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Relationship between bond ionicity, lattice energy, coefficient of thermal expansion and microwave dielectric properties of Nd(Nb$_{1-x}$Sb$_x$)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 Nd(Nb$_{1-x}$Sb$_x$)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 Nd(Nb$_{1-x}$Sb$_x$)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 $\varepsilon_r$ had a close relationship with the Nb/Sb-O bond ionicity. The increase of the $Q\times f$ and $|\tau|$ values could attribute to the lattice energy and the coefficient of thermal expansion. The microwave dielectric properties of Nd(Nb$_{1-x}$Sb$_x$)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 NdNbO$_4$ possessed $\varepsilon_r$ of 19.6, $Q\times f$ of 33, 000 GHz and $\tau_f$ 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 NdNbO$_4$ ceramics doping with CaF$_2$. NdNbO$_4$ ceramics with 2.0 wt.% CaF$_2$ sintered at 1225°C for 4 h showed excellent microwave dielectric properties, $Q\times f$ ~75, 000 GHz and $\tau_f$ ~ -19 ppm/°C[11]. And we discovered that the microwave properties of NdNbO$_4$ ceramics could be optimized using bivalent ions substituted to Nd$^{3+}$ ionic owing to the formation of solid solutions, the phase composition would be changed when Nd$^{3+}$ ionic was substituted by other bivalent ions (Sr$^{2+}$, Ca$^{2+}$, Mn$^{2+}$, Co$^{2+}$)[12,13]. Recently, we investigated the correlation of crystal structure and microwave dielectric properties Nd$_{1.02}$(Nb$_{1-x}$Ta$_x$)$_{0.988}$O$_4$ ceramics[14], and discovered that the NdNbO$_4$ 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
Nd(Nb\textsubscript{1-x}Sb\textsubscript{x})O\textsubscript{4} ceramics.

In this paper, for the first time, quantitative calculation was made in bond ionicity of the
Nd(Nb\textsubscript{1-x}Sb\textsubscript{x})O\textsubscript{4} (0≤x≤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
Nd(Nb\textsubscript{1-x}Sb\textsubscript{x})O\textsubscript{4} ceramics were really dependent on bond ionicity, lattice energy and coefficient of
thermal expansion.

2. Experimental procedure and Theory

2.1 Experimental Section

Nd(Nb\textsubscript{1-x}Sb\textsubscript{x})O\textsubscript{4} microwave dielectric ceramics were prepared using a conventional solid-state
reaction method. The starting materials were the oxides of the respective elements (Nd\textsubscript{2}O\textsubscript{3} (99.99%),
Nb\textsubscript{2}O\textsubscript{5} (99.99%) and Sb\textsubscript{2}O\textsubscript{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 Cu Kα 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\textsubscript{f}) were measured in the temperature
range from 25 °C to 85 °C and calculated by noting the change in resonant frequency ($\Delta f$)

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)}$$  \hspace{1cm} (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 $A^X B^{8-N}$ 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:

$$A_{a_1}^i A_{a_2}^j \ldots A_{a_l}^i B_{b_1}^i B_{b_2}^j \ldots B_{b_j}^j$$

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:

$$A_{a_1}^i A_{a_2}^j \ldots A_{a_l}^i B_{b_1}^i B_{b_2}^j \ldots B_{b_j}^j = \sum g A_{a_{i_g}}^i B_{b_{j_g}}^j$$  \hspace{1cm} (2)

$$m_i = \frac{N (B^i - A^i) a_i}{N_{CAI}}$$  \hspace{1cm} (3)
where $N_{CA_i}$ and $N_{CB_j}$ represent the nearest total coordination numbers of the $A_i$ and $B_j$ ions in the crystal; $N(B_j-A_i)$ 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 $f^\mu_i$ and bond covalency $f^\mu_c$ of an individual bond $\mu$ can be defined as follows:

$$f^\mu_i = \left(\frac{C^\mu}{E^\mu_d}\right)^2$$

$$f^\mu_c = \left(\frac{E^\mu_d}{E^\mu_h}\right)^2$$

where $E^\mu_d$ was the average energy gap for the type bond $\mu$, which was composed of homopolar $E^\mu_h$ and heteropolar $C^\mu$ parts as follows:

$$E^\mu_d = (E^\mu_h)^2 + (C^\mu)^2$$

where

$$(E^\mu_h)^2 = \frac{39.74}{(d^\mu)^{3.48}}$$

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

$$C^\mu = 14.4b^\mu \exp(-k^\mu r^\mu_\text{ref}) \left[ \left( \frac{(Z^\mu_A)^2}{r^\mu_\text{ref}} - \frac{n}{m} \frac{(Z^\mu_B)^2}{r^\mu_\text{ref}} \right) \right] \text{ (if n>m)}$$

$$n_j = \frac{N(B_j-A_i)b_j}{N_{CB_j}}$$
\[ C^\mu = 14.4 b^\mu \exp(-k^\mu r^\mu) \left[ \left( \frac{m}{n} \right) \frac{(Z^\mu_A)^*}{r^\mu_A} - \frac{(Z^\mu_B)^*}{r^\mu_B} \right] \text{ (if } n < m) \]  

(10)

where \( b^\mu \) was a correction factor that is proportional to the square of the average coordination number \( N^\mu_c \), \( (Z^\mu_A)^* \) was the effective number of valence electrons on the cation A and \( (Z^\mu_B)^* \) was the effective number of valence electrons on the anion B.

The correction factor \( b^\mu \) was defined as:

\[ b^\mu = \beta (N^\mu_c)^2 \]  

(11)

\[ N^\mu_c = \frac{m}{m+n} N^\mu_{ca} + \frac{n}{m+n} N^\mu_{cb} \]  

(12)

\( \beta \) was 0.089[20], \( N^\mu_{ca} \) is the coordination number of \( \mu \) type of bond for cation A, and \( N^\mu_{cb} \) is the coordination number of bond for anion B.

\( \exp(-k^\mu r^\mu) \) is the Thomas-Fermi screening factor,

\[ k^\mu_s = \left( \frac{4 k^\mu_F}{\pi a_B} \right)^{1/2} \]  

(13)

\[ k^\mu_F = \left[ 3 \pi^2 (N^\mu_c)^* \right]^{1/3} \]  

(14)

\[ r^\mu_o = d^\mu / 2 \]  

(15)

where \( a_B \) is the Bohr radius and has the value 0.5292 Å and \( r^\mu_o \) is the average radius of A and B in angstroms. \( (N^\mu_c)^* \) is the number of \( \mu \) valence electrons of bond per cubic centimeter.

\[ (n^\mu_c)^* = \frac{(n^\mu)^*}{v^\mu_b} \]  

(16)

\[ (n^\mu)^* = (Z^\mu_A)^* \left( \frac{N^\mu_{CA}}{N^\mu_c} \right)^* + (Z^\mu_B)^* \left( \frac{N^\mu_{CB}}{N^\mu_c} \right)^* \]  

(17)

where \( (n^\mu)^* \) is the number of the effective valence electrons per \( \mu \) bond, \( v^\mu_b \) is the bond volume.

\[ v^\mu_b = \sum \frac{(d^\mu)^3 N^\mu_b}{v^\mu_b} \]  

(18)
$N_b^γ$ 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:

$$U_{cal} = \sum_{b} U_{b}^\mu$$

(19)

$$U_{b}^\mu = U_{bc}^\mu + U_{bi}^\mu$$

(20)

$$U_{bc}^\mu = 2100m \frac{(Z^\mu)^{1.64}}{(d^\mu)^{0.75}} f_c^\mu$$

(21)

$$U_{bi}^\mu = 1270 \frac{(m+n)Z_v^\mu Z_-^\mu}{d^\mu} \frac{(1 - 0.4/d^\mu)}{f_i^\mu}$$

(22)

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

### 2.2.3 Coefficient of thermal expansion

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

$$\alpha = \sum_{\mu} F_{mn}^\mu \alpha_{mn}^\mu$$

(23)

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

For any binary crystal $A_mB_n$ type compounds, the coefficient of thermal expansion $\alpha_{mn}^\mu$ can be calculated as following:

$$\alpha_{mn}^\mu = -3.1685 + 0.8376\gamma_{mn}$$

(24)
\[
\gamma_{mn} = \frac{kZ_A^\mu N_{c_A}^\mu}{U_b^\mu \Delta_A} \beta_{mn} \\
\beta_{mn} = \frac{m(m+n)}{2n}
\]

where \( k \) is the Boltzmann constant, \( Z_A^\mu \) the valence states of cation, \( N_{c_A}^\mu \) is the coordination number of \( \mu \) type of bond for cation \( A \), and \( \Delta_A \) 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 Nd(Nb_{1-x}Sb_x)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 \( a=5.451 \, \text{Å}, b=11.294 \, \text{Å}, c=5.150 \, \text{Å}, \beta=94.47^\circ \) and \( V_{\text{unit}}=317.25 \, \text{Å}^3 \). With the substitution Sb^{5+} constant increased, the Nd_2Sb_5O_{10.5} peaks (indexed as Nd_2Sb_5O_{10.5}, ICDD #34-0942) can be detected when \( x=0.10 \). The formation of Nd_2Sb_5O_{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. \(r=0.60\ \text{Å}\), coordination numbers, abbr. CN = 6)) ion is smaller than the Nb\(^{5+}\) ((ionic radius, abbr. \(r=0.64\ \text{Å}\), 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 (1×1×1) 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 Nd(Nb\(_{1-x}\)Sb\(_x\))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:

\[
\text{NdNbO}_4 = \text{NdNbO}(1)\_2 + \text{O}(2)\_2
\]

\[
= \text{Nd}_{1/2}\_O(1) + \text{Nd}_{1/2}\_O(2)_{4/3} + \text{Nb}_{2/3}\_O(1) + \text{Nd}_{1/3}\_O(2)_{2/3}
\]

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 Nd\(_{1/2}\_O(1)\) bond, \(Z_{\text{O}}=55/8\) in Nd\(_{1/2}\_O(2)_{4/3}\) bond, \(Z_{\text{O}}=14/3\) in Nb\(_{2/3}\_O(1)\) bond and \(Z_{\text{O}}=11/2\) 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.
The calculated results of bond ionicity for Nd(Nb\textsubscript{1-x}Sb\textsubscript{x})O\textsubscript{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 \(A f_{i(Nd-O)}\) and the Nb/Sh-O bond \(A f_{i(Nb/Sh-O)}\) decreased with increasing the constant of Sb\textsuperscript{5+} ions, the variation of the average bond ionicity for the Nd-O bond \(\Delta A f_{i(Nd-O)}\) is not obvious. According to the calculated results shown in Table 2, we can find that \(\Delta A f_{i(Nd-O)} = 0.0026\) and \(\Delta A f_{i(Nb/Sh-O)}(\%) = 0.0567\). It is clarified that the substitution of Sb\textsuperscript{5+} has more effect on the B-site bond ionicity, and the bond ionicity of Nb/Sh-O type has dominant effect on the microwave dielectric properties of Nd(Nb\textsubscript{1-x}Sb\textsubscript{x})O\textsubscript{4} ceramics.

### 3.3 Lattice Energy and Phase Stability

The lattice energies are calculated by chemical bond method of the Nd(Nb\textsubscript{1-x}Sb\textsubscript{x})O\textsubscript{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 Nd(Nb\textsubscript{1-x}Sb\textsubscript{x})O\textsubscript{4} \((0\leq x \leq 0.08)\) ceramics increased with the Sb\textsuperscript{5+} ion constant increasing, and the \(U_{Nd-O}\) has a smaller value than the \(U_{Nb/Sh-O}\) which is demonstrated that \(U_{Nb/Sh-O}\) has more contributions to the Nd(Nb\textsubscript{1-x}Sb\textsubscript{x})O\textsubscript{4} ceramics. Based on the results from Fig 1, and combined with the analysis of the lattice energies in Table 3, the \(U_{Nb/Sh-O}\) 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\textsubscript{4} crystals could be predicted by the variation of \(U_{Nb/Sh-O}\).

### 3.4 Coefficient of Thermal Expansion Calculation of Nd(Nb\textsubscript{1-x}Sb\textsubscript{x})O\textsubscript{4} System

Table 4 shows the calculated results of coefficient of thermal expansion for Nd(Nb\textsubscript{1-x}Sb\textsubscript{x})O\textsubscript{4} \((0\leq x \leq 0.10)\) ceramics. According to the calculated results in Table 4, with the increasing of the Sb\textsuperscript{5+} ion
substitution, the coefficient of thermal expansion $\alpha$ of Nd(Nb$_{1-y}$Sb$_y$)O$_4$ ceramics decreased in the range of $x=0-0.08$. There has an increasing trend in $\alpha$ when the second phase is formed at $x=0.10$. The variation of $\alpha$ 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 $\alpha$ is also key factor on the microwave dielectric properties of Nd(Nb$_{1-y}$Sb$_y$)O$_4$ ceramics.

3.5 Microwave Dielectric Properties

The microwave dielectric properties of Nd(Nb$_{1-y}$Sb$_y$)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 $A_{fi}$ (Nb:Sb-O), the $U_{Nb:Sb-O}$ and the $\alpha$ play an important role in Nd(Nb$_{1-y}$Sb$_y$)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:

$$\varepsilon \approx \frac{n^2 - 1}{1 - f_i} + 1$$

(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 Nd(Nb$_{1-y}$Sb$_y$)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 Nd(Nb$_{1-y}$Sb$_y$)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 NdNbO\(_4\) 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 \( \tau_f \) is the relations between resonant frequency and the temperature, a small \( \tau_f \) value indicates that the system will be more stable. It is well known that the \( \tau_f \) value is a function of the temperature coefficient of the dielectric constant (\( \tau_\varepsilon \)) and the linear thermal expansion coefficient (\( \alpha_L \)), as shown in Eq.(27) [27]:

\[
\tau_f = -\frac{\tau_\varepsilon}{2} - \alpha_L
\]  

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

4. Conclusions

The Nd(Nb\(_{1-x}\)Sb\(_x\))O\(_4\) (0≤\(x\)≤0.10) ceramics were prepared by conventional oxide mixed method. The single phase with monoclinic fergusonite structure was obtained in region of 0≤\(x\)≤0.08. With a further substitution with Sb\(^{5+}\) ions, the second phase could be detected. In the Nd(Nb\(_{1-x}\)Sb\(_x\))O\(_4\) system, the lattice energy increased when Nb\(^{5+}\) ion was substituted by Sb\(^{3+}\) 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 \( \varepsilon_r \) was
dependent on the average of B-site bond ionicity \( I_b \). The Q×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, \( \tau_f \)
value had really a close relationship with the coefficient of thermal expansion \( \alpha \) for the \( \text{Nd(Nb}_{1-x}\text{Sb}_x\text{)}\text{O}_4 \)
system.

References


Figure captions

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

Fig. 2 The crystal structure patterns (1 × 1 × 1) supercell of monoclinic fergusonite structured Nd\(\text{NbO}_4\).

Fig. 3 The coordination number and charge distribution of ions in Nd\(\text{NbO}_4\) ceramics.

Fig. 4 The ε, value and the average of B-site bond ionicity \(I_b\) for Nd\((\text{Nb}_{1-x}\text{Sb})\text{O}_4\) (0≤x≤0.1) ceramics.

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

Fig. 6 The τ, value and coefficient of thermal expansion α for Nd\((\text{Nb}_{1-x}\text{Sb})\text{O}_4\) (0≤x≤0.1) ceramics.
Fig. 3

Fig. 4

Fig. 5
Fig. 6
Table 1: Crystallographic data from Rietveld refinement for Nd(Nb$_{1-x}$Sb$_x$)$_4$O$_4$ (0≤x≤0.10) ceramics

<table>
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<th>x value</th>
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<td>5.466</td>
<td>5.455</td>
<td>5.485</td>
</tr>
<tr>
<td>β</td>
<td>94.47</td>
<td>94.52</td>
<td>94.49</td>
<td>94.50</td>
<td>94.46</td>
<td>94.41</td>
</tr>
<tr>
<td>V$_{cell}$ (Å$^3$)</td>
<td>317.25</td>
<td>316.88</td>
<td>316.56</td>
<td>316.24</td>
<td>315.28</td>
<td>316.81</td>
</tr>
<tr>
<td>R$_p$</td>
<td>0.0865</td>
<td>0.0759</td>
<td>0.0929</td>
<td>0.1191</td>
<td>0.0727</td>
<td>0.0720</td>
</tr>
<tr>
<td>R$_wp$</td>
<td>0.1265</td>
<td>0.1278</td>
<td>0.1230</td>
<td>0.1272</td>
<td>0.1183</td>
<td>0.1120</td>
</tr>
<tr>
<td>Nd-O(1) (Å) × 2</td>
<td>2.4352</td>
<td>2.4352</td>
<td>2.4340</td>
<td>2.4332</td>
<td>2.4297</td>
<td>2.4354</td>
</tr>
<tr>
<td>Nd-O(2) (Å) × 2</td>
<td>2.4809</td>
<td>2.4793</td>
<td>2.4785</td>
<td>2.4779</td>
<td>2.4761</td>
<td>2.4769</td>
</tr>
<tr>
<td>Nb/Sb-O(1) (Å) × 2</td>
<td>2.3674</td>
<td>2.3656</td>
<td>2.3657</td>
<td>2.3643</td>
<td>2.3629</td>
<td>2.3697</td>
</tr>
<tr>
<td>Nb/Sb-O(2) (Å) × 2</td>
<td>2.4944</td>
<td>2.4938</td>
<td>2.4923</td>
<td>2.4921</td>
<td>2.4888</td>
<td>2.4899</td>
</tr>
</tbody>
</table>

Table 2: Bond ionicity for Nd(Nb$_{1-x}$Sb$_x$)$_4$O$_4$ (0≤x≤0.10) ceramics

<table>
<thead>
<tr>
<th>Bond type</th>
<th>Bond Ionicity $f_i$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x=0</td>
</tr>
<tr>
<td>Nd-O(1)$^1$</td>
<td>97.3292</td>
</tr>
<tr>
<td>Nd-O(1)$^2$</td>
<td>97.3542</td>
</tr>
<tr>
<td>Bond type</td>
<td>Lattice Energy $U_c$(kJ/mol)</td>
</tr>
<tr>
<td>---------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td></td>
<td>$x=0$</td>
</tr>
<tr>
<td>$Nd-O(1)^1$</td>
<td>2950</td>
</tr>
<tr>
<td>$Nd-O(1)^2$</td>
<td>2907</td>
</tr>
<tr>
<td>$Nd-O(2)^2$</td>
<td>2777</td>
</tr>
<tr>
<td>$Nd-O(2)^2$</td>
<td>2663</td>
</tr>
<tr>
<td>$Nb/Sb-O(1)^1$</td>
<td>8700</td>
</tr>
<tr>
<td>$Nb/Sb-O(1)^2$</td>
<td>7487</td>
</tr>
<tr>
<td>$Nb/Sb-O(2)$</td>
<td>5946</td>
</tr>
<tr>
<td>$U_{Nd-O}$</td>
<td>11287</td>
</tr>
</tbody>
</table>

*The $A_f$ was the average of the bond iconicity and $\Delta$ was the variation in $A_f$, $\Delta A_f = (A_{f_{\text{max}}}-A_{f_{\text{min}}})/A_{f_{\text{min}}}$.*

Table 3 Lattice energy for Nd(Nb$_{1-x}$Sb$_x$)$_2$O$_4$ (0 ≤ x ≤ 0.10) ceramics
<table>
<thead>
<tr>
<th>Bond type</th>
<th>Coefficient of thermal expansion $\alpha$ ($10^{-6}K^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x=0$</td>
</tr>
<tr>
<td>Nd-O(1)$^1$</td>
<td>4.9653</td>
</tr>
<tr>
<td>Nd-O(1)$^2$</td>
<td>5.0856</td>
</tr>
<tr>
<td>Nd-O(2)$^1$</td>
<td>5.4720</td>
</tr>
<tr>
<td>Nd-O(2)$^2$</td>
<td>5.8419</td>
</tr>
<tr>
<td>Nb/Sb-O(1)$^1$</td>
<td>0.6768</td>
</tr>
<tr>
<td>Nb/Sb-O(1)$^2$</td>
<td>1.2998</td>
</tr>
<tr>
<td>Nb/Sb-O(2)</td>
<td>2.4578</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>3.6856</td>
</tr>
</tbody>
</table>

Table 4: The coefficient of thermal expansion for Nd(Nb$_{1-x}$Sb$_x$)O$_4$ (0 ≤ x ≤ 0.10) ceramics

<table>
<thead>
<tr>
<th>$x$ value</th>
<th>$\varepsilon_r$</th>
<th>$Q\times f$ (GHz)</th>
<th>$\tau_f$ (ppm/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>22.88</td>
<td>35300</td>
<td>-18.8</td>
</tr>
<tr>
<td>0.02</td>
<td>22.49</td>
<td>38300</td>
<td>-19.9</td>
</tr>
<tr>
<td>0.04</td>
<td>21.81</td>
<td>44200</td>
<td>-20.7</td>
</tr>
<tr>
<td>0.06</td>
<td>21.37</td>
<td>55100</td>
<td>-22.1</td>
</tr>
<tr>
<td>0.08</td>
<td>20.06</td>
<td>73200</td>
<td>-23.1</td>
</tr>
<tr>
<td>0.10</td>
<td>19.93</td>
<td>58900</td>
<td>-25.2</td>
</tr>
</tbody>
</table>

Table 5: The microwave dielectric properties of Nd(Nb$_{1-x}$Sb$_x$)O$_4$ (0 ≤ x ≤ 0.10) ceramics
A table of contents entry

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