

Synthesis and microwave characterization of Bi- substituted barium lanthanum titanate

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Bi-substituted barium lanthanum titanates with the general formula $\text{Ba}_4(\text{La}_{(1-z)}\text{Bi}_z)_{9.33}\text{Ti}_{18}\text{O}_{54}$ where $z = 0.0$ to 0.2 in steps of 0.05 were synthesized by a conventional mixed oxide route. The composition and morphology were determined using scanning electron microscopy (SEM) and X-ray powder diffraction analysis (XRD). Two dielectric performance parameters, namely dielectric constant and loss tangent were measured with varying microwave frequency in the range 0.3 to 3 GHz at room temperature. It was observed that the dielectric constant and loss tangent both increased initially for $z \leq 0.10$ and then decreased. The best properties were obtained for $z = 0.20$ with a dielectric constant of 91.4 and loss tangent of 0.004 . This could be a promising microwave material with a high dielectric constant and low loss.

Key words: Ceramics, X-ray Diffraction, Scanning electron microscopy, dielectric constant, loss tangent.

Introduction

Recently, dielectric ceramic materials based on the ternary system $\text{BaO-R}_2\text{O}_3\text{-kTiO}_2$ (R = Rare earth and $k = 3$ to 5) have received much scientific and commercial attention due to significant applications as resonators and filters in microwave communication [1-3]. The properties required for these materials include high dielectric constant (ϵ') for miniaturization, high Q value (which is the inverse of the loss tangent, $\tan \delta$) for better frequency selectivity and good temperature stability.

Ceramics having excellent properties in the $\text{BaO-R}_2\text{O}_3\text{-4TiO}_2$ system with the general formula $\text{Ba}_{6-3x}\text{R}_{8+2x}\text{Ti}_{18}\text{O}_{54}$ ($x = 0.0$ to 0.7) have been extensively investigated [4-7] and identified as promising materials for application at frequencies below 2 GHz. In the rare earth family, La has the highest dielectric constant, but it has not been focused on much due to its relatively low Q value as compared with Sm and Nd [7]. Their crystal structures were reported [8] to be tungsten bronze type with a structural formula $[\text{R}_{8+2x}\text{Ba}_{2-3x}\text{V}_x]_{\text{A1}}[\text{Ba}_4]_{\text{A2}}\text{Ti}_{18}\text{O}_{54}$ in the range $0 \leq x \leq 2/3$. This structure has three types of large cation sites: ten A1 rhombic sites in 2×2 perovskite blocks, four A2 pentagonal sites and four trigonal empty sites. The special composition $\text{Ba}_4\text{R}_{9.33}\text{Ti}_{18}\text{O}_{54}$ at $x = 2/3$, in which R and Ba ions occupy the A1 and A2 sites respectively, exhibits the highest Q [8].

It has been demonstrated [9-12] that the materials in the Bi_2O_3 doped $\text{BaO-Nd}_2\text{O}_3\text{-TiO}_2$ system have high dielectric constants and low sintering temperatures.

However, the effect of Bi_2O_3 additions to $\text{BaO-La}_2\text{O}_3\text{-TiO}_2$ system has not been much studied [13]. Because of the high dielectric constant and low loss tangent (for $x = 2/3$) of the composition $\text{Ba}_4\text{La}_{9.33}\text{Ti}_{18}\text{O}_{54}$, excellent microwave ceramics are expected to be prepared by substitution of Bi for La. Therefore, in the present study, $\text{Ba}_4(\text{La}_{(1-z)}\text{Bi}_z)_{9.33}\text{Ti}_{18}\text{O}_{54}$ ($z = 0.0$ to 0.2) ceramics with different Bi contents were prepared and characterized. The effects of such substitutions on microstructures and microwave dielectric properties at room temperature were investigated.

Experimental Procedure

The ceramic samples were synthesized by a conventional mixed oxide route using reagent grade BaCO_3 (99.5%), La_2O_3 (99.9%), Bi_2O_3 (99.9%) and TiO_2 (99.5 %). The starting powders were weighted so as to agree with the composition $\text{Ba}_4(\text{La}_{(1-z)}\text{Bi}_z)_{9.33}\text{Ti}_{18}\text{O}_{54}$ where $z = 0.00, 0.05, 0.10, 0.15$ and 0.20 and mixed with methanol in an agate mortar for 12 h. The powders were then dried and calcined at 1100°C for 2 h in a linearly programmable furnace. The calcined powders were ground for 12 h, dried and mixed with $3\text{-}5$ wt% of poly vinyl alcohol (PVA). The granulated powders were pressed into circular and rectangular pellets under a pressure of 98 MPa and sintered at 1300°C for 2 h.

The sintered samples were polished and bulk densities were measured by a liquid displacement method using de-ionized water (Archimedes method). X-ray powder diffraction (XRD) patterns were recorded with powders of sintered samples using $\text{CuK}\alpha$ radiation filtered through Ni foil in the $20^\circ\text{-}80^\circ$ 2θ range (model PWQ 1729, Philip). From these patterns, lattice parameters were calculated by the least square method.

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The microstructural observation and analysis of the sintered samples were executed by scanning electron microscopy (model JSM 6100, JEOL Japan). The dielectric constant and loss tangent parameters between 0.3-3 GHz at room temperature were measured by a coaxial open ended probe method using a network analyzer (model 8714ET, Agilent Technologies) and a dielectric probe kit.

Results and Discussion

The X-ray diffraction patterns of $\text{Ba}_4(\text{La}_{(1-z)}\text{Bi}_z)_{9.33}\text{Ti}_{18}\text{O}_{54}$ with change in Bi contents are shown in Fig. 1. They show that a single phase is obtained and all peaks match with those reported for $\text{Ba}_4\text{La}_8\text{Ti}_{17}\text{O}_{50}$ (JCPDS card no 42-0419). There was no evidence of any secondary phase present for $z \leq 0.10$. Some secondary phases were seen in the XRD patterns for higher Bi contents.

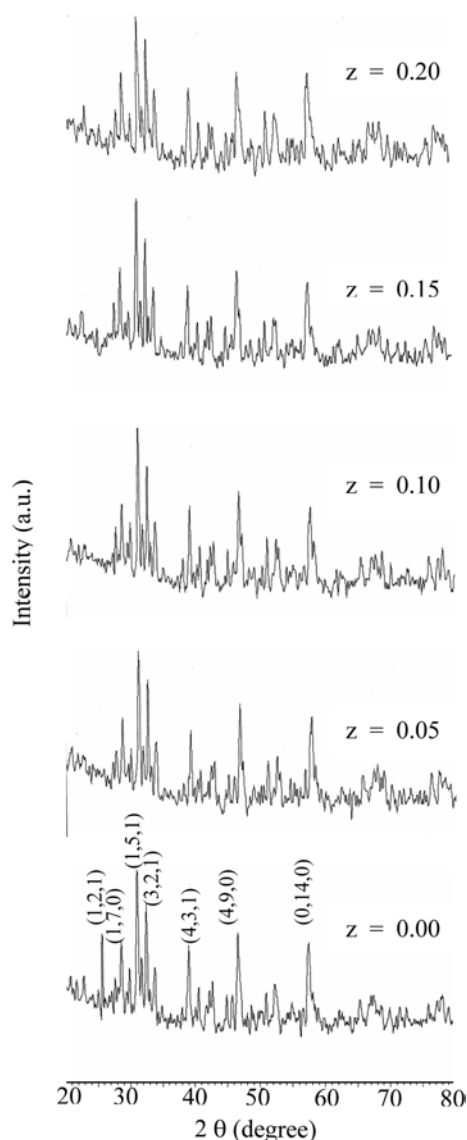


Fig. 1. X ray diffraction patterns of $\text{Ba}_4(\text{La}_{(1-z)}\text{Bi}_z)_{9.33}\text{Ti}_{18}\text{O}_{54}$ for different Bi contents.

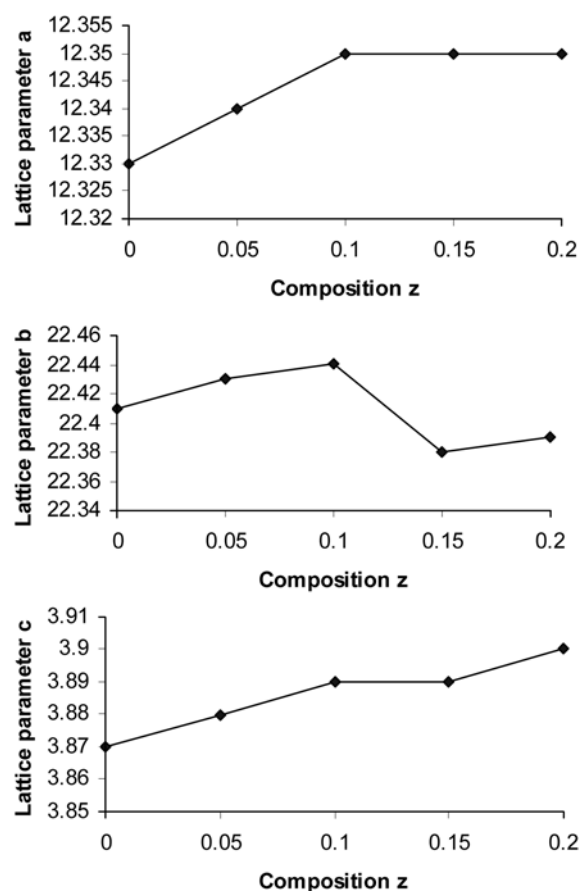


Fig. 2. Variation of lattice parameters (in Å) for different Bi contents.

The solid solutions have the perovskite structure with orthorhombic symmetry. The variation in lattice parameters for the a-axis, b-axis and c-axis with changing Bi contents are shown in Fig. 2. The lattice parameter curve for the a-axis and c-axis increase linearly with an increase in Bi substitution. But the lattice parameter curve of the b-axis has an inflection point at $y = 0.10$. This lattice parameter curve increases in the early stage for $z \leq 0.10$ and then decreases. The increase of the b-axis could be because of the substitution of Bi ions for La ions in A1 rhombic sites and also the ionic radius of Bi ion is greater than that of La ion. The ionic radius of Bi and La ions, as reported by Okawa et al. [13] and Shannon [14], are 1.45 Å and 1.36 Å respectively. Further, the decrease in lattice parameter b-axis for $z > 0.10$ might be due to substitution of Ba ion located in A2 pentagonal sites by Bi ions as the ionic radius of the Bi ion (1.45 Å) is smaller than the Ba ion (1.61 Å) as reported previously [14].

Figure 3 shows SEM micrographs of fractured surfaces of all the sintered samples. They have a close microstructure with low porosity and closely packed needle-like elongated grains (of size 4-7 μm). The data show an increase in average grain size and grains elongated in one dimension which take a rectangular shape. The EDAX spectra for all the samples are shown in

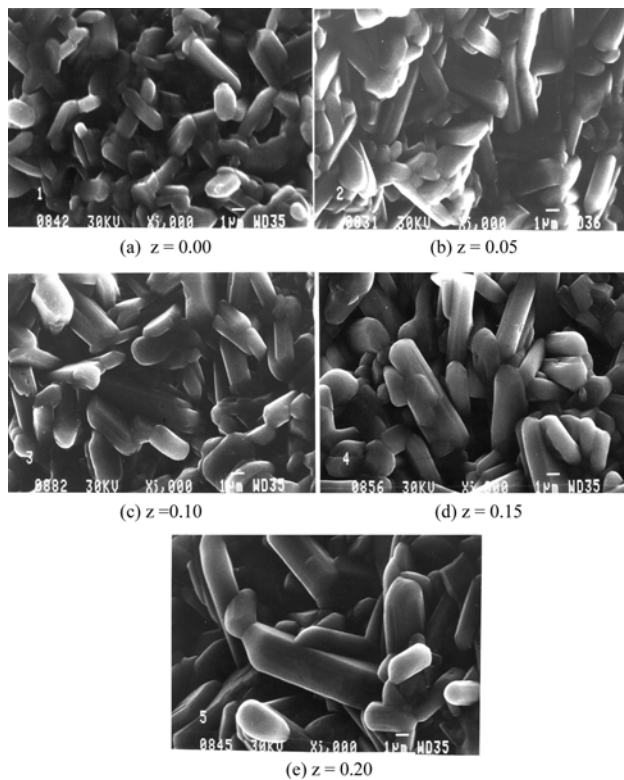


Fig. 3. SEM micrographs of $\text{Ba}_4(\text{La}_{(1-z)}\text{Bi}_z)\text{Ti}_{18}\text{O}_{54}$ for different Bi contents.

Fig. 4. This figure clearly indicates the presence of the expected elements (Ba, La, Bi and Ti) in appropriate proportions.

The bulk densities of the sintered samples versus composition are plotted in Fig. 5. These ceramics have high values ($>0.5 \text{ g/cm}^3$) of bulk density. The maximum bulk density was observed to be 5.252 g/cm^3 . This shows that a suitable sintering temperature of Bi-added samples decreases by approximately 100°C compared with non Bi-added samples [13].

Figure 6 shows the variation of dielectric constant ϵ' values of $\text{Ba}_4(\text{La}_{(1-z)}\text{Bi}_z)_{9.33}\text{Ti}_{18}\text{O}_{54}$ samples as a function of frequency with changing Bi content at room temperature. The values are 91.6 for $z = 0.0$, 112 for $z = 0.10$ and 90.5 for $z = 0.20$ at 2 GHz. This increases for $z = 0.0$ to 0.10 and then decreases for $z = 0.15$ and 0.20 . The increase in dielectric constant (ϵ') could be attributed to the fact that Bi ions have replaced La ions from A1 sites. ϵ' is affected by the polarizabilities of the R ion and it increases with an increase in ionic polarizability [8]. The Bi ion ($6.12 \text{ \AA}^3$) has a higher ionic polarizability than the La ion ($6.07 \text{ \AA}^3$) according to the table of polarizability derived by Shannon [15]. The decrease in dielectric constant beyond $z = 0.10$ could be because of replacement of the Ba ion from an A2 site instead of a La ion from A1 sites by Bi. Moreover, the Ba ion ($6.40 \text{ \AA}^3$) has higher ionic polarizability than Bi ion ($6.12 \text{ \AA}^3$) [15].

The variation of loss tangent ($\tan \delta$) of $\text{Ba}_4(\text{La}_{(1-z)}-$

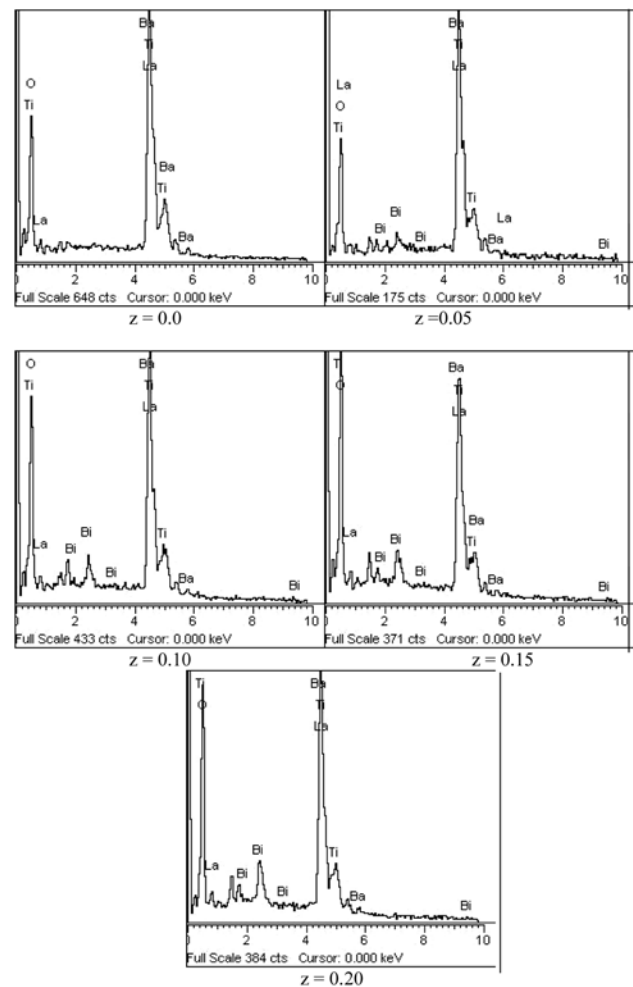


Fig. 4. Energy dispersive X-ray spectra for different Bi contents.

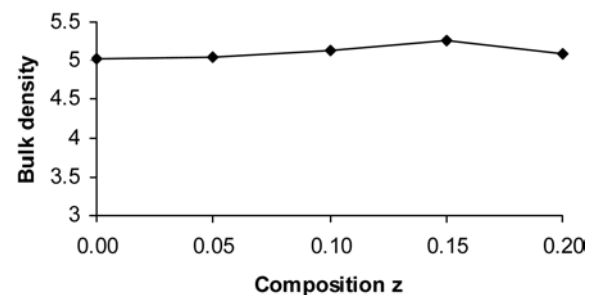


Fig. 5. Variation of bulk density (in g/cm^3) for different Bi contents.

$\text{Bi}_z)_{9.33}\text{Ti}_{18}\text{O}_{54}$ samples for different Bi contents as a function of frequency at room temperature is shown in Fig. 7. It is 0.11 for $z = 0.00$, 0.17 for $z = 0.10$ and 0.004 for $z = 0.20$. The loss tangent initially increases with an increase in Bi content upto $z = 0.10$ and then it decreases for higher Bi contents. This tendency is similar to that of the lattice parameter b-axis and the difference in ionic radius might be behind this. Moreover, Oshato and Imaeda [16] have reported that the quality factor, which is the inverse of the loss tangent, increases with a decrease of the ionic radius of R (La, Nd, Sm, Pr) ion.

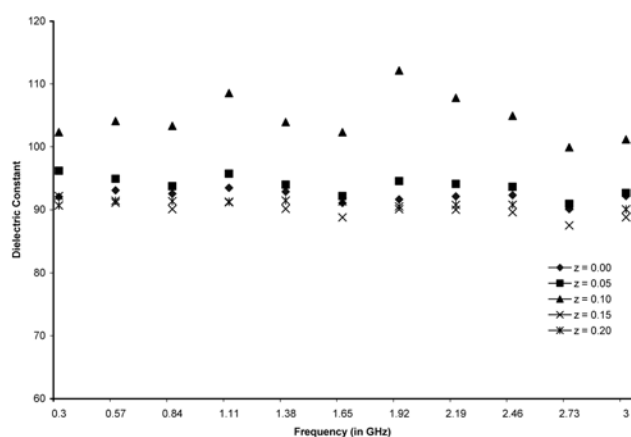


Fig. 6. Variation of dielectric constant with frequency for different Bi contents.

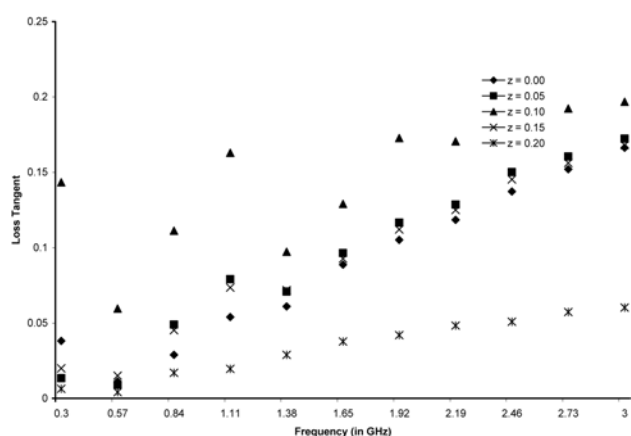


Fig. 7. Variation of loss tangent with frequency for different Bi contents.

Due to the disordered distribution of bivalent (Ba ion) and trivalent (La and Bi ion) cations on rhombic A1 and pentagonal A2 sites, the dipoles are restricted by the inhomogeneous local charge. More energy is consumed as the dipoles orientate with the alternating electric field. The inhomogeneous distribution of concentration, such as secondary phases and vacancies created by Bi vaporization, has added to the internal stress in grains, which could result in the dielectric loss or loss tangent.

Conclusions

The microstructure and microwave dielectric properties of new dielectric ceramics $\text{Ba}_4(\text{La}_{(1-z)}\text{Bi}_z)_{9.33}\text{Ti}_{18}\text{O}_{54}$ where $z = 0.0-0.2$ have been studied. The dielectric constant and loss tangent values of samples with $z = 0.0$ to 0.10 increases slightly with an increase in the amount of Bi substitution. However, the loss tangent is reduced remarkably for $z = 0.20$ without much reduction in the dielectric constant. These materials have great potential for application in wireless communication at microwave frequencies.

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