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**Structure-property relations of low sintering
temperature scheelite-structured
(1-x)BiVO₄-xLaNbO₄ microwave dielectric ceramics**

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Abstract

A series of the $(1-x)\text{BiVO}_4-x\text{LaNbO}_4$ ($0.0 \leq x \leq 1.0$) ceramics were prepared via a solid state reaction method. A scheelite-structured solid solution was formed for $x \leq 0.5$ but for $x > 0.5$, tetragonal scheelite, monoclinic LaNbO_4 -type and $\text{La}_{1/3}\text{NbO}_3$ phases co-existed. As x increased from 0 to 0.1, the room temperature crystal structure gradually changed from monoclinic to tetragonal scheelite, associated with a decrease in the ferroelastic phase transition temperature from 255 °C (BiVO_4) to room temperature or even below. High sintering temperatures were also found to accelerate this phase transition in compositions with $x \leq 0.08$. Temperature independent high quality factor $Q_f > 10,000$ GHz in wide temperature range 25 - 140 °C and high microwave permittivity $\epsilon_r \sim 76.3 \pm 0.5$ were obtained for $x = 0.06$ ceramic sintered at 800 °C. However, small changes in composition resulted in a change in sign and magnitude of the temperature coefficient of resonant frequency (TCF) due to the proximity of the ferroelastic transition to room temperature. If TCF can be controlled and tuned through zero, the $(1-x)\text{BiVO}_4-x\text{LaNbO}_4$ ($0.0 \leq x \leq 1.0$) is a strong candidate for microwave device applications.

I. Introduction

Bismuth vanadate (BiVO_4) has attracted attention due to its novel photocatalytic, dyeing, ferroelastic and dielectric properties, which make it a great candidate in catalyst, pigment and dielectric resonator applications.¹⁻⁶ BiVO_4 crystallizes in an orthorhombic phase (space group, Pnca [60]) as a natural mineral and takes on a brown color.⁷ However, the orthorhombic BiVO_4 phase has, to date, never been synthesized. Instead, BiVO_4 is readily synthesized in the monoclinic scheelite (I2/b [13]), tetragonal scheelite ($\text{I4}_1/\text{a}$ [88]) and tetragonal zircon-type ($\text{I4}_1/\text{amd}$ [141]) forms.^{1,8,9} Monoclinic scheelite BiVO_4 can be prepared via traditional solid state reaction method from Bi_2O_3 and V_2O_5 . However tetragonal scheelite and zircon-structured polymorphs may only be synthesized by soft chemical methods. Critical factors for the successful synthesis of these latter polymorphs includes pH and use of a range and different initial starting materials, such as $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, NH_4VO_3 , HNO_3 , CH_3COOH and NaOH .^{5,6} Both the tetragonal scheelite and zircon-type phases are metastable and irreversibly transform to monoclinic scheelite BiVO_4 after annealing at high temperature (300 ~ 400 °C).

Monoclinic, tetragonal scheelite BiVO_4 and their mixtures are widely used as a Pb-free complex inorganic colored pigment known as C.I. Pigment Yellow 184.³ Monoclinic scheelite BiVO_4 is an n-type photoactive semiconductor with a band gap of 2.4 eV, which has been investigated widely for water splitting applications under visible light.^{5,6,10} In addition, monoclinic BiVO_4 possesses a high microwave permittivity (ϵ_r) ~ 68 and quality factor (Qf) ~ 8,000 GHz, which make it a strong candidate for microwave device applications.^{11,12}

Monoclinic BiVO_4 undergoes a second order reversible ferroelastic phase transition to tetragonal scheelite at 255 °C,^{9,13-15} which can be induced by external pressure to

below room temperature.¹⁶ In monoclinic BiVO₄, V⁵⁺ is 4-coordinated and its ionic radius is 0.355 Å. In our previous work,¹⁷⁻²⁰ single or complex substitutions (~ 10 mol. %) for V⁵⁺ in BiVO₄ using trivalent or hexavalent ions with larger ionic radius, such as Fe³⁺ (0.49 Å), Mo⁶⁺ (0.41 Å) and W⁶⁺ (0.41 Å), increased the atomic packing factor of monoclinic scheelite structure, which resulted in an increase in the so-called “internal or chemical pressure”, meanwhile lowered the phase transition temperature from 255 °C to below room temperature. Microwave dielectric properties of scheelite-structured BiVO₄ are enhanced by using Li, Mo and Fe, Mo substitutions according to the general formulae (Li_{0.5x}Bi_{1-0.5x})(Mo_xV_{1-x})O₄ ($\epsilon_r \sim 81$)¹⁷ and Bi(Fe_{x/3}Mo_{2x/3}V_{1-x})O₄²⁰ ($\epsilon_r \sim 75$) with Qf > 8,000 and > 13,000GHz, respectively, for compositions near the ferroelastic phase boundary. Highly polarizable B-site ions such as Ti⁴⁺ and Nb⁵⁺ have a strong octahedral site preference in many crystal structures.^{21,22} In our previous work,²³ TiO₂, in which Ti⁴⁺ resides in octahedral coordination, was found to be immiscible with pure BiVO₄, forming a thermodynamically stable composite with $\epsilon_r = 86$, Qf = 9,500 GHz and near-zero TCF. Despite the strong octahedral site preference, Nb⁵⁺ ions in LaNbO₄ occupy tetrahedral sites as Kim et al.²⁴ reporting $\epsilon_r = 19.3$, Qf = 54,400 GHz and a TCF ~ + 9 ppm/°C. LaNbO₄ has the fergusonite-structure (monoclinic, C2/c) and reversibly transforms to tetragonal scheelite at ~ 480 °C,²⁵ suggesting that BiVO₄-LaNbO₄ might, at least in part form a solid solution with useful microwave dielectric properties. Therefore, ceramics in the (1-x)BiVO₄-xLaNbO₄ (0.0 ≤ x ≤ 1.0) system were prepared via a solid state reaction and their phase evolution, crystal structure, microstructure, and microwave dielectric properties were studied.

II. Experimental

Proportionate amounts of reagent-grade starting materials of Bi₂O₃, V₂O₅, Nb₂O₅ and La₂O₃ (> 99%, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) were measured according to the stoichiometric formulation (1-x)BiVO₄-xLaNbO₄ (0.0 ≤ x ≤ 1.0). Details of the processing can be found in our previous work.¹⁸⁻²⁰ Calcination and sintering temperatures were 680 ~ 800 °C and 780 ~ 1090 °C, respectively. X-ray diffraction (XRD) was performed with Cu Kα radiation (Rigaku D/MAX-2400 X-ray diffractometry, Tokyo, Japan) on crushed powders. Diffraction data were collected between 2θ of 10 ~ 65° at a step size of 0.02 °. As-fired surfaces were examined by scanning electron microscopy (SEM) (FEI; Quanta 250F). Infrared reflectivity spectra were measured using a Bruker IFS 66v FTIR spectrometer on Infrared beamline station (U4) at the National Synchrotron Radiation Lab. (NSRL), China. Microwave dielectric properties were measured with the TE_{01δ} dielectric resonator method with a network analyzer (HP 8720 Network Analyzer, Hewlett-Packard) and a temperature chamber (Delta 9023, Delta Design, Poway, CA). The temperature coefficient of resonant frequency TCF (τ_f) was calculated with the following formula:

$$\text{TCF}(\tau_f) = \frac{f_T - f_{T_0}}{f_{T_0} \times (T - T_0)} \times 10^6 \quad (1)$$

where: f_T and f_{T_0} were the TE_{01δ} resonant frequencies at temperature T and T₀, respectively.

III. Results and discussions

Figure 1 presents X-ray diffraction patterns of the (1-x)BiVO₄-xLaNbO₄ (0.0 ≤ x ≤ 1.0) ceramics calcined and sintered at different temperatures. As shown in Fig. 1 (a), after calcination for 4 h at 680 °C, only peaks associated with a monoclinic scheelite

phase were present for $0.02 \leq x \leq 0.08$. Compared with calcined samples, the (200) and (020) of $x = 0.04$ and 0.06 ceramics sintered 2 h at $780\text{ }^\circ\text{C}$ begin to converge, suggesting that the distortion of BO_4 tetrahedra decreases at high sintering temperature. Besides, as shown in Fig. S1 (Supporting Information), atomic packing factor increased slightly with x value and reached a maximum value about 62.9 % at $x = 0.08$ and 0.10 . The (200/020) peaks were still separate for $x = 0.08$ ($680\text{ }^\circ\text{C}$) but at higher temperature ($710\text{ }^\circ\text{C}$) they almost merged into a single peak, as shown in Fig. 1 (c), implying that the structure transformed from a monoclinic to tetragonal scheelite, thus illustrating the sintering temperature and compositional dependence of the ferroelastic transition temperature. The changes in the structure as a function of sintering temperature most likely relate to the rate diffusion and / or solid solubility of Nb in V tetrahedral network. Nb_2O_5 is a comparatively refractory oxide and a homogeneous distribution is difficult to obtain at low sintering temperatures. As sintering temperature increases, Nb distributes more uniformly, resulting in convergence of the (200)/(020) peaks. Moreover, the solid solubility of La and Nb ions may increase with sintering temperature. We note that the effect of sintering temperature on the ferroelastic transition temperature is negligible in other BiVO_4 based solid solutions, such as the $(\text{Li}_{0.5x}\text{Bi}_{1-0.5x})(\text{Mo}_x\text{V}_{1-x})\text{O}_4$, $(\text{Na}_{0.5x}\text{Bi}_{1-0.5x})(\text{Mo}_x\text{V}_{1-x})\text{O}_4$, $(\text{K}_{0.5x}\text{Bi}_{1-0.5x})(\text{Mo}_x\text{V}_{1-x})\text{O}_4$ and $(\text{Ag}_{0.5x}\text{Bi}_{1-0.5x})(\text{Mo}_x\text{V}_{1-x})\text{O}_4$ systems,¹⁷⁻¹⁹ presumably because of the less refractory nature of these solid solutions. A schematic of the ABO_4 scheelite structure and an illustration of how Nb reduces the distortion of the tetrahedra and related cell parameters are plotted in Fig.1 (e) and (f). The presence of $\text{La}_{1/3}\text{NbO}_3$ in XRD traces for samples with $x < 0.70$ indicates that there is limited solid solubility of La and Nb ions in the scheelite structured solid solution in the $(1-x)\text{BiVO}_4-x\text{LaNbO}_4$ ($0.0 \leq x \leq 1.0$) ceramics. For $x = 0.90$,

monoclinic LaNbO_4 was observed as the main phase but nonetheless peaks associated with $\text{La}_{1/3}\text{NbO}_3$ were present in XRD traces.²⁶ The ionic radius of 8-coordinated La^{3+} and 4-coordinated Nb^{5+} are 1.16 Å (a little smaller than that of Bi^{3+} , 1.17 Å) and 0.48 Å, respectively (much larger than that of V^{5+} , 0.355 Å).²⁷ As shown in Fig. 1 (f), both the a/b ratio and cell volume of tetragonal scheelite phase increase linearly with increase of content of LaNbO_4 , which corresponds well with our previous results in other BiVO_4 -based solid solutions.^{20,21} Pure LaNbO_4 is fergusonite-structured (monoclinic, $C2/c$)²⁵ and undergoes a ferroelastic phase transition to tetragonal scheelite structure at high temperature. The large difference in cell parameters is most likely responsible for the limited solid solubility of LaNbO_4 in BiVO_4 .

The symmetry of monoclinic scheelite-structured BiVO_4 is $I2/b$ and it gives nine Raman active modes according to group theory:^{28,29}

$$\Gamma = 3A_g + 6B_g \quad (2)$$

Room temperature Raman spectra of the $(1-x)\text{BiVO}_4-x\text{LaNbO}_4$ ($x = 0.02, 0.04, 0.06, 0.08$ and 0.10) ceramics are shown in Fig. 2. The strongest mode at about 825 cm^{-1} is assigned to the symmetric V–O stretching mode ($\nu_s(\text{V–O})$) and the weaker one at about 725 cm^{-1} to an asymmetric V–O stretching mode ($\nu_{as}(\text{V–O})$). Raman modes at about 331 and 366 cm^{-1} are assigned to asymmetric and symmetric bending modes $\delta_{as}(\text{VO}_4)$ and $\delta_s(\text{VO}_4)$, respectively. The modes below 250 cm^{-1} are external rotation / translation modes, strongly related to A site ions. Key evidence supporting the phase evolution from monoclinic to the tetragonal scheelite structure is the gradual merging of $\delta_{as}(\text{VO}_4)$ and $\delta_s(\text{VO}_4)$ with increase of x as marked in Fig. 2 (a) and plotted in Fig. 2 (b), caused by a reduction in distortion of the BO_4 tetrahedra. As shown in Fig. 2 (b), the stretching mode $\nu_s(\text{V–O})$ red-shifted with the increase of x value in the $(1-x)\text{BiVO}_4-x\text{LaNbO}_4$. The stretching mode is strongly related with the B–O bond

length. Hardcastle and Wachs gave an empirical relation between Raman shift and V-O bond length in 1991:³⁰

$$\nu = 21349 \times \exp(-1.9176R), \quad (3)$$

where ν is the Raman shift in cm^{-1} and R is the V-O bond length in \AA . The calculated B-O bond length is also plotted in Fig. 2 (b). It is only an approximate calculation due to the existence of NbO_4 tetrahedra but the substitution of Nb for V increases the B-O bond length, in agreement with the XRD results.

Un-doped BiVO_4 and LaNbO_4 densify at $800\text{ }^\circ\text{C}$ and $1250\text{ }^\circ\text{C}$, respectively.^{11,24} Optimum sintering temperature of the $(1-x)\text{BiVO}_4-x\text{LaNbO}_4$ ceramics remained around $800\text{ }^\circ\text{C}$ when $x \leq 0.10$ but then increased to $1090\text{ }^\circ\text{C}$ at $x = 0.90$. SEM images of the $(1-x)\text{BiVO}_4-x\text{LaNbO}_4$ ceramics with $0.02 \leq x \leq 0.10$ sintered at their optimal temperature are shown in Fig. 3. Dense and homogeneous microstructures were observed for all the samples. Substitution of LaNbO_4 into BiVO_4 restricted grain growth from $> 5\text{ }\mu\text{m}$ for $x = 0.02$ composition to below $5\text{ }\mu\text{m}$ for $x = 0.06$ sintered at $800\text{ }^\circ\text{C}$. With further increase of LaNbO_4 concentration, optimal sintering temperature increased and the grain size increased to $> 5\text{ }\mu\text{m}$ for $x = 0.10$ ceramic sintered at $820\text{ }^\circ\text{C}$.

ϵ_r and Q_f of the $(1-x)\text{BiVO}_4-x\text{LaNbO}_4$ ceramics as a function of x are shown in Fig. 4 (a). ϵ_r increased linearly from 68 at $x = 0$ to 80 at $x = 0.10$ within the monoclinic scheelite solid solution region and then decreased to ~ 30 for $x = 0.90$. Q_f followed a similar trend as a function of x with values $> 8,000\text{ GHz}$ for $0 \leq x \leq 0.1$ in the monoclinic scheelite phase region but for $x > 0.1$, Q_f decreased sharply to below $3,000\text{ GHz}$ for $x = 0.9$ sample. Although LaNbO_4 is reported to possess a high Q_f value $\sim 54,400\text{ GHz}$,²⁴ the poor Q_f value for $x = 0.9$ might be attributed to the existence of the $\text{La}_{1/3}\text{NbO}_3$ phase.^{31,32} The large permittivity and Q_f values of

monoclinic structured compositions are attributed to their high atomic packing factor¹⁷⁻²⁰ which is a maximum for $x = 0.1$ in the $(1-x)\text{BiVO}_4-x\text{LaNbO}_4$ system as shown in Fig. S1 from “Supporting Information”. Consequently, there is a decrease in Q_f and ϵ_r for higher values of x , although the existence of secondary phases may also increase microwave dielectric loss.

ϵ_r as a function of temperature from 25 ~ 140 °C for $x = 0.04, 0.06,$ and 0.10 is shown in Fig. 4 (b). For pure BiVO_4 , the temperature stability is influenced by the ferroelastic transition at ~ 255 °C which results in a large negative TCF of ~ - 260 ppm/°C at room temperature. Substitution of LaNbO_4 into BiVO_4 lowers the phase transition temperature to below room temperature and switches the sign of TCF to + 204 ppm/°C for $x = 0.10$, as shown in Fig. 4 (b). ϵ_r attains a maximum peak value at 134 °C for $x = 0.04$ but for $x = 0.06$, the phase transition temperature is lowered to ~ 80 °C, which resulted in equivalent TCF $\leq \pm 85$ ppm/°C. For $x = 0.10$ sample, no peak in ϵ_r was observed between 25 to 140 °C, which indicates that the phase transition temperature was about or below 25 °C, in agreement with XRD data.

For $x = 0.10$, Q_f decreased linearly with temperature to a minimum of 8,000 GHz. For $x = 0.04$ and $x = 0.06$ samples, Q_f is > 10,000 GHz and stable over a wide temperature range in contrast to $(\text{A}_{0.5}\text{Bi}_{0.5})\text{MoO}_4$ ($\text{A} = \text{Li}, \text{Na}, \text{K}$ and Ag) BiVO_4 systems,¹⁷⁻²⁰ in which Q_f decreased sharply with increasing temperature. It is concluded that substitution of La^{3+} on A site and Nb^{5+} on B site in scheelite-structured BiVO_4 improves the temperature dependence of Q_f values and increases ϵ_r .

Measured and calculated infrared reflectivity spectra (IR) of the $(1-x)\text{BiVO}_4-x\text{LaNbO}_4$ ($x = 0.02, 0.04, 0.06, 0.08$ and 0.10) ceramics are shown in Fig. 5 (a). Complex reflectivity $R(\omega)$ can be written as:

$$R(\omega) = \left| \frac{1 - \sqrt{\varepsilon^*(\omega)}}{1 + \sqrt{\varepsilon^*(\omega)}} \right|^2 \quad (4)$$

Then IR reflectivity spectra can be analyzed using a classical harmonic oscillator model as follows:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \sum_{j=1}^n \frac{\omega_{pj}^2}{\omega_{oj}^2 - \omega^2 - j\gamma_j\omega} \quad (5)$$

where $\varepsilon^*(\omega)$ is the complex dielectric function; ε_∞ is the dielectric constant caused by the electronic polarization at high frequencies; γ_j , ω_{oj} , and ω_{pj} are the damping factor, the transverse frequency, and plasma frequency of the j -th Lorentz oscillator, respectively; and n is the number of transverse phonon modes. As shown in Fig. 5 (a), all spectra fitted well by employing equations (4) and (5). As x increased, along with driving the monoclinic to tetragonal scheelite transition, some vibrational modes below 500 cm^{-1} merged continuously, e.g. $\delta_{as}(\text{BO}_4)$ and $\delta_s(\text{BO}_4)$ modes. The fitted complex dielectric spectra are shown in Fig. 5 (b) and the experimental values measured in the microwave region are also plotted. Both the fitted and measured values correspond well, which confirms that dielectric polarization at microwave frequencies is dominated by absorption of phonons at the far-infrared region and that there is no contribution from dipolar or other polarization mechanisms. The phonon parameters in the Supporting Information illustrate that external vibrational modes caused by A site ions (Bi^{3+} and La^{3+}) contributed mainly (above 85 %) to the dielectric polarization at microwave frequencies. This result also follow Shannon's additive rule in which the polarizability of Bi^{3+} (6.12 \AA^3) and La^{3+} (6.07 \AA^3) are much larger than that of Nb^{5+} (3.97 \AA^3) and V^{5+} (2.92 \AA^3). Although it is difficult to calculate every contribution to the polarization from each vibrational mode at microwave frequencies, both the infrared spectra fitting and Shannon's additive rule give a reasonable

qualitative assessment. Although the vibrational modes caused by tetrahedron bending are characteristic modes to identify the phase transition from monoclinic to tetragonal scheelite structure, their contributions to microwave dielectric permittivity are negligible. Hence, no matter monoclinic or tetragonal models were employed for $x = 0.10$ composition, there was no remarkable difference observed as shown in Fig. S2, Table S4 and Table S5.

IV. Conclusions

Scheelite structured solid solution formed in the $(1-x)\text{BiVO}_4-x\text{LaNbO}_4$ ceramics within $0 \leq x < 0.7$. Increasing x and sintering temperature accelerated the monoclinic to tetragonal scheelite phase transition for $x \leq 0.1$. For $x \leq 0.1$, samples could be densified at ~ 800 °C with a grain size 1 to 5 μm . As indicated by Raman spectroscopy, substitution of Nb^{5+} for V^{5+} increased the B-O bond length and drove the monoclinic–tetragonal phase transition to below room temperature. $\epsilon_r > 75$ with a fluctuation of ~ 1.24 % ($\text{TCF} \leq \pm 85$ ppm/°C) accompanied by a $Q_f \sim 10,000$ GHz in the range 25 ~ 140 °C were obtained in $x = 0.06$ ceramic sintered at 800 °C for 2 h. This novel system extends the understanding of ferroelastic phase transition in scheelite structure materials and provides a promising candidate for low temperature co-fired ceramic technology.

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Figure Captions:

Fig. 1 X-ray diffraction patterns of the $(1-x)\text{BiVO}_4-x\text{LaNbO}_4$ ($0.0 \leq x \leq 1.0$) ceramics calcined (a) and sintered (b), (c), (d) at different temperatures, schematic of ABO_4 scheelite structure (release of distorted tetrahedral in insert) (e), and cell parameters of the main phases as a function of x value (* — monoclinic scheelite phase, o — tetragonal scheelite phase, L — monoclinic LaNbO_4 phase, v — $\text{La}_{1/3}\text{NbO}_3$ phase)

Fig. 2 Room-temperature Raman spectra of the $(1-x)\text{BiVO}_4-x\text{LaNbO}_4$ ($x=0.02, 0.04, 0.06, 0.08$ and 0.10) ceramics sintered at their optimal temperatures

Fig. 3 SEM images of the $(1-x)\text{BiVO}_4-x\text{LaNbO}_4$ ceramics (a) for $x=0.02$ sintered 2 h at 780°C , (b) for $x=0.04$ sintered 2 h at 800°C , (c) for $x=0.06$ sintered 2 h at 800°C , and (d) for $x=0.10$ sintered 2 h at 820°C

Fig. 4 Microwave dielectric permittivity and Qf values of the $(1-x)\text{BiVO}_4-x\text{LaNbO}_4$ ceramics as a function of x value (a) and temperature (b) in range $25 \sim 140^\circ\text{C}$

Fig. 5 Measured and calculated infrared reflectivity spectra of the $(1-x)\text{BiVO}_4-x\text{LaNbO}_4$ ($x=0.02, 0.04, 0.06, 0.08$ and 0.10) ceramics (a) (solid line for fitting values and circle for measured values) and their complex dielectric spectra (b) (circles are experimental at microwave region, solid lines represent the fit of IR spectra)

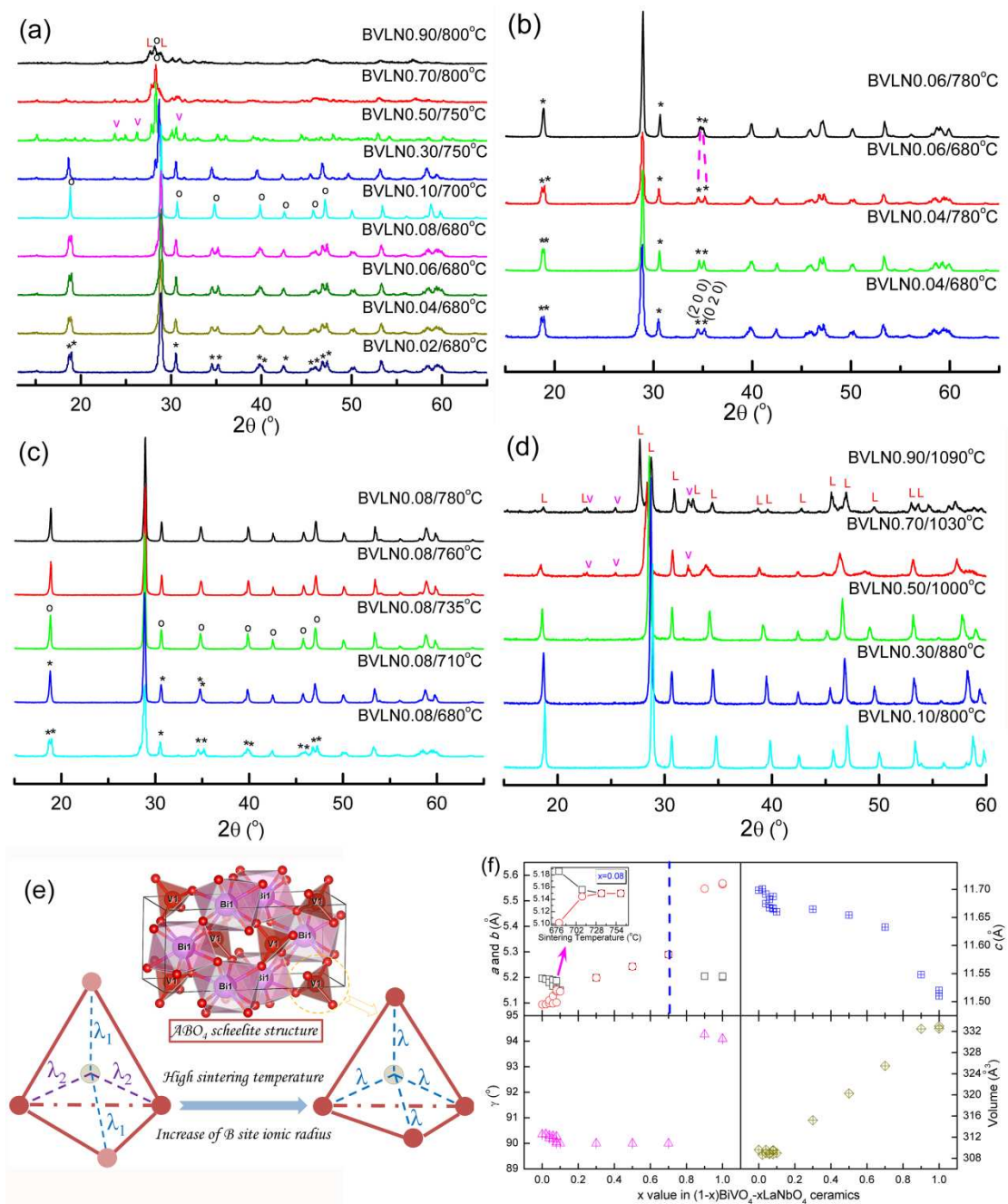


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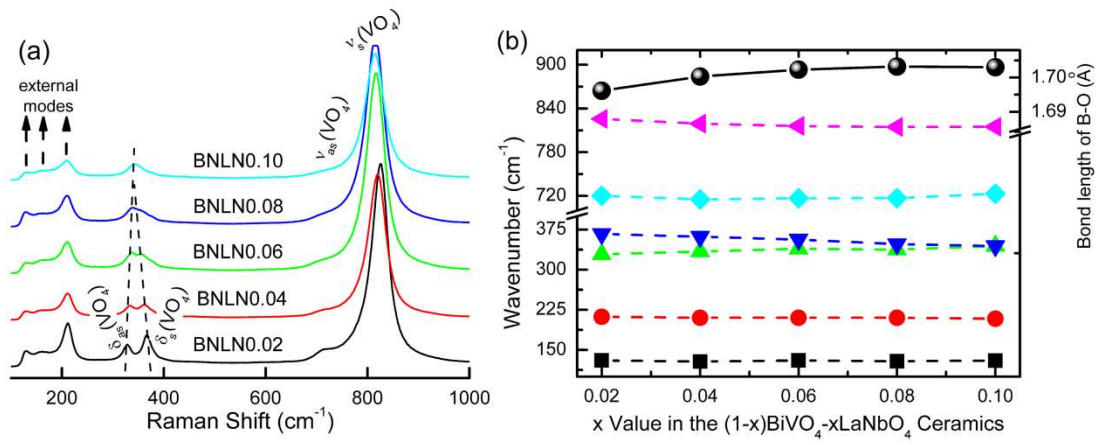


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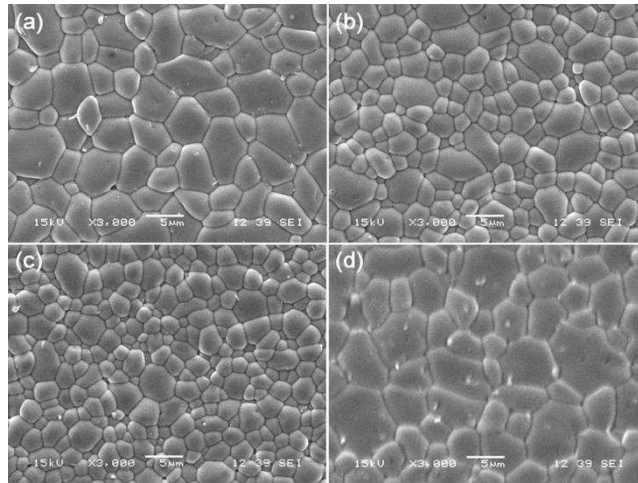


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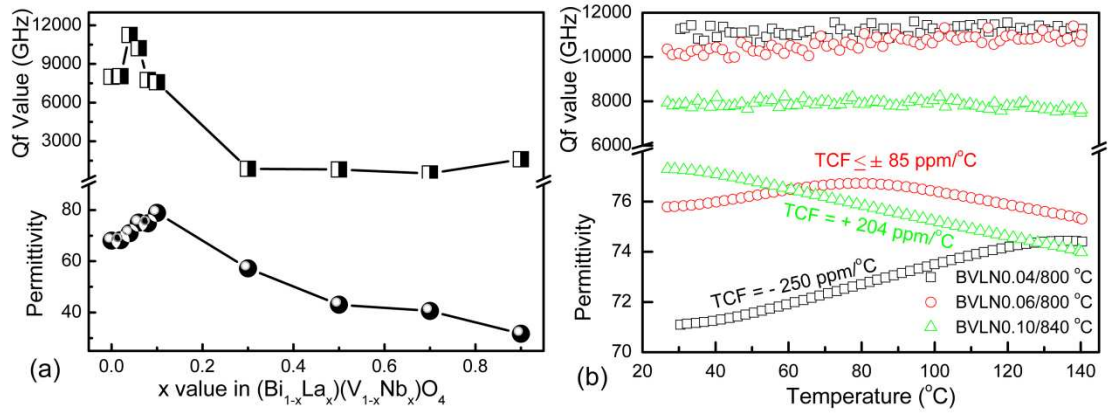


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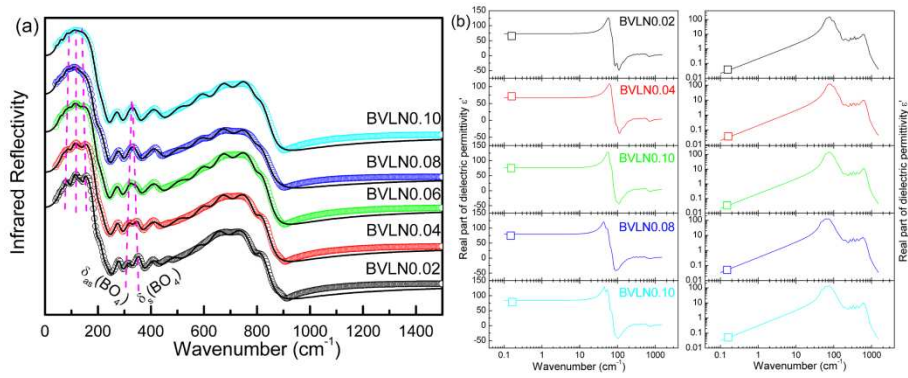
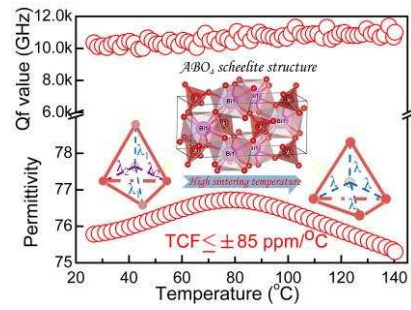


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Permittivity $\sim 76.3 \pm 0.5$ and quality factor $> 10,000$ GHz were obtained in $0.94\text{BiVO}_4\text{-}0.06\text{LaNbO}_4$ ceramic sintered at 800°C .