Synthesis and microwave dielectric behavior of $(\text{Bi}_{1-x}\text{Pb}_x)\text{NbO}_4$ ceramics

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Ceramic samples of $(\text{Bi}_{1-x}\text{Pb}_x)\text{NbO}_4$ ($x = 0, 0.025, 0.05, 0.10, 0.15, 0.20$) with 0.75 wt.% V_2O_5 addition sintered at 920°C , 940°C and 960°C are investigated. Pb is selected as a substitute for Bi^{3+} in BiNbO_4 ceramics as it exists in two stable valence states of +2 and +4 and the average valency matches to that of Bi^{3+} . The average Shannon radius (for octahedral coordination) of Pb^{2+} (1.19 Å) and Pb^{4+} (0.775 Å) cations is 0.9825 Å, which is similar to that of Bi^{3+} ion (1.03 Å). The dense (> 94%) polycrystalline $(\text{Bi}_{1-x}\text{Pb}_x)\text{NbO}_4$ samples fabricated mostly reveal orthorhombic (Pnna) phase ($\alpha\text{-BiNbO}_4$, Sp. Gp. 52) by powder XRD. Presence of satellite $\text{Pb}_2\text{Nb}_2\text{O}_7$ phase, the amount of which is increasing with increase in Pb content, is also noticed. The microwave dielectric constant (ϵ'_r) values of the niobates are found to increase from 42 to 71, whereas the quality factor (Q_{uf}) values are found to decrease from 5400 to 550 GHz with increasing substitution of Pb. The compositions so synthesized are important as hardly there are any microwave dielectric ceramics available with $45 < \epsilon'_r < 75$.

Keywords: Ceramics; sintering; BiNbO_4 ; microwave dielectric properties; quality factor.

1. Introduction

In recent past, civilian electronic communication system adopted the microwave (GHz) frequency regime. This necessitated development of new dielectric materials and also reduction in size and weight of RF and microwave dielectric components.^{1,2} A special class of dielectric materials, viz. low temperature co-fired ceramics (LTCCs) have extensively been incorporated in multilayer RF and microwave components such as chip LC and planar filters.^{2,3} The useful values of dielectric constant (ϵ'_r) required for the microwave resonator and the internal capacitor applications in LTCCs are usually between 20 and 100.³ It is noteworthy to mention here that materials with $45 \leq \epsilon'_r \leq 75$ are currently not available.⁴ Bismuth niobate (BiNbO_4) based ceramics have been explored as potential dielectrics for LTCCs on the grounds of their low sintering temperatures (STs) ($< 1000^\circ\text{C}$), making co-firing under reducing atmosphere possible with copper (melting point 1083°C) as electrode, besides having the desirable microwave dielectric constant ($\epsilon'_r \sim 43$).^{5,6} However, these ceramics are invariably difficult to densify above 85% theoretical density (TD), nevertheless, density can be improved to $\geq 95\%$ using various sintering

additives.⁶ Hence, CuO or V_2O_5 (or CuO– V_2O_5 mixture) as a sintering aid is often used, which lowers the ST to $< 1000^\circ\text{C}$.⁷ For BiNbO_4 ceramics, the room temperature stable form is $\alpha\text{-BiNbO}_4$ which is orthorhombic (space group Pnna), and transforms irreversibly above 1020°C to a lower symmetry triclinic form $\beta\text{-BiNbO}_4$ (sp. gp. P1).⁸

Kageta *et al.*⁶ reported the dielectric properties of BiNbO_4 ceramics at microwave frequency for the first time, i.e., dielectric constant $\epsilon'_r \sim 43$, quality factor $Q \sim 4260$ (at 4.3 GHz). However, a large scatter in Q_{uf} (1800–17,000 GHz) exists amongst the reported literature.^{1,5,6,9} Some of the earlier interesting reports on polycrystalline BiNbO_4 include BiNbO_4 ceramics with sintering aids such as (i) CuO (0.125–1.5 wt.%)⁸ and (ii) V_2O_5 (0.125–1.5 wt.%) to improve ϵ'_r and Q_{uf} .⁷ Subsequently, several researchers attempted to modify the quality factor (Q_{uf}) and the τ_f (temperature coefficient of resonant frequency) by discretely substituting La^{3+} , Sm^{3+} , Nd^{3+} , Dy^{3+} or Y^{3+} in place of Bi^{3+} ,^{10–14} and Ta^{5+} or Sb^{5+} in place of Nb^{5+} .^{12,15} The phase-transition temperature of BiNbO_4 ceramics got decreased due to the lattice distortion caused by the ionic size difference between Ln^{3+} ($\text{Ln} = \text{La}, \text{Sm}, \text{Y}$) and Bi^{3+} .^{5,9,10}

Shihua *et al.*¹ studied $(\text{Bi}_{1-x}\text{Ln}_x)\text{NbO}_4$ ($x = 0.03$ and $\text{Ln} = \text{Ce}^{3+}$, Nd^{3+} , Dy^{3+} , Er^{3+}) ceramics and correlated the decrease in Q_u value to decrease in both the bond valence and the size of Ln-ion, whereas the decrease of ϵ'_r was correlated to the decrease in polarizability with Ln-ion. Kim *et al.*¹⁶ associated the changes in microwave dielectric properties to phase transitions from orthorhombic to triclinic. Wang *et al.*¹⁷ did complex substitution of both 0.38 at.% La and 0.62 at.% Nd to match their effective ionic radius to the ionic radius of Bi^{3+} , i.e., made $\text{Bi}_{1-x}(\text{La}_{0.38}\text{Nd}_{0.62})_x\text{NbO}_4$, ($x \leq 0.07$), and observed that phase transition temperature for α - to β - BiNbO_4 was lowered below 900°C . Huang *et al.*¹¹ also observed decrease of phase-transition temperature when Bi^{3+} ($1.030 \text{ \AA}$) was partly substituted by La^{3+} ($1.032 \text{ \AA}$). Later, Shihua *et al.*¹⁸ reported the dielectric properties of BiNbO_4 doped with B_2O_3 and explained the dielectric relaxation behavior on the basis of $(2V_{\text{Bi}}''' - 3V_{\text{O}}'')$ defect pair model and also correlated it with microwave dielectric properties. Mao *et al.*¹⁹ also made a similar attempt by doping MoO_3 in BiNbO_4 viz. $\text{BiNb}_{1-x}\text{Mo}_x\text{O}_4$.

In this work, Pb^{2+} – Pb^{4+} is selected as a substitute for Bi^{3+} since the average valency charge can be assumed to be same and small ionic size difference (Bi^{3+} : $1.03 \text{ \AA}$, Average of Pb^{2+} – Pb^{4+} : $0.9825 \text{ \AA}$) is expected to fetch very interesting properties. V_2O_5 (0.75 wt.%) was used as a sintering aid. The main purpose of our work is to correlate the effects of Pb substitution on the sintering behavior and microwave dielectric properties of $(\text{Bi}_{1-x}\text{Pb}_x)\text{NbO}_4$ ceramics.

2. Experimental Work

$(\text{Bi}_{1-x}\text{Pb}_x)\text{NbO}_4$ ceramics samples ($x = 0, 0.025, 0.05, 0.10, 0.15, 0.20$) were prepared by conventional solid-state reaction method. High-purity AR grade oxide powers, i.e., Bi_2O_3 (> 99.99%, Sigma-Aldrich), Pb_3O_4 (> 99.99%, Fluka), and Nb_2O_5 (> 99.99%, Sigma-Aldrich), were used as raw materials. These oxide powders were mixed according to desired stoichiometry of the ceramics to be prepared and hand ground for 4 h in an agate mortar pestle. The milled mixtures were collected, dried and solid state reacted at 850°C for 3 h, the resulting powders were mixed with a mixture of V_2O_5 (0.75 wt.%), and then reground for 4 h. After drying, the powders were mixed with 3 wt.% polyvinyl alcohol (PVA) binder and were uniaxially pressed into pellets of 10 mm diameter and 5 mm height at a compaction pressure of 100 MPa to form green compacts. The green compacts so formed were subsequently sintered at various temperatures from 920°C to 960°C in air for 3 h and furnace cooled. Fabrication of a few $(\text{Bi}_{1-x}\text{Pb}_x)\text{NbO}_4$ ceramic samples without the addition of V_2O_5 was also attempted. However, the sintered density obtained was very low. This suggested that only Pb_3O_4 addition did not wet the samples and further did not cause any densification.

The bulk densities of the sintered ceramics were measured using the Archimedes' method following the guidelines of

ASTM method C 373 1988 (2006).²⁰ Phase identification was carried out using an X-ray diffractometer (PanAlytical XPERT-PRO Diffractometer) in 2θ range of 20° – 70° with a Cu K α radiation at an operating voltage of 40 kV and current of 30 mA. The TD was calculated by applying the rule of mixture as: TD = (volume fraction of BiNbO_4 phase $\times$ its theoretical density) + (volume fraction of PbNb_2O_7 phase $\times$ its TD). The experimentally measured density was then divided by this value to convert it into %TD value. The lattice parameters were refined using Wincell software.²¹ To prevent bismuth loss, the pellets were sintered within a sealed alumina crucible. Microstructures of the polished and thermally etched surfaces of the sintered pellets samples were observed by a scanning electron microscopy (FEI Quanta 200). Dielectric post (DP) resonator technique was employed for microwave characterization of the ceramic samples. The sample under test was placed over a low electric loss support material and was enclosed in a microwave cylindrical cavity, which acted as a resonating structure. The TE_{011} mode was identified for each resonator. The measurements were done using Agilent 8722ES vector network analyzer (VNA) at room temperature and ~ 4 – 5 GHz frequencies. The real part (ϵ'_r) of relative permittivity was computed from the measured resonance frequency (f) of the resonator containing the sample under test. The loaded Q factor (Q_L) of the resonator was measured directly from the VNA and the unloaded Q factor (Q_u) was calculated using a computer program which took into account the cavity losses and coupling conditions.^{22,23} Temperature coefficient of dielectric constant was measured at 1 kHz frequency Novocontrol alpha analyzer from room temperature to 125°C .

3. Results and Discussion

The phases in the $(\text{Bi}_{1-x}\text{Pb}_x)\text{NbO}_4$ ceramics were obtained using powder X-ray diffraction (XRD) technique. The shift of all the peak towards left (Fig. 1(a)) indicated that the volume of the basic orthorhombic unit cell was increasing along with the formation of a substitutional solid solution for the addition of Pb made. The XRD patterns of sintered sample of $(\text{Bi}_{1-x}\text{Pb}_x)\text{NbO}_4$ (Fig. 1(a)), revealed a primary orthorhombic phase formation for all the different STs along with a secondary lead niobium oxide ($\text{Pb}_2\text{Nb}_2\text{O}_7$) phase for higher lead substitutions ($x > 0.05$). All the observed (hkl) reflections could be indexed satisfactorily to either of the orthorhombic BiNbO_4 unit cell (JCPDS file No. 820348) or rhombohedral $\text{Pb}_2\text{Nb}_2\text{O}_7$ phase (JCPDS file No. 400829). Figure 1(b) shows the normalized XRD patterns of all the sintered samples. The bulk density (%TD), lattice parameters and cell volume along with the volume fractions of the secondary $\text{Pb}_2\text{Nb}_2\text{O}_7$ phase computed for the sintered samples are presented in Table 1.

It was noted from Table 1 that the samples crystallize in single orthorhombic phase up to addition of 0.05 Pb/mol (x), beyond which secondary $\text{Pb}_2\text{Nb}_2\text{O}_7$ phase appeared and its

Fig. 1. (a) XRD data of the $(\text{Bi}_{1-x}\text{Pb}_x)\text{NbO}_4$ samples sintered at 920–960°C and (b) XRD data (normalized to highest peak by dividing with the highest intensity peak amongst all the samples and multiplying with the common multiplier generated) of sintered $(\text{Bi}_{1-x}\text{Pb}_x)\text{NbO}_4$ samples. (*-planes corresponding to secondary $\text{Pb}_2\text{Nb}_2\text{O}_7$ phase).

Table 1. Bulk density as %TD, refined lattice parameters, cell volume and volume fractions of the Secondary $\text{Pb}_2\text{Nb}_2\text{O}_7$ phase.

x	Sintering Temp.	%TD	Refined lattice parameters for orthorhombic $\alpha\text{-BiNbO}_4(\text{\AA})$			Cell Volume ($\text{\AA}^3$)	Vol% $\text{Pb}_2\text{Nb}_2\text{O}_7$
			a	b	c		
0	920	94.2	5.6731	11.7101	4.9782	330.715	0.0
0.025	920	94.2	5.6682	11.6786	4.9808	329.707	0.0
0.05	920	94.3	5.6803	11.7002	4.9933	331.850	0.0
0.1	920	94.9	5.6801	11.7090	4.9983	332.419	35.8
0.15	920	95.2	5.6713	11.6853	4.9839	330.284	34.2
0.2	920	96.8	5.6765	11.7057	4.9755	330.610	42.0
0.2	940	97.5	5.6838	11.7206	4.9806	331.768	44.1
0.2	960	96.8	5.6913	11.7325	4.9923	333.346	44.4

amount increased for higher Pb additions. The extent (or fraction) of orthorhombic phase transition to $\text{Pb}_2\text{Nb}_2\text{O}_7$ was found to be at a maximum of 44% by volume for 0.20 Pb/mol (x). It was determined from the intensity ratio ($R = I_{\text{secondary}} / [I_{\text{secondary}} + I_{\text{ortho}}]$), where $I_{\text{secondary}}$ and I_{ortho} represented the intensities of secondary [(006)+(202)] and orthorhombic [(121)+(040)] peaks, respectively. Increase of ST from 920°C to 960°C resulted in a marginal increase of secondary $\text{Pb}_2\text{Nb}_2\text{O}_7$ phase from 42% to 44% by volume for 0.20 Pb/mol (x). All the sintered $(\text{Bi}_{1-x}\text{Pb}_x)\text{NbO}_4$, ($x = 0\text{--}0.20$) showed good sintered density ($> 94\%$ TD), ($\text{TD} \approx 7.4 \text{ g/cm}^3$). The change in lattice parameter and cell volume was not uniform with increase in Pb addition from 0 to 0.20 Pb/mol (x), whereas a small monotonic rise for all the a , b and c lattice parameters and cell volume was noted for the increase in temperature from 920°C to 960°C. No triclinic BiNbO_4 phase was observed for the entire range of Pb substitution and ST.²⁴

The correlation of the bulk densities to the STs (920–960°C) is shown in Fig. 2. It was noted that Pb substitution for Bi improved sinterability mostly due to increase in the

amount of Pb-based low-firing-temperature oxides (m.pt. of $\text{Pb}_3\text{O}_4 \sim 800^\circ\text{C}$) apart from 0.75 wt.% V_2O_5 (m.pt. 690°C) added as sintering aid. In our previous work, seldom addition of 0.50 wt.% V_2O_5 to BiNbO_4 resulted in $\sim 93\%$ TD for the samples sintered at 960°C . The grains also were slightly elongated in shape.²⁵ A much higher sintered density of 97.5%TD was obtained for the samples with 0.20 Pb/mol (x) sintered at 940°C (see Table 1). The rise in %TD value in spite of an increase in cell volume for $x = 0.20$ is mainly because of decrease in the porosity content for a higher ST of 940°C . A limited solid solubility of 0.05 Pb/mol (x) in place of Bi in BiNbO_4 compound was noted for the range of samples studied (0.05–0.20 Pb/mol (x)). The reason may be partial fulfilment of either of the factors such as difference of crystal structures, electronegativity difference (leading to increased chemical reactivity) or valency difference as per Hume-Rothery rules of solid solubility. A marginal variation in sintered density was noted till the solid solubility limit of 0.05 Pb/mol (x) in BiNbO_4 , followed by a steep rise for the two phase mixture of $\alpha\text{-BiNbO}_4$ and $\text{Pb}_2\text{Nb}_2\text{O}_7$. An overall increase as seen from the rise in %TD as shown in Table 1

Fig. 2. Bulk densities (as %TD) of (Bi_{1-x}Pb_x)NbO₄ ceramics at different STs.

(also in Fig. 2) in the density value was observed for the substitution of heavier Bi (at. wt. ≈ 209 amu) by the marginally lighter Pb (at. wt. ≈ 207 amu) ion. The increase in density was mostly attributed to the higher occurrence of liquid phase for higher Pb₃O₄ content, causing better elimination of porosity. The four important factors for liquid phase sintering to occur are higher wettability, solubility, and capillary pressure apart from sufficient amount of liquid phase to be present. Evidently, it could be assessed that the wetting was good as no swelling or liquid extrusion from the compact surface was noted.^{25,26} The individual effect of these parameters was not studied as it was beyond the scope of this work. For sintering at 920°C for 3 h, the maximum sintered density increased from 7.0 g/cm³ (94.2%TD) to 7.2 g/cm³ (96.8%TD) when x increased from 0 to 0.2. For all samples with different Pb additions, as the ST increased from 920°C to 960°C, the sintered densities of samples first increased and

reached the maximum values at 940°C, beyond which there was a fall in the density. This may be attributed to increase in concentration of defects such as oxygen vacancies. The likely causes of defects can be identified as mentioned below.

The evaporation of bismuth oxide in layered ceramics such as BiNbO₄ is very difficult to prevent and it leads to formation of oxygen vacancies.²⁷ These vacancies usually get created during sintering and the charge compensation follows the reaction as given below,²⁸ leaving behind free electrons and making these ceramics *n*-type (In the present work, it is attempted to minimize this loss by sintering these ceramics in a sealed alumina crucible).

During cooling (after sintering) certain reoxidation occurs, which however is restricted only to the surface and grain boundaries due to inadequacy of available time, hence not affecting the defects generated within bulk.²⁹ Another possibility that could exist is the formation of oxygen vacancies because of predominant Schottky equilibrium.³⁰ The defect reaction then can be written as;

Both these reactions result in an oxygen deficient oxide. These oxygen vacancies are also likely to adversely affect the dielectric loss by forming defect dipoles.

The SEM micrographs of the polished and thermally etched (Bi_{1-x}Pb_x)NbO₄, ($x = 0-0.2$) samples sintered at 920–960°C are shown in Figs. 3(a)–3(e). When results of samples with varying x from 0 to 0.20 were compared, the effect of liquid phase sintering became quite distinctly visible from spheroidized grains and fused grain boundaries. For $x \leq 0.1$, the grain shape was either prismatic or relatively flattened due to the less volume fraction of the liquid and tendency of the grains to accommodate into a shape that eliminated the pores. Comparison of microstructures for the samples sintered at 920°C as shown in Figs. 3(a)–3(c)

Fig. 3. SEM images showing effect of Pb content and ST on microstructure of (Bi_{1-x}Pb_x)NbO₄, ($x = 0-0.2$) (ST). (a) ($x = 0$, ST = 920°C), (b) ($x = 0.1$, ST = 920°C), (c) ($x = 0.2$, ST = 920°C), (d) ($x = 0.2$, ST = 940°C) and (e) ($x = 0.2$, ST = 960°C).

Fig. 3. (Continued)

revealed that at the higher solid contents (lower volume of liquid phase as in case of $x = 0$ and $x = 0.1$) having more solid–solid contacts the grains were less spherical as compared to $x = 0.20$ substitution. The spheroidizing and coarsening took place because of the breaking of the grain boundaries in polycrystalline particles and their conversion into single crystal particles due to wetting of the grains, particularly in the initial stages of liquid phase sintering. This aspect became quite clearly visible from Fig. 3(c). Closed and spheroidized pores were observed for $x = 0.20$ samples sintered at 920°C (Fig. 3(c)). During sintering at higher temperatures of 940°C and 960°C (Figs. 3(d) and 3(e)), the number of grains decreased over time due to grain coalescence, with the large grains absorbing the smaller grains, leading to formation of elongated grains in the microstructure. In Fig. 3(d), evidence of merger of grains taking place could be seen in the microstructures. The SEM photomicrograph of the sample sintered at 960°C as shown in Fig. 3(e) revealed a marginal nonhomogeneous grain growth and larger pores due to coalescence of smaller pores. These microstructure features supported the marginally lower density of 96.8%TD observed for the samples sintered at 960°C *vis-à-vis* a density of 97.5%

TD noted for samples sintered at 940°C. The average grain size measured by line intercept method was much finer, which was observed to be in the range of 1.5–2 μm for the samples sintered at different temperatures. At a given temperature (Figs. 3(a)–3(c) for sintering at 920°C), the grain size remained more or less constant with the increase in lead content. However, temperature was found to have a relatively higher effect on the increase in grain size as evident from Figs. 3(d)–3(e).

Table 2 shows the dielectric properties of $(\text{Bi}_{1-x}\text{Pb}_x)\text{NbO}_4$ ceramics sintered at 920–960°C. Figure 4 shows plots of the dielectric constant at various STs of $(\text{Bi}_{1-x}\text{Pb}_x)\text{NbO}_4$ as a function of Pb/mol (x). With the increase in Pb content up to 0.05 Pb/mol (x), the change in dielectric constant was negligible. However, beyond 0.05 Pb/mol (x), there was a remarkable increase in the dielectric constant with the increase in Pb content as clearly visible from Fig. 4. This increase could be attributed to the formation of the $\text{Pb}_2\text{Nb}_2\text{O}_7$ secondary phase which could be seen being formed in considerable amount at $x \geq 0.10$ (refer Table 1). This secondary $\text{Pb}_2\text{Nb}_2\text{O}_7$ phase formed has a high dielectric constant of about $\epsilon'_r \sim 110$.³¹

Table 2. Dielectric properties of $(\text{Bi}_{1-x}\text{Pb}_x)\text{NbO}_4$ ceramics sintered at 920–960°C.

x	Sintering Temp. (°C)	ϵ'_r calculated	ϵ'_r observed	ϵ'_r corrected	$Q_{u,f}$ (GHz)	τ_ϵ (ppm/°C)
0	920	34.8	42.5	46.3	5406	192.9
0.025	920	36.4	42.0	46.1	2638	473.2
0.05	920	33.9	42.8	46.6	2061	1000.3
0.1	920	33.8	49.4	52.8	1740	162.4
0.15	920	37.1	55.4	59.1	1750	98.9
0.2	920	37.2	70.7	73.4	558	88.0
0.2	940	35.6	68.9	72.4	791	—
0.2	960	33.7	70.7	74.3	555	—

Fig. 4. Dielectric constant values of $(\text{Bi}_{1-x}\text{Pb}_x)\text{NbO}_4$ ceramics as a function of Pb/mol (x).

For most of the samples, no significant change in the dielectric constant was noted with the rise in ST from 920°C to 960°C, except for the composition $x = 0.05$ corresponding to the transition region, beyond which secondary $\text{Pb}_2\text{Nb}_2\text{O}_7$ phase formation started. This particular composition needs further more detailed investigation.

Fig. 5. $Q_{u,f}$ values of $(\text{Bi}_{1-x}\text{Pb}_x)\text{NbO}_4$ ceramics as a function of Pb/mol (x).

The $Q_{u,f}$ values of $(\text{Bi}_{1-x}\text{Pb}_x)\text{NbO}_4$ ceramics sintered at different temperatures are presented in Fig. 5. The saturated $Q_{u,f}$ value of the $(\text{Bi}_{1-x}\text{Pb}_x)\text{NbO}_4$ ceramics showed a strong dependence on the x values. It decreased steadily from 5400 GHz to 550 GHz with an increase in x from 0 to 0.2. For all the compositions ($x = 0-0.20$), the $Q_{u,f}$ values first showed an increase with increase in ST from 920°C to 940°C and dropped further when the ST was raised further to 960°C, the $Q_{u,f}$ value remaining higher than that observed for samples sintered at 920°C. The maximum $Q_{u,f}$ value of 5400 GHz was obtained for the pure BiNbO_4 sample when sintered at 920°C. The decrease in the saturated $Q_{u,f}$ values with the increasing of x was partially attributed to the composition causing intrinsic loss and partially to existence of the secondary $\text{Pb}_2\text{Nb}_2\text{O}_7$ phase in the sintered samples, which may cause some extra extrinsic losses (amongst the two components of dielectric loss, the intrinsic loss is caused by an anharmonic phonon decay process in a pure crystal lattice, while, the extrinsic loss is presumably correlated to the existence of crystal defects, grain boundaries, secondary phases and pores in the bulk ceramics). The cause of the intrinsic losses could be thought to arise from the differential straining of the adjacent lattices due to the substitution of Bi ions ($r_{\text{Bi}}^{3+} = 1.03 \text{ \AA}$) by the different sized and valanced Pb ions ($r_{\text{Pb}}^{2+} = 0.79 \text{ \AA}$ and $r_{\text{Pb}}^{4+} = 1.19 \text{ \AA}$) in neighboring unit cells, thereby straining the lattices to different extent. The one with Pb^{2+} ions is strained more as compared to the one containing Pb^{4+} in place of Bi^{3+} , with overall negligible change in volume of the unit cell as determined from the refined lattice parameters (see Table 1). Also, the grain size of the $(\text{Bi}_{1-x}\text{Pb}_x)\text{NbO}_4$ ceramics was observed to increase with ST (see Fig. 3). The grain growth was likely to contribute to a decrease in both the number of pores and total grain boundary area. This decrease was further likely to result in a higher density and thereby lower the extrinsic loss and improve the quality factor. It could be seen that the quality factor was lower at the lowest ST of 920°C. The samples sintered at 940°C showed the highest sintered density and also the highest $Q_{u,f}$ values. At further higher ST of 960°C, the structure was likely to become more inhomogeneous due to occurrence of defects associated with bismuth evaporation leading to formation of oxygen vacancies (see Eqs. (1.1) and (1.2)). These lowered the density and also the $Q_{u,f}$ value

Fig. 6. τ_ϵ values of $(\text{Bi}_{1-x}\text{Pb}_x)\text{NbO}_4$ ceramics (sintered at 940°C) as a function of $\text{Pb/mol}(x)$.

due to defect dipoles so produced contributing to dielectric relaxation and an increase in the ionic conductivity.³²

The temperature coefficient of dielectric constant (τ_ϵ) values of $(\text{Bi}_{1-x}\text{Pb}_x)\text{NbO}_4$ ceramics (sintered at 940°C) as a function of $\text{Pb/mol}(x)$ are shown in Fig. 6. A positive τ_ϵ value was noted for all the compositions sintered. The τ_ϵ value steeply increased up to 0.05 $\text{Pb/mol}(x)$, beyond which a steep fall was noticed. The initial rise was attributed to the distortion of the orthorhombic unit cell caused due to tilting of the vertex-sharing NbO_6 octahedra. Once the secondary $\text{Pb}_2\text{Nb}_2\text{O}_7$ phase started separating out, the properties were governed by the combination of the τ_ϵ values of the two phases separated out, may be as per the rule of mixture. Such combinations of high positive τ_ϵ ceramics with high permittivity (and low loss) are rare. Combining these ceramics with high negative τ_ϵ ceramics like TiO_2 ($\epsilon'_r = 100$, $\tau_\epsilon \sim -750 \text{ ppm}/^\circ\text{C}$) may yield ceramics with zero τ_ϵ values.^{4,33} The τ_ϵ is related to τ_f as; $\tau_\epsilon = -2(\tau_f + \alpha_L)$, where α_L is linear coefficient of thermal expansion. The τ_ϵ value steeply increased up to 0.05 $\text{Pb/mol}(x)$, the solubility limit of Pb in BiNbO_4 , beyond which a steep fall in τ_ϵ value was noticed.

4. Conclusions

Ceramic samples of $(\text{Bi}_{1-x}\text{Pb}_x)\text{NbO}_4$, ($x = 0, 0.025, 0.05, 0.10, 0.15, 0.20$) with uniform microstructures were successfully prepared by solid-state reaction route. It was noted that the samples crystallized in single orthorhombic phase up to 0.05 $\text{Pb/mol}(x)$, beyond which secondary $\text{Pb}_2\text{Nb}_2\text{O}_7$ phase appeared and its amount increased for higher Pb additions. The extent (or fraction) of orthorhombic phase transition to $\text{Pb}_2\text{Nb}_2\text{O}_7$ was found to be at a maximum of 44% by volume for $x = 0.20 \text{ Pb/mol}(x)$. Substitution of Pb for Bi improved sinterability. As the ST increased from 920°C to 960°C , the sintered densities of samples first increased and reached the

maximum values at 940°C , beyond which there was a fall in the density. The effect of liquid phase sintering became quite distinctly visible from spheroidized grains and fused grain boundaries. The average grain size measured was much finer ($1.5\text{--}2\mu\text{m}$) for the samples sintered at different temperatures. The grain size remained more or less constant with the increase in Pb content. The microwave dielectric constant (ϵ'_r) values of the niobates increased from 42 to 71, whereas the quality factor ($Q_{u,f}$) values decreased from 5400 to 550 GHz with increasing substitution of Pb from 0 to 0.2 $\text{Pb/mol}(x)$. Such enhancement of ϵ'_r from 42 to 71 has never been reported for BiNbO_4 system. This increase could be attributed to the formation of the $\text{Pb}_2\text{Nb}_2\text{O}_7$ secondary phase. The decrease in the saturated $Q_{u,f}$ values with the increasing of x was partially attributed to the composition causing intrinsic loss and partially to existence of the secondary $\text{Pb}_2\text{Nb}_2\text{O}_7$ phase in the sintered samples. Temperature coefficient of resonant frequency (τ_ϵ) showed a steep increase upto 0.05 mole fraction of Pb resulting from the distortion of the orthorhombic unit cell caused due to tilting of the vertex-sharing NbO_6 octahedra. However, τ_ϵ decreased with increasing Pb fraction owing to presence of the secondary $\text{Pb}_2\text{Nb}_2\text{O}_7$ phase.

References

- D. Shihua, Y. Xi, M. Yu and L. Puling, Microwave dielectric properties of $(\text{Bi}_{1-x}\text{R}_x)\text{NbO}_4$ ceramics ($\text{R} = \text{Ce}, \text{Nd}, \text{Dy}, \text{Er}$), *J. Eur. Ceram. Soc.* **26**, 2003 (2006).
- S. Kamba, H. Wang, M. Berta, F. Kadlec, J. Petzelt, D. Zhou and X. Yao, Correlation between infrared, THz and microwave dielectric properties of vanadium doped antiferroelectric BiNbO_4 , *J. Eur. Ceram. Soc.* **26**, 2861 (2006).
- M. T. Sebastian and H. Jantunen, Low loss dielectric materials for LTCC applications: A Review, *Int. Mater. Rev.* **53**, 57 (2008).
- I. M. Reaney and D. Iddles, Microwave dielectric ceramics for resonators and filters in mobile phone networks, *J. Am. Ceram. Soc.* **89**, 2063 (2006).
- C. L. Huang, M. H. Weng, C. C. Wu and C. T. Lion, Low fire BiNbO_4 microwave dielectric ceramics modified by Sm_2O_3 Addition, *Mater. Res. Bull.* **35**, 827 (2001).
- H. Kagata, T. Inoue, J. Kato and I. Kameyama, Low-fire bismuth based dielectric ceramics for microwave use, *Jpn. J. Appl. Phys.* **31**, 3152 (1992).
- W. C. Tzou, C. F. Yang, Y. C. Chen and P. S. Cheng, Improvements in the sintering and microwave properties of BiNbO_4 microwave ceramics by V_2O_5 addition, *J. Eur. Ceram. Soc.* **20**, 991 (2000).
- R. S. Roth and J. L. Waring, Phase-equilibrium relations in the binary system bismuth sesquioxide-niobium pentoxide, *J. Res. Natl. Bur. Stand.* **66A**, 451 (1962).
- Y. Yong, D. Shihua and Y. Xi, Influences of Fe_2O_3 additives on the dielectric properties of BiNbO_4 ceramics under different sintering atmosphere, *Ceram. Int.* **30**, 1341 (2004).
- C. M. Cheng, S. H. Lo and C. F. Yang, The effect of CuO on the sintering and properties of BiNbO_4 microwave ceramics, *Ceram. Int.* **26**, 113 (2000).

- ¹¹C. L. Huang, M. H. Weng and C. C. Wu, The microwave dielectric properties and the microstructures of La_2O_3 -modified BiNbO_4 ceramics, *Jpn. J. Appl. Phys.* **39**, 3506 (2000).
- ¹²N. Wang, M. Y. Zhao, W. Li and Z. W. Yin, The sintering behavior and microwave dielectric properties of $\text{Bi}(\text{Nb,Sb})\text{O}_4$, *Ceram. Int.* **30**, 1017 (2004).
- ¹³W. Choi, K. Y. Kim, M. R. Moon and K. S. Bae, Effects of Nd_2O_3 on the microwave dielectric properties of BiNbO_4 ceramics, *J. Mater. Res.* **13**, 2945 (1998).
- ¹⁴H. Lim and Y. J. Oh, Microwave dielectric properties of Dy_2O_3 substituted BiNbO_4 ceramics, *Jpn. J. Appl. Phys.* **45**, 5865 (2006).
- ¹⁵M. H. Weng and C. L. Huang, Shifting τ_f value of BiNbO_4 ceramics by BiTaO_4 addition, *J. Mater. Sci. Lett.* **19**, 375 (2000).
- ¹⁶E. S. Kim and W. Choi, Effect of phase transitions on the microwave dielectric properties of BiNbO_4 , *J. Eur. Ceram. Soc.* **26**, 1761 (2006).
- ¹⁷N. Wang, M. Y. Zhao, Z. W. Yin and W. Li, Effects of complex substitution of La and Nd for Bi on the microwave dielectric properties of BiNbO_4 ceramics, *Mater. Res. Bull.* **39**, 439 (2004).
- ¹⁸D. Shihua, Y. Xi and Y. Yong, Dielectric properties of B_2O_3 -doped BiNbO_4 ceramics, *Ceram. Int.* **30**, 1195 (2004).
- ¹⁹Y. Mao, S. H. Ding, X. Yao and L. Y. Zhang, Microwave dielectric properties of $\text{BiNb}_{1-x}\text{Mo}_x\text{O}_4$ ceramics, *Mater. Chem. Phys.* **98**, 198 (2006).
- ²⁰ASTM Method C 373 1988, Standard test method for water absorption, bulk density, apparent porosity, and apparent specific gravity of fired whiteware products, ASTM Int West Conshohocken, PA, United States (2006), pp. 1–2.
- ²¹F. A. Rajabalee, *Wincell 1.1: A Windows Package of DOS Routines for Unit Cell Refinements*, ed. F. A. Rajabalee (Bordeaux, France, 2000).
- ²²E. L. Ginzton, *Microwave Measurement*, 1st edn. (McGraw Hill, USA, 1957).
- ²³M. V. Jacob, J. Mazierska, K. Leong and J. Krupka, Simplified method for measurements and calculations of coupling coefficients and q_o -factor of high temperature superconducting dielectric resonators, *IEEE Trans. Microw. Theory Tech.* **49**, 2401 (2001).
- ²⁴D. Zhou, H. Wang, X. Yao, X. Wei, F. Xiang and L. Pang, Phase transformation in BiNbO_4 ceramics, *J. Appl. Phys.* **90**, 172910 (2007).
- ²⁵S. P. Butee, A. R. Kulkarni, O. Prakash, R. P. R. C. Aiyar, K. Sudheendran and K. C. James Raju, Effect of lanthanide ion substitution on r.f. and microwave dielectric properties of BiNbO_4 ceramics, *J. Alloys Compd.* **492**(1–2), 351 (2010).
- ²⁶R. M. German, Pavan Suri and S. J. Park, Review: Liquid phase sintering, *J. Mater. Sci.* **44**, 1 (2009).
- ²⁷B. H. Venkataraman and K. B. R. Varma, Microstructural, dielectric, impedance and electric modulus studies on vanadium-doped and pure strontium bismuth niobate ($\text{SrBi}_2\text{Nb}_2\text{O}_9$) ceramics, *J. Mater. Sci., Mater. Electron.* **16**, 335 (2005).
- ²⁸F. A. Kröger and H. J. Vink, *Solid State Physics*, eds. F. Seitz and D. Turnbull, Vol. 3 (Academic Press, New York, 1956), pp. 307–435.
- ²⁹C. K. Suman, K. Prasad and R. N. P. Choudhary, Complex impedance studies on tungsten-bronze electroceramic: $\text{Pb}_2\text{Bi}_3\text{LaTi}_5\text{O}_{18}$, *J. Mater. Sci.* **41**, 369 (2006).
- ³⁰M. W. Barsoum, *Fundamentals of Ceramics*, 1st edn. (McGraw-Hill, USA, 1997).
- ³¹R. Ulic and I. M. Reaney, Microwave properties of doped lead pyroniobate, *J. Eur. Ceram. Soc.* **21**, 2659 (2001).
- ³²H. Tamura, T. Konoike, Y. Sakabe and K. Wakino, Improved high-Q dielectric resonator with complex perovskite structure, *J. Am. Ceram. Soc.* **67**, C59 (1984).
- ³³A. J. Moulson and J. M. Herbert, *Electroceramics, Materials, Properties, Applications*, 2nd edn. (John Wiley & Sons, USA, 2003).