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**Crystal Structure, Infrared Spectra and Microwave
Dielectric Properties of Temperature Stable Zircon-Type
(Y,Bi)VO₄ Solid Solution Ceramics**

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ABSTRACT

A series of $(\text{Bi}_{1-x}\text{Y}_x)\text{VO}_4$ ($0.4 \leq x \leq 1.0$) ceramics were synthesized by using the traditional solid state reaction method. In the composition range $0.4 \leq x \leq 1.0$, a zircon-type solid solution was formed between $900 \sim 1550$ °C. Combined with our previous work (scheelite monoclinic and zircon type coexist in the range $x < 0.40$), a pseudo binary phase diagram of BiVO_4 - YVO_4 is presented. As x decreased from 1.0 to 0.40, the microwave permittivity (ϵ_r) of $(\text{Bi}_{1-x}\text{Y}_x)\text{VO}_4$ ceramics increased linearly from 11.03 to 30.9 coincident with an increase in the temperature coefficient of resonant frequency (TCF) from -61.3 to +103 ppm/°C. Excellent microwave dielectric properties were obtained for $(\text{Bi}_{0.3}\text{Y}_{0.7})\text{VO}_4$ sintered at 1025 °C and $(\text{Bi}_{0.2}\text{Y}_{0.8})\text{VO}_4$ sintered at 1075 °C with $\epsilon_r \sim 19.35$, microwave quality factor (Qf) $\sim 25,760$ GHz and TCF $\sim +17.8$ ppm/°C, and $\epsilon_r \sim 16.3$, a Qf $\sim 31,100$ GHz, and TCF ~ -11.9 ppm/°C, respectively. Raman spectra, Shannon's additive rule, a classical oscillator model and far-infrared spectra were employed to study structure/property relations in detail. All evidence supported the premise that Bi-based vibrations dominate the dielectric permittivity in the microwave region.

INTRODUCTION

Microwave dielectric ceramics have played an important role in modern wireless communication systems as dielectric resonators (DR), filters, capacitors and duplexers. To meet the requirement of miniaturization and reliability of microwave devices, large dielectric permittivity (ϵ_r), large microwave quality factor (Qf) and near-zero temperature coefficient of frequency (TCF) must be achieved.¹⁻⁴

Many classic microwave dielectric ceramics based on ABO_3 perovskite structure have been explored and the relation between structure-property has been extensively studied.^{5,6} Recently, many complex oxides with classic ABO_4 type, such as scheelite ($CaMoO_4$, $BiVO_4$),^{7,8} Fergusonite ($LaNbO_4$, $NdNbO_4$),⁹ stibiotantalite ($BiNbO_4$, $BiTaO_4$),^{10,11} wolframite ($ZnWO_4$, $MgWO_4$),¹² zircon ($CeVO_4$)¹³ and rutile ($(Zn,Nb)TiO_4$, $(Cu,Nb)TiO_4$)^{14,15} structures, have been reported to have good microwave dielectric properties. Zircon-type ($I4_1/amd$) vanadates (AVO_4 , $A = Sc^{3+}$, Ln^{3+} , Bi^{3+}) are a subset of ABO_4 -type compounds and were widely investigated due to their potential optical, magnetic, elastic, and electric properties.^{4,13} The zircon structure is composed of alternating $[VO_4]$ tetrahedra and edge-sharing $[AO_8]$ dodecahedra forming chains parallel to the c axis. Two $[AO_8]$ dodecahedra are arranged along a, b and c axes, which results in a linear increase of cell volumes with A site ionic radius.^{4,16} As reported by Watanabe and Zuo,^{13,17} $LaVO_4$ prefers to crystallize in a monoclinic monazite-type structure with a space group $P2_1/n$. Microwave dielectric properties of zircon-type $CeVO_4$ ceramic were first reported by Wang et al.¹³ with a $\epsilon_r \sim 12.3$, a Qf $\sim 41,460$ GHz and a TCF ~ -34.4 at a sintering temperature of ~ 950 °C. It can be deduced that other rare-earth orthovanadates, such as YVO_4 , $SmVO_4$, $NdVO_4$, may also possess similar microwave dielectric properties.

However, their large negative TCF values must be modified to near zero. There are two traditional methods to modify TCF value of microwave dielectric ceramic to near zero broadly separated into a composite and solid solution approach.¹⁸ In our previous work, a temperature stable microwave dielectric composite ceramic, which contains both scheelite BiVO₄ and zircon-type (Bi_{0.6}Y_{0.4})VO₄ phases with a $\epsilon_r = 45$, a Qf ~ 14 000 GHz and a TCF = +10 ppm/°C was achieved.⁴ The end member (Bi_{0.6}Y_{0.4})VO₄ takes on the zircon structure with positive TCF (+32 ppm/°C). This result inspired the design of a zircon-type solid solution ceramics in (Bi,Y)VO₄ system with near-zero TCF. Undoped BiVO₄ ceramic prepared via solid state reaction method crystallizes in the monoclinic scheelite not zircon structure. As reported by Watanabe,¹⁷ solid solubility of Bi³⁺ ion in zircon structured (Bi_xCe_{1-x})VO₄ ceramics is $\geq 60\%$, as confirmed in our previous work,¹⁹ attributed to the presence of the zircon-type BiVO₄ synthesized by a precipitation method.^{20,21} Undoped zircon-type BiVO₄ is not stable and irreversibly transforms to the monoclinic scheelite structure at > 300 °C²¹ and it is plausible that the substitution of Bi into for Y in YVO₄ stabilises the zircon-type lattice. In the present work, a comprehensive study on the phase assemblage and evolution in (Bi,Y)VO₄ system was performed with the zircon-type solid solution region and its associated sintering behavior, microstructure and microwave dielectric properties were studied in detail.

RESULTS AND DISCUSSIONS

X-ray diffraction patterns of the (Bi_{1-x}Y_x)VO₄ ceramics calcined and sintered at their optimal temperatures are presented in Figure 1 (a). All peaks were indexed as a zircon-type phase for $x \geq 0.4$. As Bi concentration increased (decrease of x), all diffraction peaks shifted to the lower 2θ , commensurate with an increase in cell

volume attributed to the larger ionic radius of Bi^{3+} (1.17 Å) compared with Y^{3+} (1.019 Å). Cell parameters of $(\text{Bi}_{1-x}\text{Y}_x)\text{VO}_4$ ($x \geq 0.4$) ceramics as a function x value are presented in Figure 1 (b). a and c parameters increased from 7.116 Å to 7.225 Å and 6.287 Å to 7.394 Å, respectively, as x decreased from 1.0 to 0.4 commensurate with an increase in cell volume from 318.35 Å³ to 333.79 Å³. As shown in Figure 1 (c), the refined values of lattice parameters for the $(\text{Bi}_{0.3}\text{Y}_{0.7})\text{VO}_4$ sample are $a = b = 7.163(7)$ Å, $c = 6.336(2)$ Å with a space group $I4_1/amd$ (141). All the atomic fractional coordinates are listed in Table 1. The goodness of fit of refinement, which is defined as the ratio of R_{wp}/R_{exp} , is ~ 3.15 . The V-O distance in the zircon-type $(\text{Bi}_{0.3}\text{Y}_{0.7})\text{VO}_4$ sample is 1.7005 Å, similar to that in YVO_4 (1.7058 Å). The long and short (Bi,Y)-O bond distances are 2.3301 Å and 2.4520 Å, respectively, which are larger than that in YVO_4 (2.2986 Å and 2.4434 Å, respectively),²² consistent with the larger ionic radius of Bi^{3+} than Y^{3+} . Combined with our previous work,⁴ the schematic phase diagram of $(1-x)\text{BiVO}_4-x\text{YVO}_4$ binary system is presented in Figure 1 (d). In the region $x \geq 0.4$, a zircon-type solid solution phase field was formed. In the region $x < 0.4$, both monoclinic BiVO_4 and zircon $(\text{Bi}_{0.6}\text{Y}_{0.4})\text{VO}_4$ coexisted with stable cell parameters.

Undoped YVO_4 belongs to the D_{4h}^{19} crystal structure ($I4_1/amd$) and the theoretical group analysis gives an irreducible representation of the vibrational modes after Miller et al.²³ and Vali²⁴:

$$\Gamma_{36} = (2A_{1g} + 2B_{1u}) + (B_{1g} + A_{1u}) + (A_{2g} + B_{2u}) + (4B_{2g} + 4A_{2u}) + (5E_g + 5E_u), \quad (1)$$

The $2A_{1g}$, B_{1g} , B_{2g} and $5E_g$ are Raman active optical modes whereas $3A_{2u}$ and $4E_u$ modes are infrared active. In addition, there are two further inactive translational modes $A_{2u} + E_u$. From Figure 2 (a), the main Raman modes created by stretching and bending of $[\text{VO}_4]$ tetrahedra at $\sim 890 \text{ cm}^{-1}$, 378 cm^{-1} , 815 cm^{-1} and 488 cm^{-1} are assigned to $A_{1g}(v_1)$, $A_{1g}(v_2)$, $B_{2g}(v_3)$ and $B_{2g}(v_4)$, respectively. The weak mode at 837

cm^{-1} , which is close to $B_{2g}(v_3)$ mode, is assigned to E_g . The peaks at 260 cm^{-1} and overlapping at about 160 cm^{-1} are external modes caused by translation. From Figure 2 (b), the main Raman modes shift to the lower wave-number as x decreases, along with broadening and a decrease in peak intensity, due to A-site disorder in the solid solution. According to Hardcastle and Wach's study on the relation ($\nu = 21349 \times e^{(-1.9176R)}$),²⁵ in which ν is the Raman shift and R is the bond length of V-O) between Raman shift and V-O bond length, the decrease in the $A_{1g}(v_1)$ Raman mode (stretching mode of $[\text{VO}_4]$, Figure 2 (b)) is caused by the increase of V-O bond length.

SEM images of the $(\text{Bi}_{1-x}\text{Y}_x)\text{VO}_4$ ceramics are shown in Figure 3. For pure YVO_4 ($x=1.0$), the densification temperature is above $1550 \text{ }^\circ\text{C}$ and many pores are observed in ceramics sintered at $1550 \text{ }^\circ\text{C}$ for 2 hr. As seen from Figure 3 (a), (b) and (c), substitution of Bi for Y effectively lowered the sintering temperature and induced a homogeneous dense microstructure in $(\text{Bi}_{1-x}\text{Y}_x)\text{VO}_4$ ceramics with $x = 0.7, 0.8$ and 0.9 . As x decreased from 1.0 to 0.7, sintering temperatures of $(\text{Bi}_{1-x}\text{Y}_x)\text{VO}_4$ ceramics were lowered from $1550 \text{ }^\circ\text{C}$ to $1025 \text{ }^\circ\text{C}$ along with a decrease of grain size from $\sim 5 \text{ }\mu\text{m}$ to $\sim 1 \text{ }\mu\text{m}$.

Microwave ϵ_r and Q_f of the $(\text{Bi}_{1-x}\text{Y}_x)\text{VO}_4$ ceramics as a function of sintering temperature are shown in Figure 4. ϵ_r of $(\text{Bi}_{1-x}\text{Y}_x)\text{VO}_4$ ceramics increased with sintering temperature due to the elimination of pores before reaching a stable value. Q_f increased with sintering temperature, reaching a maximum value before decreasing sharply for all samples except for $x = 1.0$. Q_f is composed of intrinsic and extrinsic contributions and affected by grain size, grain boundaries and pores. For $(\text{Bi}_{1-x}\text{Y}_x)\text{VO}_4$ ceramics high Q_f values were only attained at a relatively narrow sintering temperature range. Optimal microwave properties of $(\text{Bi}_{1-x}\text{Y}_x)\text{VO}_4$ ceramics are listed

in Table 2, in which ϵ_r decreases linearly from 30.9 at $x = 0.4$ to 11.1 at $x = 1.0$ in accordance with Shannon's additive rule. Shannon²⁶ suggested that polarizabilities of oxides may be estimated by summing the polarizabilities of constituent ions. The polarizabilities α_x of $(\text{Bi}_{1-x}\text{Y}_x)\text{VO}_4$ may be calculated as follows:

$$\alpha_x = (1-x)\alpha_{\text{Bi}^{3+}} + x\alpha_{\text{Y}^{3+}} + \alpha_{\text{V}^{5+}} + 4\alpha_{\text{O}^{2-}} \quad (2)$$

where $\alpha_{\text{Bi}^{3+}}$, $\alpha_{\text{Y}^{3+}}$, $\alpha_{\text{V}^{5+}}$, $\alpha_{\text{O}^{2-}}$ are the polarizabilities of Bi^{3+} , Y^{3+} , V^{5+} and O^{2-} , respectively.

Due to the smaller polarizabilities of Y^{3+} relative to Bi^{3+} ($\alpha_{\text{Bi}^{3+}} = 6.12^3 \text{ \AA}^3 > \alpha_{\text{Y}^{3+}} = 3.81^3 \text{ \AA}^3$)²⁶, there should be a linear decrease in $(\text{Bi}_{1-x}\text{Y}_x)\text{VO}_4$ as x increases. Using the Clausius-Mossotti relation which relates ϵ_x , α_x and the molar cell volume, V_x , ϵ_r may be calculated:

$$\epsilon_x = \frac{3V_x + 8\pi\alpha_x}{3V_x - 4\pi\alpha_x} \Leftrightarrow \alpha_x = \frac{3V_x}{4\pi} \frac{\epsilon_x - 1}{\epsilon_x + 2} \quad (3)$$

The calculated molecular α_x from equations (2) and (3) along with the macroscopic microwave dielectric properties are listed in Table 2. As x decreases, the relative deviation between $\alpha_{\text{cal.}}$ and $\alpha_{\text{meas.}}$ increases. Employing equation (3), it can be obtained that $\alpha_{\text{Bi}^{3+}} - \alpha_{\text{Y}^{3+}} = (\alpha_{x_2} - \alpha_{x_1}) / (x_1 - x_2) \approx 5.8^3 \text{ \AA}^3$. This result is greater than that reported by Shannon (2.31^3 \AA^3), which suggests that within its coordination in the zircon-type structure, Bi^{3+} contributes much more than Y^{3+} to the dielectric polarizability, compared with higher symmetry systems.

The highest Qf ($\sim 40,700$ GHz) was obtained for $(\text{Bi}_{0.1}\text{Y}_{0.9})\text{VO}_4$ but as x decreased to 0.65 and 0.40, Qf decreased linearly to 16,000 GHz. The intrinsic dielectric loss determines the upper limit of Qf and is quantitatively described by the classical one-phonon damped oscillator model as following:²⁷

$$\varepsilon^*(\omega) - \varepsilon(\infty) = \frac{(ze)^2 / mV\varepsilon_0}{\omega_T^2 - \omega^2 - j\gamma\omega} \quad (4)$$

where $\varepsilon^*(\omega)$ is the complex permittivity, $\varepsilon(\infty)$ is the electronic part of the static permittivity, ω_T is the transverse frequency of the polar phonon mode, γ is the damping parameter, z is the equivalent electric charge number, e is the electric charge for a electron, m is the equivalent atom weight and V is the unit volume. In the microwave region, considering $\omega^2 \ll \omega_T^2$, the relationship between Qf and ε_r is obtained as following:

$$Q \times f \approx \frac{(ze)^2 / mV\varepsilon_0}{2\pi\gamma \times (\varepsilon'(\omega) - \varepsilon(\infty))}, \quad (5)$$

The above relation was successfully used to explain the reciprocal relationship between ε_r and Qf in scheelite solid solutions.²⁸ The same qualitative relationship holds for zircon-type solid solution in $(\text{Bi}_{1-x}\text{Y}_x)\text{VO}_4$ ceramics. The decrease in Qf for undoped YVO_4 is attributed to the absence of a sintering temperature at which the density of the end member compound may be optimized. TCF of undoped YVO_4 is ~ -61.3 ppm/ $^\circ\text{C}$. As x decreased to 0.40, TCF linearly increased to $+103$ ppm/ $^\circ\text{C}$. In contrast, $+17.8$ ppm/ $^\circ\text{C}$ and -11.9 ppm/ $^\circ\text{C}$ were obtained in the $(\text{Bi}_{0.3}\text{Y}_{0.7})\text{VO}_4$ and $(\text{Bi}_{0.2}\text{Y}_{0.8})\text{VO}_4$ ceramics, respectively, suggesting that zero TCF may be achieved for $0.7 < x < 0.8$. TCF is usually defined as following:

$$\text{TCF} = -\alpha_1 - \frac{1}{2}\tau_\varepsilon, \quad (6)$$

where α_1 is thermal expansion coefficient and τ_ε is temperature coefficient of dielectric constant. Usually α_1 of microwave dielectric is $< +20$ ppm/ $^\circ\text{C}$ and independent of x . Hence, TCF value mainly depends on τ_ε . Using the Clausius-Mosotti relation, Bosman and Havinga²⁹ derived an expression for τ_ε at constant pressure, as follows:

$$\tau_{\varepsilon} = \frac{1}{\varepsilon} \left(\frac{\partial \varepsilon}{\partial T} \right)_P = \frac{(\varepsilon-1)(\varepsilon+2)}{\varepsilon} (A+B+C) = \left(\varepsilon - \frac{2}{\varepsilon} + 1 \right) (A+B+C) \quad (7)$$

$$A = \frac{1}{3V} \left(\frac{\partial V}{\partial T} \right)_P, B = \frac{1}{3\alpha_m} \left(\frac{\partial \alpha_m}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P, C = \frac{1}{3\alpha_m} \left(\frac{\partial \alpha_m}{\partial T} \right)_V$$

The sum of the A and B terms is approximately 6 ppm/°C. Term C usually lies between $-1 \sim -10$ ppm/°C. The term C represents the direct dependence of the polarizability on temperature. Figure 5 (a) shows a plot of the temperature dependence of permittivity (α_l was assumed to be + 20 ppm/°C) as a function of $(\varepsilon-1)(\varepsilon+2)/\varepsilon$ for all the $(\text{Bi}_{1-x}\text{Y}_x)\text{VO}_4$ ceramics to extrapolate the (A+B+C) value ~ -16.1 ppm/°C, which is within acceptable range. By using this relation, any TCF value can be achieved by precisely adjusting the composition. Furthermore, it is similar to the empirical logarithmic rule $(\ln \varepsilon = y_1 \ln \varepsilon_1 + y_2 \ln \varepsilon_2 / \text{TCF} = y_1 \ln \tau_{f1} + y_2 \ln \tau_{f2})$ ³⁰ suitable for composites. The temperature dependence of ε_r and Qf of the $(\text{Bi}_{0.3}\text{Y}_{0.7})\text{VO}_4$ and $(\text{Bi}_{0.2}\text{Y}_{0.8})\text{VO}_4$ ceramics in the temperature range 25 ~ 130 °C are shown in Figure 5 (b). ε_r is stable at ~ 19 and 16 for the $(\text{Bi}_{0.3}\text{Y}_{0.7})\text{VO}_4$ and $(\text{Bi}_{0.2}\text{Y}_{0.8})\text{VO}_4$ ceramics, respectively. Qf decreased linearly with temperature from 28,000 GHz to $\sim 20,000$ GHz confirming that the dielectric loss increased with temperature. Taking into account the above arguments, temperature stable microwave dielectric ceramics may be achieved for $0.7 < x < 0.8$ with $16 \leq \varepsilon_r \leq 19$ and $\text{Qf} > 20,000$ GHz between 25 ~ 130 °C. Compared with the SrLnAlO_4 (Ln = Nd and Sm) microwave dielectric ceramics³¹ with similar properties (permittivity 17.8~18.8, Qf values 25,700 ~ 54,880 GHz, and TCF values $-9 \sim +2$ ppm/°C), sintering temperature (below 1050 °C) of this system is much lower than that of SrLnAlO_4 (Ln = Nd and Sm) ceramics (1475 ~ 1500 °C) and this can save lots of energy during processing.

Far-Infrared reflectivity is a useful tool to investigate intrinsic dielectric properties of microwave ceramics. As discussed above, there are seven infrared active modes

including three A_{2u} and four E_u mode. In Vali et al.'s work,²⁴ a perpendicular electric field of the incident light to the c axis of YVO_4 single crystal was employed to obtain the infrared reflectivity and only four E_u modes, at 195 cm^{-1} , 263 cm^{-1} , 309 cm^{-1} and 780 cm^{-1} , were observed. As shown in Figure 6, besides the four E_u modes, another two at 439 and 916 cm^{-1} , assigned to A_{2u} modes, were also observed to contribute to the infrared reflectivity spectra of YVO_4 ceramic sample. The high wave number peak at 916 cm^{-1} belongs to the stretching mode of $[VO_4]$, which is similar to that at 977 cm^{-1} caused by the Si-O stretching in $ZrSiO_4$ material.³² As x decreased to 0.8, four new modes are observed, at 69 , 136 , 233 and 749 cm^{-1} . These new modes are also assigned to E_u modes caused by the partial occupation by Bi on the A site of the zircon structure. The external E_u modes below 450 cm^{-1} are conventionally caused by translation and rotation between A site ions and $[VO_4]$ tetrahedral, as shown in Figure 6 (b). Due to the different relative mass of Bi and Y atoms, the translation and rotation strength are different and lead to different Raman shifts, consequently the strength of the E_u modes increased with Bi concentration.

By using the Equation (4) and the relation between complex reflectivity $R(\omega)$ and permittivity as following:

$$R(\omega) = \left| \frac{1 - \sqrt{\varepsilon^*(\omega)}}{1 + \sqrt{\varepsilon^*(\omega)}} \right|^2, \quad (8)$$

The fitting of infrared reflectivity was employed to study the intrinsic dielectric contribution from each vibrational mode. Infrared reflectivity spectra of the $(Bi_{0.3}Y_{0.7})VO_4$ was fitted using eight modes as shown in Figure 7 (a) and the related parameters are listed in Table 3. Among the eight modes, No. 1, 2, 4 and 6 modes belong to Bi-based vibrations and their total contribution to the microwave permittivity was ~ 8 while all the others were attributed to the Y-based and $[VO_4]$

tetrahedral vibrations (value about ~ 7.2). The optical permittivity is ~ 4.41 . This result indicates that Bi-based vibrations mainly contribute to permittivity in the microwave region, in accordance with the analysis using the Shannon's additive rule. The measured and fitted real and imaginary part of permittivity were plotted in Figure 7 (b). The measured corresponded well with the fitted values, confirming that in the microwave region the dielectric polarization is mainly caused by phonon absorption in the infrared region.

CONCLUSIONS

Zircon-type solid solution formed in the $(\text{Bi}_{1-x}\text{Y}_x)\text{VO}_4$ ($0.4 \leq x \leq 1.0$) ceramics. Substitution of Bi effectively lowered sintering temperatures from above $1550\text{ }^\circ\text{C}$ for undoped YVO_4 to $\sim 900\text{ }^\circ\text{C}$ for $(\text{Bi}_{0.6}\text{Y}_{0.4})\text{VO}_4$. As x decreased from 1.0 to 0.4, cell parameters increased linearly, along with the increase of ϵ_r from 11.03 to 30.9 accompanied by a shift of TCF value from -61.3 to $+103\text{ ppm}/^\circ\text{C}$. Excellent microwave dielectric properties with a $\epsilon_r \sim 19.35$, a $Q_f \sim 25,760\text{ GHz}$ and a TCF $\sim +17.8\text{ ppm}/^\circ\text{C}$ were obtained in $(\text{Bi}_{0.3}\text{Y}_{0.7})\text{VO}_4$ ceramic sintered at $1025\text{ }^\circ\text{C}$. For $(\text{Bi}_{0.2}\text{Y}_{0.8})\text{VO}_4$ ceramic sintered at $1075\text{ }^\circ\text{C}$, $\epsilon_r \sim 16.3$, $Q_f \sim 31,100\text{ GHz}$ and TCF $\sim -11.9\text{ ppm}/^\circ\text{C}$ were obtained. It is demonstrated that temperature stable microwave dielectric ceramics obtained for compositions with $0.7 < x < 0.8$. We conclude therefore, with reference to our previous work,⁴ that there are two methods to design temperature stable microwave dielectric ceramics in the $(\text{Bi}_{1-x}\text{Y}_x)\text{VO}_4$ system for GHz frequency applications: i) the fabrication of composites of scheelite and zircon phase, and ii) the formation of zircon structured solid solution with $0.7 < x < 0.8$.

EXPERIMENTAL SECTION

The $(\text{Bi}_{1-x}\text{Y}_x)\text{VO}_4$ ($x = 0.4, 0.65, 0.7, 0.8, 0.9$ and 1.0) (as abbreviated BYVx) samples were prepared via solid state reaction method as described in our previous work.^{2,3} Samples were sintered at temperatures from $850\text{ }^\circ\text{C}$ to $1550\text{ }^\circ\text{C}$ for 2 h.

XRD was performed with $\text{Cu K}\alpha$ radiation (Rigaku D/MAX-2400 X-ray diffractometry, Tokyo, Japan) using powder sample. Diffraction pattern was collected over $5 - 65\text{ }^\circ$ (2θ) at a step size of 0.02 ° . Rietveld profile refinement method was employed to analyze the data using FULLPROF program. As-fired surfaces were observed by scanning electron microscopy (SEM, FEI, Quanta 250 F). Raman spectra were performed with a Raman spectrometer (inVia, Renishaw, England), excited by an Ar^+ laser (514.5 nm). Infrared reflectivity spectra were measured using a Bruker IFS 66v FT-IR spectrometer on the Infrared beamline station (U4) at the National Synchrotron Radiation Lab. (NSRL), China. Microwave dielectric properties were measured using the $\text{TE}_{01\delta}$ method with a network analyzer (HP 8720 Network Analyzer, Hewlett-Packard) and a temperature chamber (Delta 9023, Delta Design, Poway, CA). Temperature coefficient of resonant frequency TCF (τ_f) was calculated with the following formula:

$$\text{TCF}(\tau_f) = \frac{f_T - f_{T_0}}{f_{T_0} \times (T - T_0)} \times 10^6, \quad (9)$$

where f_T and f_{T_0} are the $\text{TE}_{01\delta}$ resonant frequencies at temperature T and T_0 , respectively.

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FIGURE CAPTIONS:

Figure 1 X-ray diffraction patterns of $(\text{Bi}_{1-x}\text{Y}_x)\text{VO}_4$ ceramics calcined and sintered at different temperatures (a), the cell parameters as a function x value (b), the experimental (circles) and calculated (line) X-ray powder diffraction profiles of the $(\text{Bi}_{0.3}\text{Y}_{0.7})\text{VO}_4$ composition sintered at 960 °C for 2 h at room temperature (c) ($R_p = 12.7\%$, $R_{wp} = 12.9\%$, $R_{exp} = 7.27\%$); The short vertical lines below the patterns mark the positions of Bragg reflections. The bottom continuous line is the difference between the observed and the calculated intensity), and the schematic phase diagram of BiVO_4 - YVO_4 system (d)

Figure 2 Raman spectra of $(\text{Bi}_{1-x}\text{Y}_x)\text{VO}_4$ ($x \geq 0.4$) ceramics (a) and as a function of x value (b)

Figure 3 SEM images of $(\text{Bi}_{1-x}\text{Y}_x)\text{VO}_4$ ceramics sintered at different temperatures: $x=0.70$ at 1025 °C (a), $x=0.80$ at 1075 °C (b), $x=0.90$ at 1225 °C (c), and $x=1.00$ at 1550 °C (d)

Figure 4 Microwave dielectric permittivity (a) and Qf values (b) of $(\text{Bi}_{1-x}\text{Y}_x)\text{VO}_4$ ceramics as a function of sintering temperature

Figure 5 τ_ϵ (temperature dependence of permittivity) as a function of $(\epsilon-1)(\epsilon+2)/\epsilon$ (a), permittivity and Qf as a function of temperature (b) for the $(\text{Bi}_{0.3}\text{Y}_{0.7})\text{VO}_4$ and $(\text{Bi}_{0.2}\text{Y}_{0.8})\text{VO}_4$ ceramics

Figure 6 Far-Infrared reflectivity of $(\text{Bi}_{1-x}\text{Y}_x)\text{VO}_4$ ceramics (a) and schematic of external E_u modes caused by translation and rotation (b)

Figure 7 Measured and calculated infrared reflectivity spectra (a) (solid line for fitting values and circle for measured values) and fitted complex dielectric spectra (b) of the $(\text{Bi}_{0.3}\text{Y}_{0.7})\text{VO}_4$ ceramic (circles are experimental at microwave region).

Table 1 Refined atomic fractional coordinates from XRD data for the $(\text{Bi}_{0.3}\text{Y}_{0.7})\text{VO}_4$ sample and the lattice parameters at room temperature are $a = b = 7.163(7) \text{ \AA}$, $c = 6.336(2) \text{ \AA}$ with a space group $I 4_1/amd (141)$.

| Atom | Site | Occ. | x | y | z | Biso. |
|------|------|---------|---------|---------|---------|---------|
| Y | 4a | 0.08750 | 0.00000 | 0.75000 | 0.12500 | 0.27426 |
| Bi | 4a | 0.03750 | 0.00000 | 0.75000 | 0.12500 | 0.27426 |
| V | 4b | 0.12500 | 0.00000 | 0.25000 | 0.37500 | 0.14327 |
| O | 16h | 0.50000 | 0.00000 | 0.06795 | 0.20273 | 0.12035 |

Table 2 Densification temperature, microwave dielectric properties and molecular polarizability of the (Bi_{1-x}Y_x)VO₄ ceramics

| x | S.T. (°C) | ϵ_r | Qf (GH) | TCF(ppm/°C) | V(Å ³) | $\alpha_{cal.}$ (Å ³) | $\alpha_{meas.}$ (Å ³) |
|------|-----------|--------------|---------|-------------|--------------------|-----------------------------------|------------------------------------|
| 0.4 | 975 | 30.9 | 15,570 | +103 | 333.79 | 16.16 | 18.11 |
| 0.65 | 995 | 20.5 | 16,380 | +32 | 325.43 | 15.58 | 16.83 |
| 0.7 | 1025 | 19.35 | 25,760 | +17.8 | 324.55 | 15.46 | 16.65 |
| 0.8 | 1075 | 16.3 | 30,100 | -11.9 | 322.76 | 15.23 | 16.11 |
| 0.9 | 1225 | 13.49 | 40,720 | -31.2 | 319.96 | 15.00 | 15.40 |
| 1.0 | 1550 | 11.03 | 28,600 | -61.3 | 318.35 | 14.77 | 14.63 |

Table 3 Phonon parameters obtained from the fitting of the infrared reflectivity spectra of the $(\text{Bi}_{0.3}\text{Y}_{0.7})\text{VO}_4$ ceramic (bold type present the modes coming from Bi-based vibrations)

| Mode | ω_{oj} | ω_{pj} | γ_j | $\Delta\epsilon_j$ |
|----------|---------------|------------------------|--------------------|--------------------|
| 1 | 86.97 | 170.99 | 32.31 | 3.77 |
| 2 | 142.85 | 245.14 | 45.68 | 2.74 |
| 3 | 187.97 | 444.15 | 26.78 | 5.38 |
| 4 | 229.35 | 266.24 | 39.57 | 1.25 |
| 5 | 256.07 | 168.85 | 15.32 | 0.44 |
| 6 | 750.00 | 365.67 | 54.21 | 0.24 |
| 7 | 803.83 | 967.63 | 93.02 | 1.35 |
| 8 | 871.76 | 154.23 | 32.06 | 0.03 |
| | | $\epsilon_\infty=4.41$ | $\epsilon_0=19.61$ | |