has a smaller value than the $U_{\text{Nb/Sb-O}}$, which is demonstrated that $U_{\text{Nb/Sb-O}}$ has more contributions to the $\text{Nd}(\text{Nb}_{1-x}\text{Sb}_x)\text{O}_4$ ceramics. Based on the results from Fig.1, and combined with the analysis of the lattice energies in Table.3, the $U_{\text{Nb/Sb-O}}$ has a decreased trend when the formation of second phase is observed at $x=0.10$. It is suggested that the phase change of the NdNbO_4 crystals could be predicted by the variation of $U_{\text{Nb/Sb-O}}$.

3.4 Coefficient of Thermal Expansion Calculation of $\text{Nd}(\text{Nb}_{1-x}\text{Sb}_x)\text{O}_4$ System

Table.4 shows the calculated results of coefficient of thermal expansion for $\text{Nd}(\text{Nb}_{1-x}\text{Sb}_x)\text{O}_4$ ($0 \leq x \leq 0.10$) ceramics. According to the calculated results in Table.4, with the increasing of the Sb^{5+} ion

substitution, the coefficient of thermal expansion α of $\text{Nd}(\text{Nb}_{1-x}\text{Sb}_x)\text{O}_4$ ceramics decreased in the range of $x=0-0.08$. There has an increasing trend in α when the second phase is formed at $x=0.10$. The variation of α can attribute to the formation of second phase, and the phase change has a close relationship with microwave dielectric properties. It is suggested that the α is also key factor on the microwave dielectric properties of $\text{Nd}(\text{Nb}_{1-x}\text{Sb}_x)\text{O}_4$ ceramics.

3.5 Microwave Dielectric Properties

The microwave dielectric properties of $\text{Nd}(\text{Nb}_{1-x}\text{Sb}_x)\text{O}_4$ ($0 \leq x \leq 0.10$) ceramics are illustrated in Table.5. The microwave dielectric properties of these compounds are varied regularly with Nb^{5+} ion substitution for Sb^{5+} ionic. Combined with the chemical bond ionicity, the lattice energy and the coefficient of thermal expansion in the compounds, the Af_i (Nb/Sb-O), the $U_{\text{Nb/Sb-O}}$ and the α play an important role in $\text{Nd}(\text{Nb}_{1-x}\text{Sb}_x)\text{O}_4$ ceramics with monoclinic fergusonite structure.

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

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

where n is the refractive index. It is indicated that the dielectric constant decreased with the bond ionicity decreasing. Fig.4 shows the variation of the dielectric and the average of B-site bond ionicity I_b as a function of the x values of $\text{Nd}(\text{Nb}_{1-x}\text{Sb}_x)\text{O}_4$ ceramics. The dielectric constant keeps the same change with the I_b in the range of $x=0-0.08$ from Fig.4. When $x>0.08$, although the dielectric constant is still decreasing with the increase of x values, the I_b has an improper change. This abnormal change of the I_b could attribute to the formation of the second phase.

The $Q \times f$ values and the B-site lattice energy U_{bc} for $\text{Nd}(\text{Nb}_{1-x}\text{Sb}_x)\text{O}_4$ ($0 \leq x \leq 0.10$) 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, was 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 $Q \times f$ values are strongly dependent on the lattice energy. As shown in Fig.5, the $Q \times f$ values have a same variation trend with the U_{bc} . The results of variation of the $Q \times f$ values are suggested that the B-site lattice energy plays a non-negligible role in NdNbO₄ system. It indicates 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, a small τ_f value indicates that the system will be more stable. It is well known that the τ_f value is a function of the temperature coefficient of the dielectric constant (τ_ϵ) and the linear thermal expansion coefficient (α_L), as shown in Eq.(27) [27]:

$$\tau_f = -\frac{\tau_\epsilon}{2} - \alpha_L \quad (27)$$

In this paper, the τ_f value has a close relationship with the coefficient of thermal expansion α . With the decreasing of α , τ_f value decreased in the range $x=0-0.08$. The reason why α suddenly increase when $x=0.10$ could attribute to the formation of the second phase.

4. Conclusions

The Nd(Nb_{1-x}Sb_x)O₄ ($0 \leq x \leq 0.10$) ceramics were prepared by conventional oxide mixed method. The single phase with monoclinic fergusonite structure was obtained in region of $0 \leq x \leq 0.08$. With a further substitution with Sb⁵⁺ ions, the second phase could be detected. In the Nd(Nb_{1-x}Sb_x)O₄ system, the lattice energy increased when Nb⁵⁺ ion was substituted by Sb⁵⁺ ion in the range of $x=0$ to $x=0.08$, the lattice energy had a decreasing trend when the second phase was formed, which indicated that the

phase change could be predicted by the variation of the lattice energy. And the dielectric constant ϵ_r was dependent on the average of B-site bond ionicity I_b . The $Q \times f$ values had a same variation trend with the lattice energy of the B-site bond U_{bc} which was considered as an intrinsic factor. And in the finally, τ_f value had really a close relationship with the coefficient of thermal expansion α for the $\text{Nd}(\text{Nb}_{1-x}\text{Sb}_x)\text{O}_4$ system.

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Figure captions

Fig.1 The X-ray diffraction patterns of $\text{Nd}(\text{Nb}_{1-x}\text{Sb}_x)\text{O}_4$ ($0 \leq x \leq 0.1$) ceramics sintered at 1250 °C for 4h.

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 value and the average of B-site bond ionicity I_b for $\text{Nd}(\text{Nb}_{1-x}\text{Sb}_x)\text{O}_4$ ($0 \leq x \leq 0.1$) ceramics.

Fig.5 The $Q \times f$ value and the B-site lattice energy U_{bc} for $\text{Nd}(\text{Nb}_{1-x}\text{Sb}_x)\text{O}_4$ ($0 \leq x \leq 0.1$) ceramics.

Fig.6 The τ_f value and coefficient of thermal expansion α for $\text{Nd}(\text{Nb}_{1-x}\text{Sb}_x)\text{O}_4$ ($0 \leq x \leq 0.1$) ceramics.

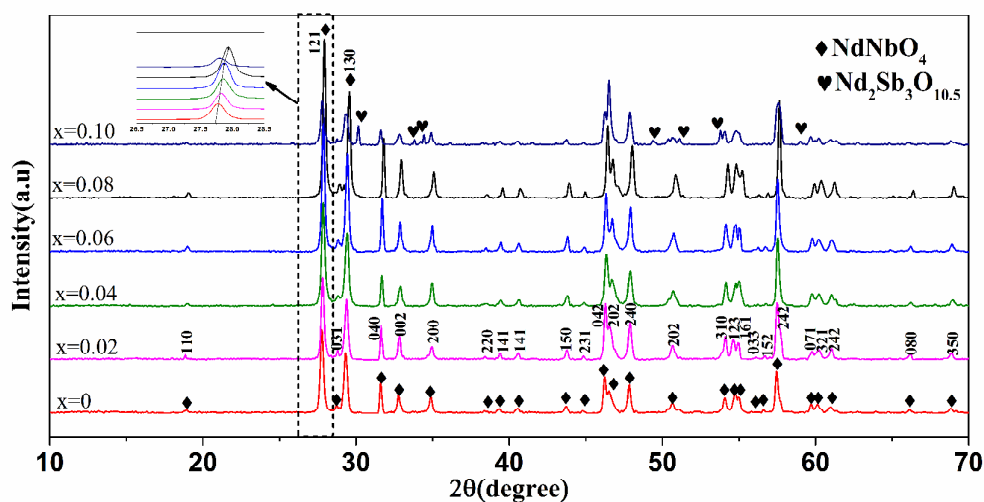


Fig.1

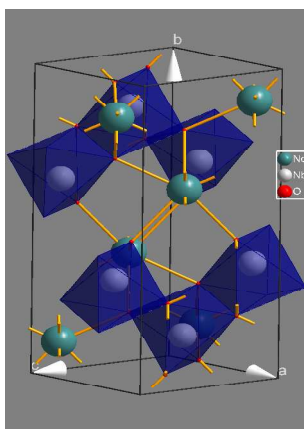


Fig.2

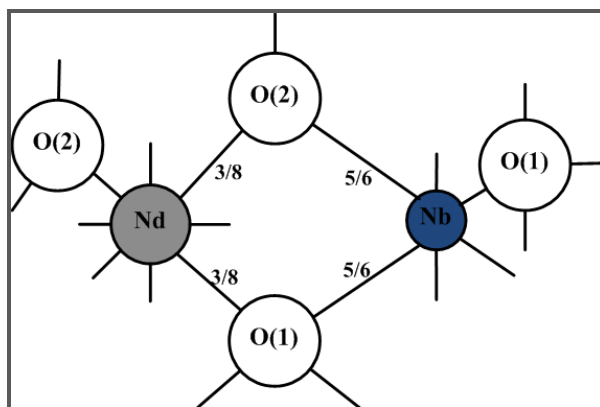


Fig.3

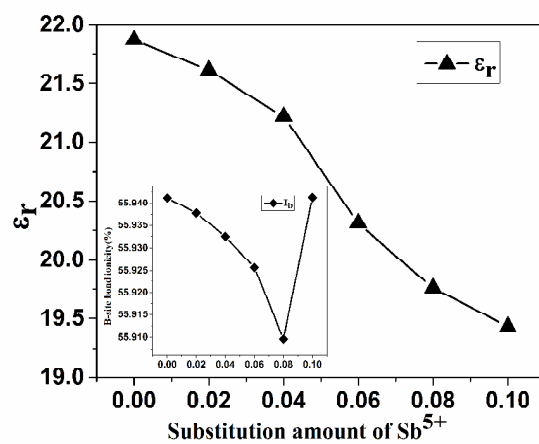


Fig.4

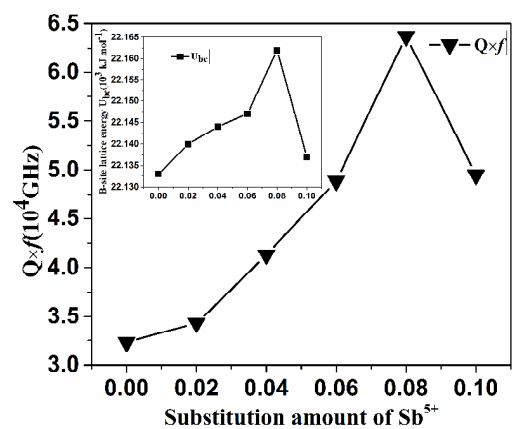


Fig.5

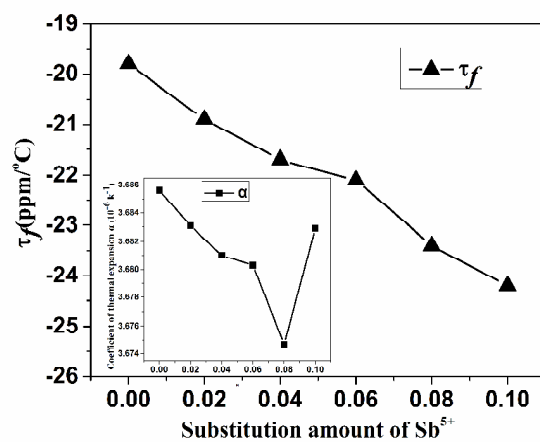


Fig. 6

Table.1 Crystallographic data from Rietveld refinement for Nd(Nb_{1-x}Sb_x)O₄ (0≤x≤0.10) ceramics

<i>x</i> value	<i>x=0</i>	<i>x=0.02</i>	<i>x=0.04</i>	<i>x=0.06</i>	<i>x=0.08</i>	<i>x=0.10</i>
<i>a</i>	5.150	5.148	5.148	5.144	5.143	5.153
<i>b</i>	11.294	11.288	11.280	11.282	11.272	11.242
<i>c</i>	5.471	5.470	5.468	5.466	5.455	5.485
β	94.47	94.52	94.49	94.50	94.46	94.41
$V_{cell}(\text{\AA}^3)$	317.25	316.88	316.56	316.24	315.28	316.81
R_p	0.0865	0.0759	0.0929	0.1191	0.0727	0.0720
R_{wp}	0.1265	0.1278	0.1230	0.1272	0.1183	0.1120
<i>Nd-O(1)¹(\AA) × 2</i>	2.4352	2.4352	2.4340	2.4332	2.4297	2.4354
<i>Nd-O(1)²(\AA) × 2</i>	2.4809	2.4793	2.4785	2.4779	2.4761	2.4769
<i>Nd-O(2)¹(\AA) × 2</i>	2.3674	2.3656	2.3657	2.3643	2.3629	2.3697
<i>Nd-O(2)²(\AA) × 2</i>	2.4944	2.4938	2.4923	2.4921	2.4888	2.4899
<i>Nb/Sb-O(1)¹(\AA) × 2</i>	1.9126	1.9126	1.9117	1.9110	1.9086	1.9126
<i>Nb/Sb-O(1)²(\AA) × 2</i>	2.4857	2.4841	2.4835	2.4828	2.4804	2.4850
<i>Nb/Sb-O(2)(\AA) × 2</i>	1.8794	1.8782	1.8777	1.8772	1.8751	1.8790

Table.2 Bond ionicity for Nd(Nb_{1-x}Sb_x)O₄ (0≤x≤0.10) ceramics

Bond type	Bond Ionicity f_i (%)					
	<i>x=0</i>	<i>x=0.02</i>	<i>x=0.04</i>	<i>x=0.06</i>	<i>x=0.08</i>	<i>x=0.10</i>
<i>Nd-O(1)¹</i>	97.3292	97.3295	97.3288	97.3281	97.3263	97.3296
<i>Nd-O(1)²</i>	97.3542	97.3536	97.3532	97.3526	97.3519	97.3523

$Nd-O(2)^1$	96.7617	96.7610	96.7610	96.7599	96.7579	96.7634
$Nd-O(2)^2$	96.8289	96.8289	96.8282	96.8278	96.8265	96.8271
$Nb/Sb-O(1)^1$	44.8442	44.8465	44.8372	44.8279	44.8044	44.8465
$Nb/Sb-O(1)^2$	49.1511	49.1456	49.1426	49.1367	49.1264	49.1502
$Nb/Sb-O(2)$	73.8284	73.8214	73.8177	73.8124	73.7981	73.8273
$Af_{i(Nd-O)}$	97.0685	97.0683	97.0678	97.0671	97.0660	97.0681
$Af_{i(Nb/Sb-O)}$	55.9412	55.9378	55.9325	55.9257	55.9096	55.9413
$\Delta Af_{i(Nd-O)}(\%)$	0.0026	-	-	-	-	-
$\Delta Af_{i(Nb/Sb-O)}(\%)$	0.0567	-	-	-	-	-

*The Af_i was the average of the bond ionicity and Δ was the variation in Af_i , $\Delta Af_i = (Af_{i\max} - Af_{i\min}) / Af_{i\min}$.

Table.3 Lattice energy for $Nd(Nb_{1-x}Sb_x)O_4$ ($0 \leq x \leq 0.10$) ceramics

Bond type	Lattice Energy U_c (kJ/mol)					
	$x=0$	$x=0.02$	$x=0.04$	$x=0.06$	$x=0.08$	$x=0.10$
$Nd-O(1)^1$	2950	2950	2952	2952	2956	2950
$Nd-O(1)^2$	2907	2908	2909	2909	2911	2910
$Nd-O(2)^2$	2777	2779	2779	2780	2781	2775
$Nd-O(2)^2$	2663	2664	2665	2665	2668	2667
$Nb/Sb-O(1)^1$	8700	8700	8702	8703	8709	8700
$Nb/Sb-O(1)^2$	7487	7491	7492	7493	7498	7489
$Nb/Sb-O(2)$	5946	5949	5950	5951	5955	5948
U_{Nd-O}	11287	11301	11305	11306	11316	11302

$U_{Nb/Sb-O}$	22133	22140	22144	22147	22162	22137
Total	33430	33441	33449	33453	33478	33439

Table.4 The coefficient of thermal expansion for $Nd(Nb_{1-x}Sb_x)O_4$ ($0 \leq x \leq 0.10$) ceramics

Bond type	Coefficient of thermal expansion α ($10^{-6}K^{-1}$)					
	$x=0$	$x=0.02$	$x=0.04$	$x=0.06$	$x=0.08$	$x=0.10$
$Nd-O(1)^1$	4.9653	4.9653	4.9598	4.9598	4.9488	4.9653
$Nd-O(1)^2$	5.0856	5.0828	5.0799	5.0799	5.0742	5.0771
$Nd-O(2)^1$	5.4720	5.4658	5.4658	5.4627	5.4596	5.4782
$Nd-O(2)^2$	5.8419	5.8385	5.8351	5.8351	5.8250	5.8284
$Nb/Sb-O(1)^1$	0.6768	0.6768	0.6759	0.6755	0.6728	0.6768
$Nb/Sb-O(1)^2$	1.2998	1.2974	1.2968	1.2962	1.2932	1.2986
$Nb/Sb-O(2)$	2.4578	2.4550	2.4540	2.4531	2.4493	2.4559
α	3.6856	3.6831	3.6810	3.6803	3.6747	3.6829

Table.5 The microwave dielectric properties of $Nd(Nb_{1-x}Sb_x)O_4$ ($0 \leq x \leq 0.10$) ceramics

x value	ϵ_r	$Q \times f$ (GHz)	τ_f (ppm/ $^\circ C$)
0	22.88	35300	-18.8
0.02	22.49	38300	-19.9
0.04	21.81	44200	-20.7
0.06	21.37	55100	-22.1
0.08	20.06	73200	-23.1
0.10	19.93	58900	-25.2

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Bond ionicity, lattice energy, and coefficient of thermal expansion were calculated using a semiempirical method

