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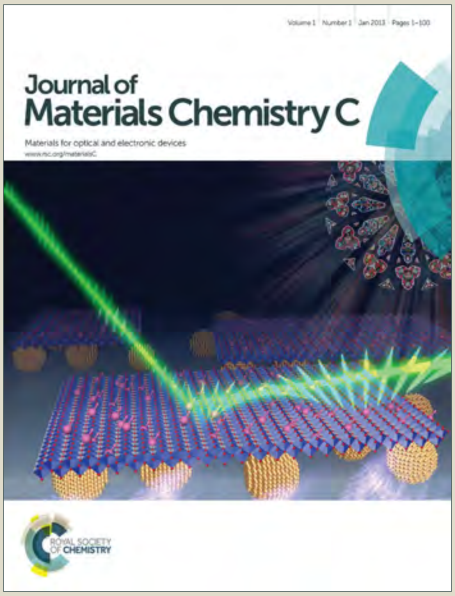

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Novel temperature stable high-ε_r microwave dielectrics in the Bi_2O_3-TiO_2-V_2O_5 system

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Abstract

In the present work, a series of low temperature firing (1-x)$BiVO_4$-xTiO_2 (x=0.4, 0.50, 0.55 and 0.60) microwave dielectric ceramics was prepared using traditional solid state reaction method. From back-scattered electron images (BEI), X-ray diffraction (XRD) and energy dispersive analysis (EDS), there was negligible reaction between $BiVO_4$ and TiO_2 at the optimal sintering temperature ~ 900 ^oC. As x increased from 0.4 to 0.60, permittivity (ε_r) increased from 81.8 to 87.7, quality factor value (Qf) decreased from 12,290 to 8,240 GHz and temperature coefficient (TCF) shifted from -121 to +46 ppm/^oC. Temperature stable microwave dielectric ceramic was obtained in 0.45$BiVO_4$-0.55TiO_2 composition sintered at 900 ^oC with a ε_r ~ 86, a Qf ~ 9,500 GHz and a TCF ~ -8 ppm/^oC. Far-infrared reflectivity fitting indicated that stretching of Bi-O and Ti-O bonds in this system dominated dielectric polarization. This series of ceramics are promising not only for low temperature co-fired ceramic (LTCC) technology but also as substrates for physically and electrically small dielectrically loaded micro-strip patch antennas.

Keywords: (Ceramics, Dielectrics)

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I. Introduction

Microwave dielectric (MW) ceramics are widely used as dielectric resonators (DR), filters, substrates for radio frequency (RF) components and waveguides.[1,2] The driving force for development in MW ceramics depends on applications. For low temperature co-fired ceramics (LTCC) technology, the driving forces are compatibility with low cost electrodes (Ag, Cu, etc.) and reduced sintering temperatures. For resonators and filters, ultra-high quality factors (Qf> *40,000 GHz*) are required to ensure selectivity to in a narrow frequency range and for dielectrically loaded antennas in handheld devices, reduction of size and cost of the component is critical.[3,4] LTCC technology has played an important role in fabrication of modern microwave devices and requires materials with permittivity (ε_r) values between 10 - 100, Qf values > 5000 GHz, near-zero temperature coefficients of resonant frequency (TCF < ±15 ppm/^{o}C). Many low ε_r materials for LTCC technology have been developed and several are commercially available through companies such as Ferro and Dupont.[5,6] However, materials with ε_r above 70 are rare. The classic method to develop LTCC materials is to add low melting point oxides or glasses to high Qf microwave dielectric ceramics to lower their sintering temperatures.[3,7,8] The best known commercial high ε_r microwave dielectric ceramics are the BaO-RE_2O_3-TiO_2 (BRET, RE = La, Nd and Sm) system with properties of $70 < \varepsilon_r < 85$, $8{,}000 < Qf <$ 12,000 GHz, and tunable TCF values near zero but these compositions can only be sintered above 1300 ^{o}C.[9-12] Moreover, their sintering temperatures cannot be lowered to below 1100 ^{o}C using sintering aids without decreasing ε_r to less than 70 accompanied by a significant deterioration in Qf values.[12]

$Bi_2Ti_4O_{11}$-TiO_2 composites[13,14] belong to the Bi_2O_3-TiO_2 binary system, in which there are five known single phase compounds: $Bi_2Ti_4O_{11}$; $Bi_2Ti_2O_7$; $Bi_4Ti_3O_{12}$; $Bi_8Ti_4O_{14}$ and $Bi_{12}TiO_{20}$ as shown in Fig. 1 (a).[15,16] Single phase $Bi_2Ti_4O_{11}$ ceramic was reported to possess a ε_r = 53.2, a Qf ~ 4,500 GHz (at 5 GHz), and a TCF = -550 ppm/^{o}C. Temperature stable microwave dielectric ceramic with composition $0.919TiO_2$-$0.081Bi_2O_3$, which is composed of TiO_2 and $Bi_2Ti_4O_{11}$, was found to possess a high ε_r ~ 80, a high Q (1800 at 5 GHz) and a TCF ~ +21 ppm/°C.[14] In our previous work,[17] CuO was used as sintering aid in $0.92TiO_2$-$0.08Bi_2Ti_4O_{11}$ and it lowered the sintering temperature to 900 ^{o}C whilst maintaining a ε_r = 81, Qf value ~3,500 GHz and a TCF ~ -5.1 ppm/^{o}C. Formation of semiconducting $Cu_9Bi_2Ti_{12}O_{36}$ was thought to be responsible for the reduction in Qf value. Valant et al.[18] also found that nano-TiO_2 additions can further improve Qf. Besides $Bi_2Ti_4O_{11}$, sillenite-structured $Bi_{12}TiO_{20}$ ceramic was reported to possess a ε_r ~ 41, Qf between 3,300 ~ 10,400 GHz, and TCF between – 2 ~ –10.8 ppm/°C, according to Valant and Jeong et al.'s reports[19-21]

In Bi-rich part of the Bi_2O_3-V_2O_5 binary system, there are at least seven known phases, Bi_7VO_{13}, Bi_5VO_{10}, $Bi_{14}V_4O_{31}$, $Bi_7V_3O_{18}$, $Bi_6V_4O_{19}$, $BiVO_4$, and $Bi_2V_8O_{23}$, according to Touboul and Vachon's report.[22] Lv et al. studied this system via solid state reaction method[23] and based on their XRD analysis, five binary compounds: $Bi_{8.1}V_{0.9}O_{14}$, Bi_7VO_{13}, $Bi_8V_2O_{17}$, $Bi_4V_2O_{11}$ and $BiVO_4$were obtained along with two solid solutions: $xBi_2O_3:V_2O_5$ ($5 \leq x \leq 6$) and $(Bi_2O_3)_{1-x}(V_2O_5)_x$ ($0 \leq x \leq 0.069$). In the V-rich part, only a meta-stable $Bi_2V_8O_{23}$ was reported as shown in Fig. 1 (a). Among all the phases in the Bi_2O_3-V_2O_5 binary system, only $BiVO_4$ was reported to possess good microwave properties with a ε_r ~ 68, a Qf value between 6,500 ~ 8,000 GHz, and a TCF between –243 ~ –260 ppm/°C.[24,25] Although reported to react with Ag,[24] $BiVO_4$-based ceramics were found to be chemically compatible with Al and Cu

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electrodes in our previous work[26] which might extend its application in LTCC technology.

According to Lv's report,[23] three single phase compounds, $Bi_{17}V_2TiO_{32.5}$, $Bi_4V_{1.5}Ti_{0.5}O_{10.85}$ and $Bi_{13}V_5TiO_{34}$ exist in the Bi_2O_3–TiO_2–V_2O_5 ternary system and no single phase compounds were reported in the V_2O_5-TiO_2 and TiO_2-$BiVO_4$ binary systems. This indicates that TiO_2 and $BiVO_4$ phases do not react with each other and can co-exist. The absence of single phase compounds in the TiO_2-$BiVO_4$ binary system suggests that immiscible composites may be fabricated. TiO_2 was reported to have a $\varepsilon_r = 100$ and a $Qf \sim 14{,}000$ GHz but a TCF > + 400 ppm/°C.[27] $BiVO_4$ was also reported to possess excellent MW properties (a $\varepsilon_r \sim 68$, a Qf value between 6,500 ~ 8,000 GHz, and a TCF between –243 ~ –260 ppm/°C) and a low sintering temperature about 820 °C. Hence, it attracts us to design novel high permittivity and low sintering temperature composite microwave dielectric ceramics based on the TiO_2-$BiVO_4$ binary system.

In the present work, a series of composite ceramic samples in the TiO_2-$BiVO_4$ binary system were designed and prepared via traditional solid state reaction method. Phase composition, microstructure, microwave dielectric properties and infrared reflectivity were investigated. A wide ternary region in the Bi_2O_3–TiO_2–V_2O_5 phase diagram was discovered with high ε_r and easily adjustable TCF values.

II. Experimental

Proportionate amounts of reagent-grade starting materials of Bi_2O_3 (> 99 %, Shu-Du Powders Co. Ltd., Chengdu, China), TiO_2 and V_2O_5 (> 99 %, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) were measured according to the stoichiometric formulations$(1-x)BiVO_4$-$xTiO_2$ (x=0.4, 0.50, 0.55 and 0.60). Powders were mixed

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and milled for 4 h using a planetary mill (Nanjing Machine Factory, Nanjing, China) by setting the running speed at 150 rpm with the zirconia balls (2 mm in diameter) as milling media. The powder mixture was then dried and calcined at 800 ^{o}C for 4 h. The calcined powders were ball milled for 5 h with a running speed of 200 rpm to obtain fine powders. Then the powders were pressed into cylinders in a steel die with 5 wt. % PVA binder addition under a uniaxial pressure of 150 MPa. Samples were sintered in the temperature range from 850 ^{o}C to 920 ^{o}C for 2 h. Room temperature X-ray diffraction (XRD) was performed using a XRD with Cu Kα radiation (Rigaku D/MAX-2400 X-ray diffractometry, Tokyo, Japan). Prior to examination sintered pellets were crushed in a mortar and pestle to powder. Diffraction pattern was obtained between 2θ of 10-65^{o} at a step size of 0.02 ^{o}. To examine the grain morphology, as-fired and fractured surfaces were investigated by scanning electron microscopy (SEM, FEI, Quanta 250 F). The room temperature infrared reflectivity spectra were measured using a Bruker IFS 66v FTIR spectrometer on Infrared beamline station (U4) at National Synchrotron Radiation Lab. (NSRL), China. Dielectric properties at microwave frequency were measured with the $TE_{01\delta}$ 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:

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

where the f_{T} and f_{T0} were the $TE_{01\delta}$ resonant frequencies at temperature T and T_0, respectively.

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III. Results and Discussions

X-ray diffraction patterns of the (1-x)$BiVO_4$-xTiO_2 (x=0.4, 0.50, 0.55 and 0.60) ceramic samples sintered at their optimal temperatures are presented in Fig. 2. Two sets of peaks corresponding to both rutile TiO_2 and monoclinic scheelite $BiVO_4$ phases were revealed, indicating that $BiVO_4$ and TiO_2 coexist at their sintering temperatures, which is consistent with reported data.[23]

In the monoclinic $BiVO_4$ structure, V^{5+} ions (0.355 Å) occupy tetrahedral (CN4) sites and may be substituted for by Mo^{6+} (0.41 Å), W^{6+}(0.41 Å), Fe^{3+}(0.49 Å) and In^{3+}(0.62 Å).[28] Ti^{4+} has similar ionic radius (0.42 Å in CN4) to that of V^{5+} but prefers to remain in octahedral coordination within the rutile structure (note Ti^{4+} has a strong octahedral site preference in most structures, such as ABO_3 perovskite[29]), permitting chemical and structural immiscibility between $BiVO_4$ and TiO_2.

Back-scattering electron images (BEI) of the as-fired and fractured surfaces of 0.45$BiVO_4$-0.55TiO_2 ceramics sintered at 890 °C for 2 hr and EDS results are shown in Fig. 3. Dense microstructure are revealed and there are two different kinds of grains with white and black contrast. According to EDS analysis, the regions of white and dark contrast are $BiVO_4$ and TiO_2, respectively. The grain size of $BiVO_4$ is ~ 5 μm, which is similar to the reported value,[26] even though the sintering temperature is higher than that of pure $BiVO_4$ ceramic (840 °C). Usually rutile TiO_2 can be densified at high sintering temperature above 1300 °C and here the grain size remains < 1 μm. Fractured surfaces corresponded well with as-fired ones and BEI further confirmed the coexistence of $BiVO_4$ and TiO_2 phases.

ε_r, Q*f*, and TCF as a function of composition and temperature in (1-x)$BiVO_4$-xTiO_2 are shown in Fig. 4. ε_r of $BiVO_4$ and TiO_2 are 68 and 104, respectively, at microwave

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frequencies. Here ε_r increased linearly from 68.5 at x=0.0 to 87.7 at x=0.6. This was accompanied by a commensurate increase in TCF values from – 260 ppm/°C for pure $BiVO_4$ to + 46 ppm/°C at x=0.6. A near-zero TCF (-8 ppm/°C) was achieved in compositions with x=0.55. Sintering temperature increased from 840 °C for pure $BiVO_4$ to 890 °C at x = 0.4, after which it remained stable up to x=0.6. In contrast to the linear trends described above for ε_r and TCF values, Q*f* values exhibited non-linear behavior as a function of x. First Q*f* increased to ~12,290 GHz at x = 0.4 but decreased to 9,500 GHz at x = 0.55. As reported by Alford,[30] the dielectric loss of TiO_2 ceramics doped with divalent and trivalent ions with ionic radii in the range of 0.5 ~ 0.95 Å can be very low (Q ~17 000) at room temperature, which might be attributed to the prevention of formation of Ti^{3+}. In the present work, small amount of V^{5+} might hold the Ti site in rutile structure. A series of modifications based on $0.45BiVO_4$-$0.55TiO_2$ composite were designed on the premise that the large difference in sintering temperatures between $BiVO_4$ and TiO_2 ceramics may cause defects at grain boundaries.[30,31] Therefore, a series of modified rutile structured $Ti_{1-x}(Cu_{1/4}Nb_{3/4})_xO_2$ (ε_r ~ 95, Q*f* ~ 35,000 GHz, TCF ~ + 400 ppm/°C)[32] and $Ti_{1-x}(Cu_{1/3}Ta_{2/3})_xO_2$ materials with low sintering temperatures were chosen to replace pure TiO_2 in the $0.45BiVO_4$-$0.55TiO_2$ composite. Moreover, we have previously shown that Q*f* of $BiVO_4$ was improved by substitution on both A and B sites. Hence, $Bi(Fe,Mo,V)O_4$, $(Na,Bi)(Mo,V)O_4$ series[33,34] were chosen to replace pure $BiVO_4$ in $0.45BiVO_4$-$0.55TiO_2$ composite. In addition, nano-sized TiO_2 (20 nm) particles were also utilized to form composites. The results of these studies are listed in Table I. Despite modification to sintering temperature, properties of the composite end members did not increase as expected and Q*f* remained between 9,000 ~ 12,330 GHz. Furthermore, to avoid any possibility of interfacial defects between $BiVO_4$ and TiO_2

caused during the sintering process, macroscopic composites of well sintered and polished $BiVO_4$ and TiO_2 ceramics samples bonded with adhesive were also measured. Similar Q*f* values were obtained suggesting that the unexpected decrease of Q*f* might not arise from defects during sintering but were intrinsic. It is important to note that for a given sample dimension, the resonant frequency of composites with larger ε_r will be less than those with lower ε_r. Consequently, Q*f* values for $BiVO_4$, TiO_2 and $0.45BiVO_4$-$0.55TiO_2$ composite samples were measured at different resonant frequencies. To a first approximation, Q*f* is considered as a material constant, however, it is well known that[35] for different materials Q*f* values usually change slightly as a function of frequency and this might be the reason of the unexpected decrease in Q*f* values. Anyway, there is no strong evidence here supporting the intrinsic or extrinsic decrease in $BiVO_4$-TiO_2 composites when $x > 0.4$ and this needs further study in detail.

The temperature dependence of ε_r and Q*f* of the $(1\text{-}x)BiVO_4$-$xTiO_2$(x=0.4, 0.5 and 0.55) are presented in Fig. 4 (c). Temperature stable ε_r= 86 and Q*f*=9,500 GHz were obtained over a wide temperature range 20 ~ 125 °C, which is illustrating that compensation of TCF was achieved using composites of $BiVO_4$ and TiO_2. According to Ref,[26] $BiVO_4$ does not react with copper and aluminum at low sintering temperatures and TiO_2 was also reported to be chemically compatible with silver.[18] It is therefore possible that a compatible base metal electrode system could be developed for co-firing with $(1\text{-}x)BiVO_4$-$xTiO_2$ composites. The sintering temperatures and microwave dielectric properties of some high ε_r microwave dielectric ceramics are listed in Table II for comparison[34-36] with the composites fabricated in this study. The $(1\text{-}x)BiVO_4$-$xTiO_2$ composites possess both low sintering temperatures and good microwave dielectric properties. Therefore, based on the data

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shown in Fig. 1 (b), a series of temperature stable microwave dielectric ceramics might be achievable in the Bi_2O_3-TiO_2-V_2O_5 ternary system along the composition line ($0.88TiO_2$-$0.12Bi_2Ti_4O_{11}$)-($0.45BiVO_4$-$0.55TiO_2$). Besides LTCC technology with suitable electrode, such materials also have great potential for dielectric substrates in ultra-small dielectrically-loaded micro-strip patch antennas. The current generation of substrates utilize compositions based on BRET,[36-38] which have sintering temperatures above 1300 °C. Moreover, BRET compositions with comparable ε_r (86.2) have lower Q*f* than that of the composites described in this contribution. $BiVO_4$–TiO_2 composites therefore offer a low sintering temperature, RE-free, and high Q*f* alternative to BRET.

To further study the intrinsic microwave dielectric properties, infrared reflectivity spectra of the $0.45BiVO_4$-$0.55TiO_2$ ceramic were analyzed using a classical harmonic oscillator model:

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

where $\varepsilon^*(\omega)$ is 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. ε_∞ is the dielectric constant caused by the electronic displacive polarization at optical frequency. Assuming that within the microwave region $\omega \ll \omega_{oj}$, the real part and imaginary part of microwave permittivity can be written as:

$$\varepsilon'(\omega) = \varepsilon_\infty + \sum_{j=1}^{n} \Delta\varepsilon_j' = \varepsilon_\infty + \sum_{j=1}^{n} \frac{\omega_{pj}^2}{\omega_{oj}^2}, \qquad (3)$$

$$\varepsilon''(\omega) = \sum_{j=1}^{n} \frac{\gamma_j \omega_{pj}^2}{\omega_{oj}^2}\omega, \qquad (4)$$

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and the complex reflectivity R(ω) can be written as:

$$R(\omega)=\left|\frac{1-\sqrt{\varepsilon^*(\omega)}}{1+\sqrt{\varepsilon^*(\omega)}}\right|^2 . \tag{5}$$

Fitted infrared reflectivity values, complex permittivities and phonon parameters are shown in Fig. 5 and Table III. The calculated ε_r and dielectric loss values match well those measured using $TE_{01\delta}$ method, which implies that the majority of the dielectric contribution to this system at microwave frequencies may be attributed to the absorptions of structural phonon oscillations in the infrared region and very little contribution was from defect phonon scattering. The optical dielectric constant calculated from the infrared spectra is about 5.87, which is only7 % percent of the total polarizability contribution at microwave frequencies, and this implies that the main polarization contributions to microwave permittivity of high ε_r materials come from ionic polarization rather than electronic. Contributions from each mode is listed as $\Delta\varepsilon_j$ in Table III. The contributions from the first four modes, which are below 200 cm^{-1}, can reach 70.15 and about 85% of the total value, which means that the stretching of Bi-O and Ti-O bond lengths determine the main dielectric polarization rather than bending modes. This conclusion corresponds well with our previous studies.[2, 33]

IV. Conclusions

In the present work, temperature stable high ε_r microwave dielectric ceramics were explored in the Bi_2O_3-TiO_2-V_2O_5 ternary system. The 0.45$BiVO_4$-0.55TiO_2 ceramics sintered at 900 ^oC for 2 h possessed excellent microwave dielectric properties with a ε_r ~ 86, a Qf ~ 9,500 GHz and a near-zero TCF ~ -8 ppm/^oC. These composite ceramics were composed of both scheelite-structured $BiVO_4$ (with large negative TCF)

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and rutile TiO_2 (with large positive TCF), which was supported both by the XRD and EDS analysis. Far-infrared reflectivity fitting indicated that stretching of the Bi-O and Ti-O bonds in this system dominate the dielectric polarization. Therefore, along with the TiO_2-$Bi_2Ti_4O_{11}$ system, the Bi_2O_3-TiO_2-V_2O_5 ternary system presents a wide compositional region with easily adjustable ε_r and TCF that can be fabricated by a traditional solid state reaction method at 900°C. The materials therefore have great potential for exploitation both in LTCC technology and ultra-small, dielectrically-loaded micro-strip patch antennas applications with RE-free composition, lower sintering temperature, and higher *Qf* alternative to BRET materials.

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Table Captions:

Table I. Microwave dielectric properties of some modifications of $0.45BiVO_4$-$0.55TiO_2$ ceramics

Table II. Sintering temperatures (S.T.) and microwave dielectric properties of high-K microwave dielectric ceramics

Table III. Phonon parameters obtained from the fitting of the infrared reflectivity spectra of $0.45BiVO_4$-$0.55TiO_2$ceramic

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Table I. Microwave dielectric properties of some modifications of $0.45BiVO_4$-$0.55TiO_2$ ceramics

Compositions	S.T. (^oC)	ε_r	Qf (GHz)	TCF (ppm/^oC)
$0.45Bi(Fe,Mo,V)O_4$-$0.55TiO_2$	880	74.8	9,300	+22
$Bi(Fe,Mo,V)O_4$-TiO_2	stack	75.4	9,240	+18
$0.45(Na,Bi)(Mo,V)O_4$-$0.55TiO_2$	870	83.8	8,300	+15
$0.45BiVO_4$-0.55 $Ti_{1-x}(Cu_{1/4}Nb_{3/4})_xO_2(x=0.15)$	870	79.8	12,330	-65
$0.45BiVO_4$-0.55 $Ti_{1-x}(Cu_{1/4}Ta_{3/4})_xO_2(x=0.15)$	890	78.7	10,240	-46
$0.45BiVO_4$-$0.55TiO_2$ (nano~20μm)	870	80.5	9,500	+10
$0.45BiVO_4$-$0.55TiO_2$	900	86.2	9,500	-8

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Table II. Sintering temperatures (S.T.) and microwave dielectric properties of high-K microwave dielectric ceramics

Compositions	S.T. (^{o}C)	ε_r	Qf (GHz)	TCF (ppm/^{o}C)	Ref.
$BiVO_4$	820	68	8,500	-260	24,25
$0.88TiO_2$-$0.12Bi_2Ti_4O_{11}$	>1150	81	6,500~8,500	+8~15	13,14,17
TiO_2 (nano)-$Bi_2Ti_4O_{11}$-CuO	915	80	9,500	0	19
$Ba_{6-x}Sm_{8+2x}Ti_{18}O_{54}$ (x=2/3)	1400	80	10,700	-15	31
$Ba_{6-x}(Sm,Nd)_{8+2x}Ti_{18}O_{54}$	1350	78.9	9,060	-5.3	36
TiO_2-$Bi_2Ti_4O_{11}$-CuO	900	81.5	3,500	-5.1	18
Bi(Fe,Mo,V)O_4	820	74.8	13,000	+20	30
(Li,Bi)(MoV)O_4	650	81	8,000	-90~+9.7	26
$0.5BiVO_4$-$0.5TiO_2$	900	85.6	11,650	-55	This work
$0.45BiVO_4$-$0.55TiO_2$	**900**	**86.2**	**9,500**	**-8**	**This work**
$0.45BiVO_4$-$0.55TiO_2$ (nano)	870	80.5	9,500	+10	This work
$0.4BiVO_4$-$0.6TiO_2$	900	87.7	8,240	+46	This work
TiO_2	1300	100	20,000	+400	13
CaO-Li_2O-Ln_2O_3-TiO_2	1400	110	4,500	+7	38

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Table III. Phonon parameters obtained from the fitting of the infrared reflectivity spectra of 0.45$BiVO_4$-0.55TiO_2ceramic

Mode	ω_{oj}	ω_{pj}	γ_j	$\Delta\varepsilon_j$
1	82.52	412.86	23.27	25.0
2	109.60	607.09	44.64	30.7
3	145.62	483.00	43.22	11.0
4	177.53	329.58	42.45	3.45
5	255.28	263.79	53.14	1.07
6	273.07	126.68	17.50	0.22
7	310.41	289.19	43.68	0.87
8	346.43	224.05	35.31	0.42
9	400.66	344.27	57.39	0.74
10	535.28	559.14	102.07	1.09
11	632.53	821.63	106.98	1.69
12	675.01	610.32	108.10	0.82
0.45$BiVO_4$ -0.55TiO_2	ε_∞=5.87		ε_0=82.2	

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Figure Captions:

Fig. 1. Schematic of phase diagram of the Bi_2O_3-TiO_2-V_2O_5 binary system after Touboul and Lv's reports (a)[22,23] and a promising region for temperature stable microwave dielectrics (b)

Fig. 2. X-ray diffraction patterns of the (1-x)$BiVO_4$-xTiO_2 (x=0.4, 0.50, 0.55 and 0.60) ceramic samples sintered at their optimal temperatures (o—rutile phase; *—scheelite).

Fig. 3. Back-scattered electron images of the as-fired (a) and fractured (b) surfaces of the 0.45$BiVO_4$-0.55TiO_2 ceramics sintered 2h at 890 ^{o}C (The associated energy dispersive X-ray spectrum is inserted)

Fig. 4. Microwave ε_r and Q*f* (a), sintering temperature and TCF (b) as a function of x in the (1-x)$BiVO_4$-xTiO_2 compositions and their temperature dependence (c).

Fig. 5. Measured and calculated infrared reflectivity spectra (solid line for fitting values and circle for measured values) and fitted complex dielectric spectra of 0.45$BiVO_4$-0.55TiO_2 ceramic (circles are experimental in microwave region).

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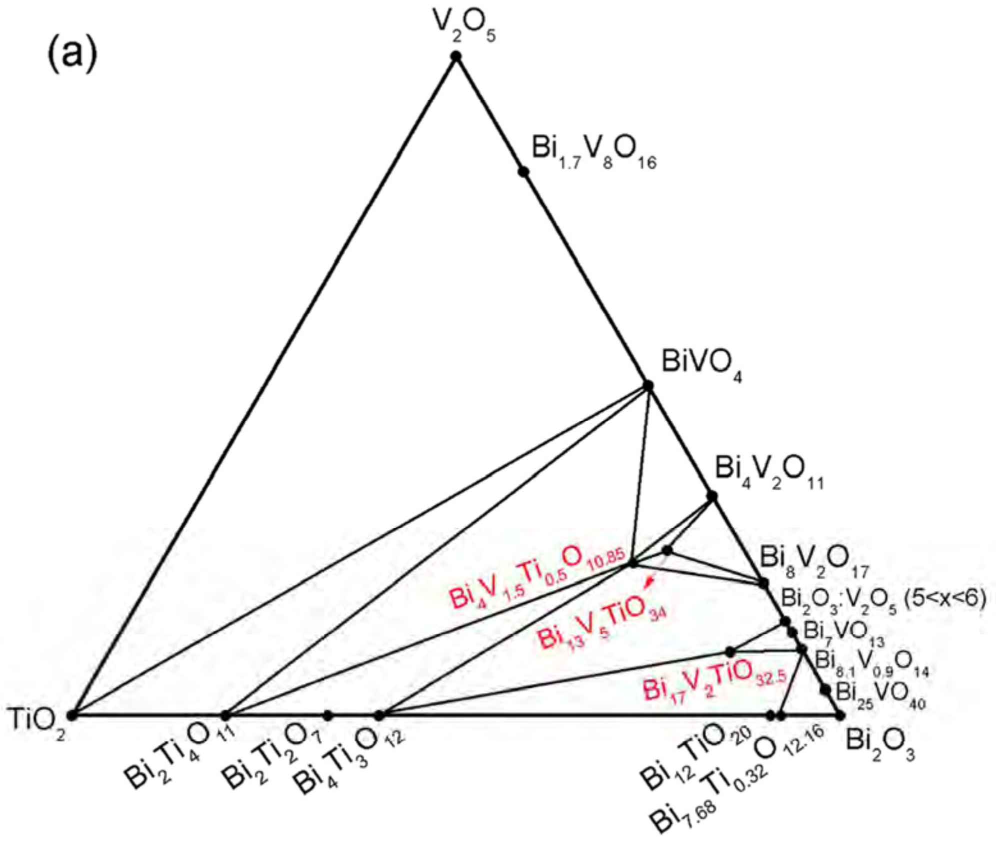

Fig. 1. Schematic of phase diagram of Bi2O3-TiO2-V2O5binary system after Touboul and Lv’(a) [22, 23] and a promising region for temperature stable microwave dielectrics (b)
84x72mm (300 x 300 DPI)

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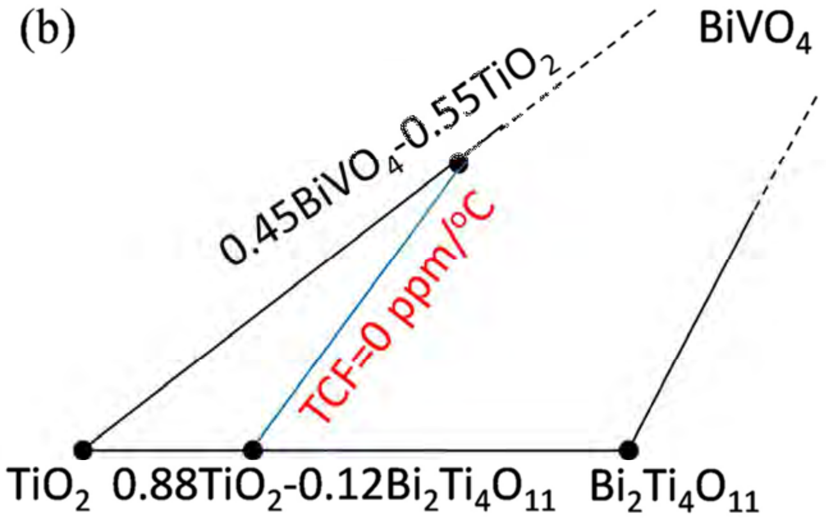

Fig. 1. Schematic of phase diagram of Bi2O3-TiO2-V2O5binary system after Touboul and Lv'(a) [22, 23] and a promising region for temperature stable microwave dielectrics (b)
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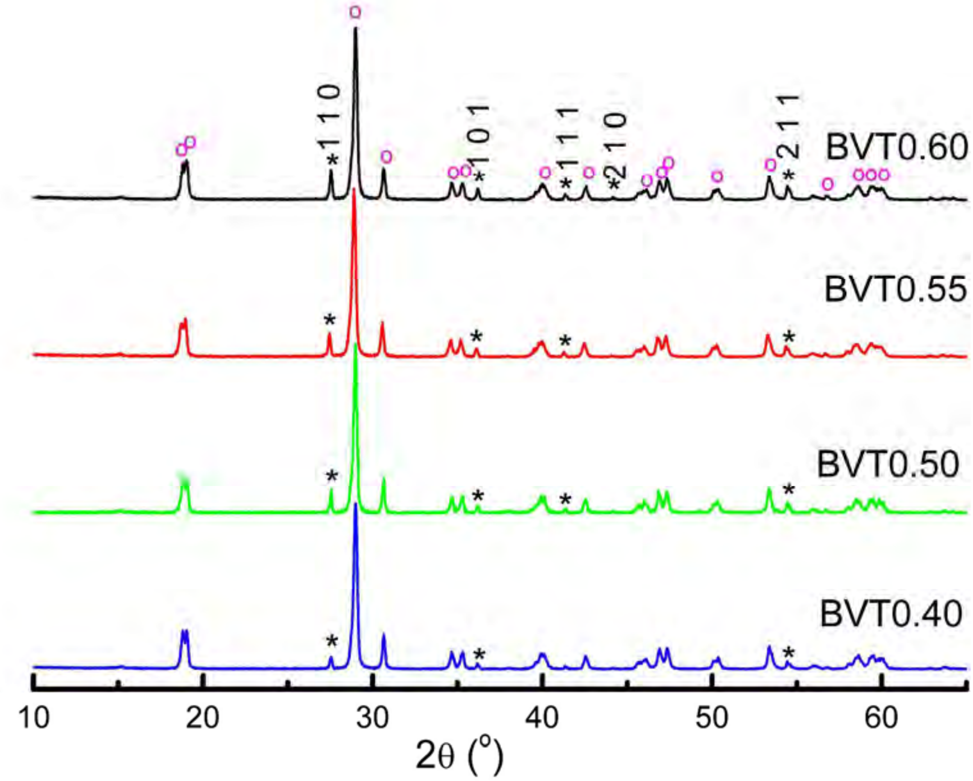

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87x72mm (600 x 600 DPI)

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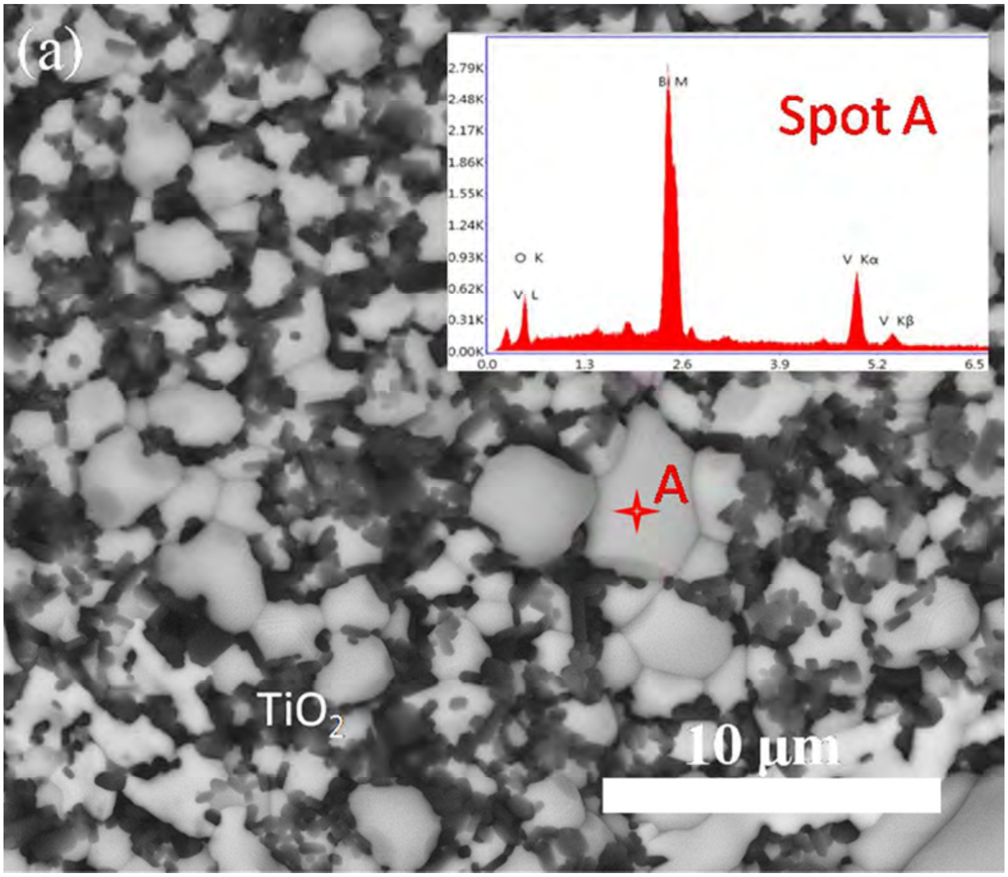

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84x73mm (300 x 300 DPI)

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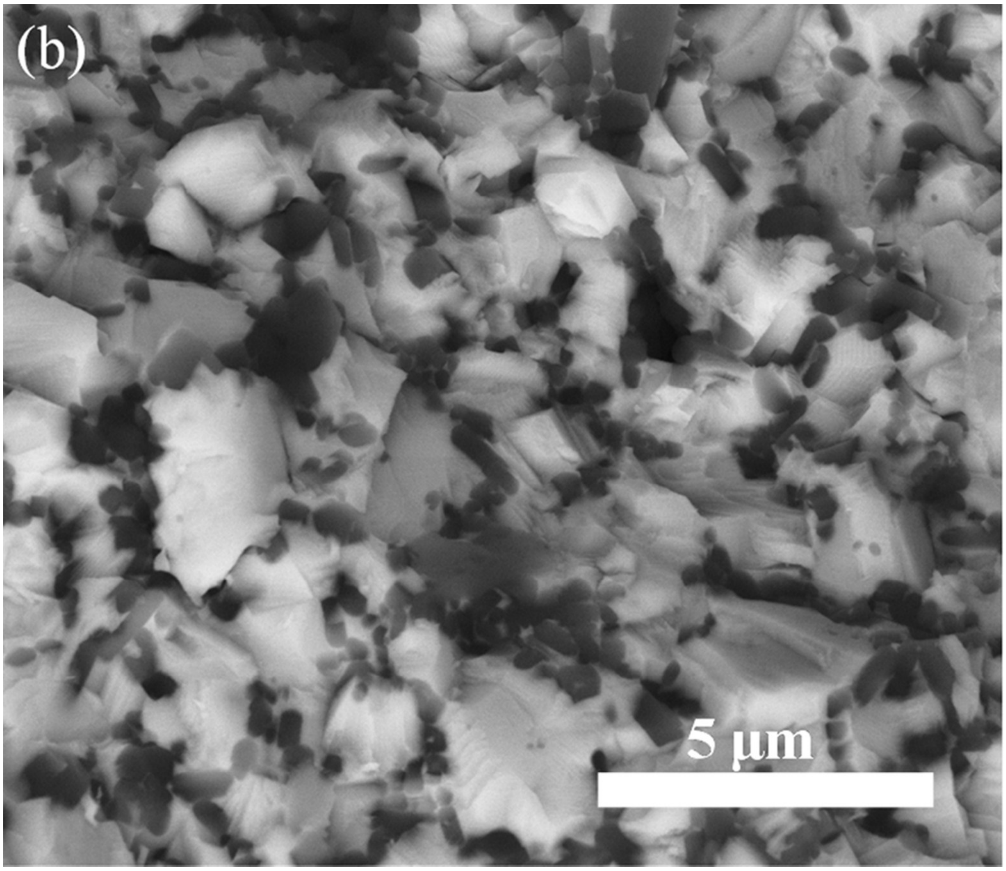

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84x72mm (300 x 300 DPI)

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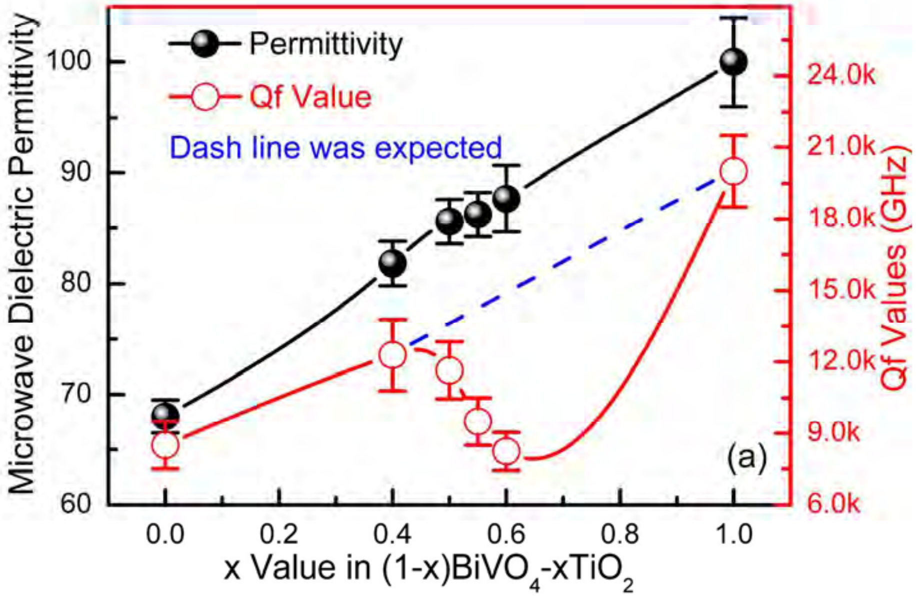

Fig. 4. Microwave εr and Qf (a), sintering temperature and TCF (b) as a function of x in (1-x)BiVO4-xTiO2 compositions and their temperature dependence (c).
95x66mm (600 x 600 DPI)

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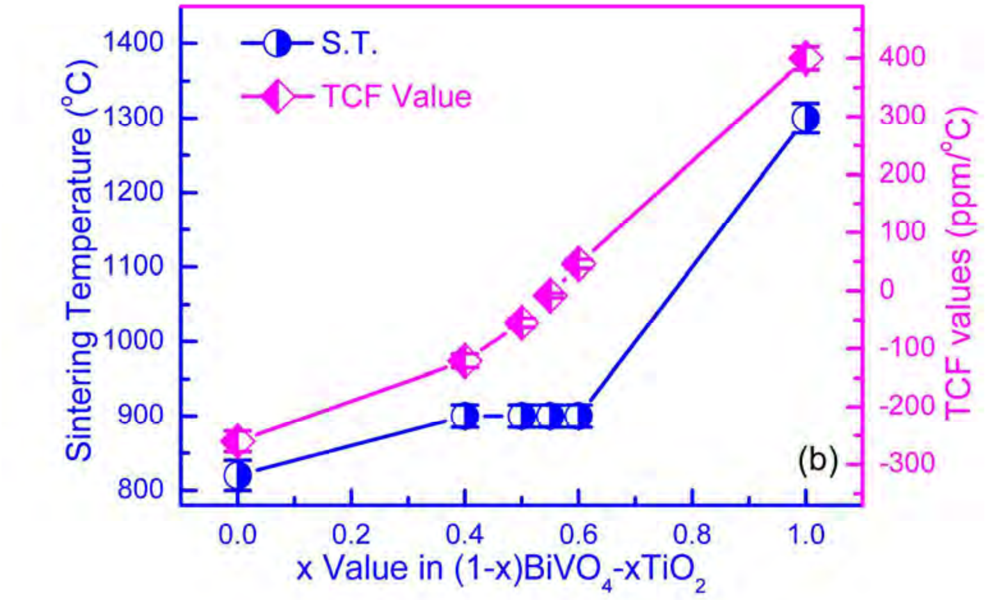

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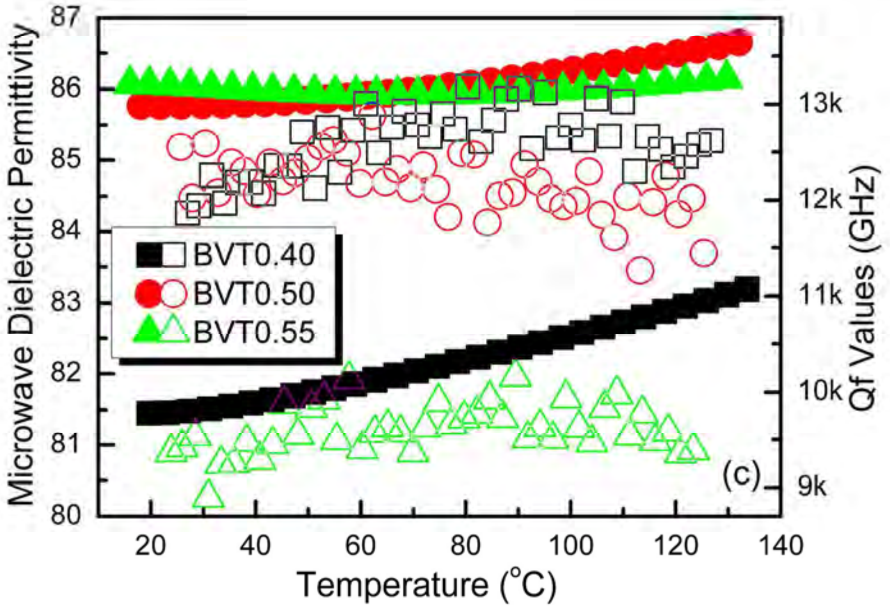

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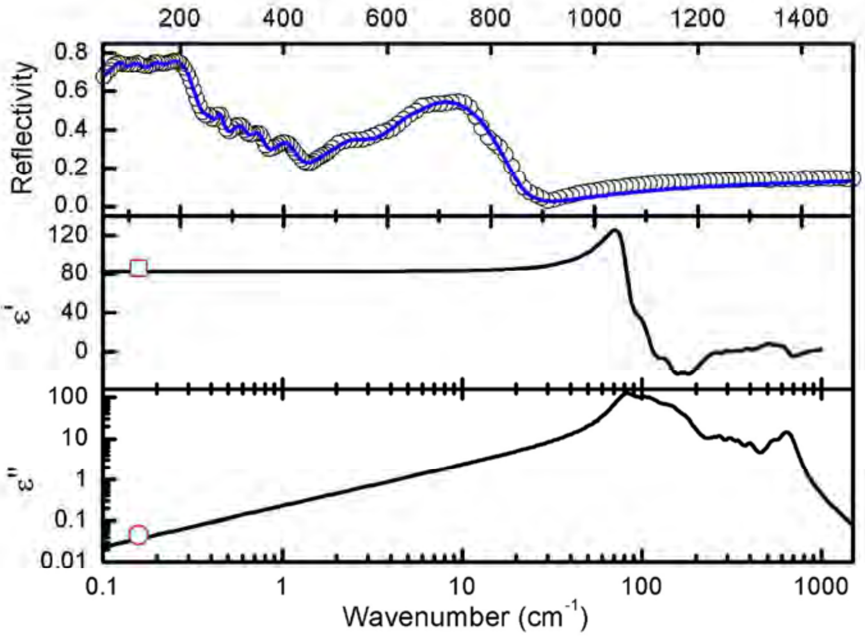

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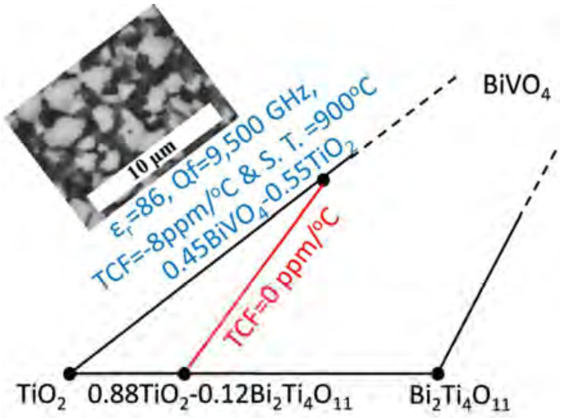

Temperature stable microwave dielectric ceramics were obtained for compositions with 0.45$BiVO_4$-0.55TiO_2 sintered at 900 °C with ε_r ~ 86, a Q*f* ~ 9,500 GHz and TCF ~ -8 ppm/°C. It is promising for both low temperature co-fired ceramic technology and dielectrically loaded micro-strip patch antennas substrates. Far-infrared reflectivity fitting indicated that stretching of Bi-O dominated dielectric polarization.