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Optimization of dielectric properties of barium rare earth titanate by complex substitution

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Abstract

The optimization of dielectric properties of barium rare earth titanate was carried out by simultaneous substitution of Sm, La and Bi ions. The effects of substitution of Bi on dielectric and structural characteristics of $Ba_4(La_{0.3}Sm_{0.7})_{9.33}Ti_{18}O_{54}$ were investigated. The solid solutions, $Ba_4(La_{(1-y-z)}Sm_yBi_z)_{9.33}Ti_{18}O_{54}$ with $y = 0.7$ and $z = 0.0$–0.2, synthesized by solid state reaction technique were characterized by X-ray diffraction, scanning electron microscopy and energy dispersive X-ray analysis. The dielectric properties were measured using a network analyzer in the frequency range 0.3–3.0 GHz. It has been found that Bi substitution not only increases the dielectric constant but also improves the temperature coefficient of resonant frequency. However the tangent loss increases with increase in Bi substitution. Among the investigated compositions, $Ba_4(La_{(1-y-z)}Sm_yBi_z)_{9.33}Ti_{18}O_{54}$ dielectric ceramic with $y = 0.7$ and $z = 1.0$ has got high dielectric constant (82), low tangent loss (3.3×10^{-3}) at 3 GHz and near zero temperature coefficient of resonant frequency (−5 ppm/°C). It could be suitable candidate for applications in wireless communication systems.

Keywords: A. Powder: solid state reaction; C. Dielectric properties; Ceramics

1. Introduction

The growing importance of dielectric ceramics in wireless communication has led to development of new materials. High dielectric constant ($\varepsilon_r > 80$), low tangent loss (tan δ) and near zero temperature coefficient of resonant frequency (τ_f) are the desirable properties of these materials.

Among the various candidates, microwave dielectric ceramics based on the ternary system BaO–R_2O_3–TiO_2 (R = rare earth) are given much attention due to their suitability for applications at microwave frequencies in resonators, filters, etc. [1–7]. Matveeva et al. [3] first reported the crystal structure of $Ba_{3.75}Pr_{9.5}Ti_{18}O_{54}$ based on the fundamental unit cell by single crystal X-ray diffraction, which was confirmed by many researchers [4,5]. In this system, formation of tungsten bronze-type structure with orthorhombic symmetry has been established with general formula $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R = Sm, Nd, Pr, La). The fundamental structural formula of this compound was reported as $[R_{8+2x}Ba_{2-3x}V_x]_{A1}[Ba_4]_{A2}\ [V_4]_CTi_{18}O_{54}$. The A1-site is rhombic with 2×2 perovskite blocks, the A2-site is pentagonal and the C-site is trigonal which is usually vacant. Ohsato [6] found that at $x = 2/3$, the quality factor becomes highest due to ordering of R and Ba ions in the rhombic and pentagonal sites, respectively.

Recent studies mainly concerned with the improvement in dielectric properties of BaO–R_2O_3–TiO_2 ceramics by adjusting ionic substitution and modifying the structure in wide range. Ohsato et al. [8] studied the microwave dielectric properties of $Ba_{6-3x}(Sm_{1-y}R_y)_{8+2x}Ti_{18}O_{54}$ (R = Nd and La; $x = 0.6$, $0.0 \leq y \leq 1.0$) solid solutions in which Nd or La ions were substituted for Sm ions and near zero temperature coefficient of resonant frequency was reported. Kolar et al. [9] first reported that the addition of Bi_2O_3 or $Bi_4Ti_3O_{12}$ could improve the dielectric constant and temperature stability of $BaNd_2Ti_4O_{12}$ and $BaNd_2Ti_5O_{14}$ ceramics with increase in dielectric loss. Since then, many researchers have proposed to improve the dielectric properties of BaO–Nd_2O_3–TiO_2 system by Bi_2O_3 addition [10–13]. The modification of the microwave dielectric properties in $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$, $x = 0.5$ solid solutions by Sm/Bi co-substitution for Nd were studied by Wu and Chen [14] and it was

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confirmed that Bi^{3+} ions could increase ε_r. $Ba_{6-3x}La_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$) ceramics were also modified with Bi_2O_3 substitution [15]. The site occupancy of Bi ions in Bi-doped $Ba_{6-3x}R_{8+2x}$-$Ti_{18}O_{54}$ (R = rare earth, $x = 2/3$) ceramics was researched by Okawa et al. [16]. However until now there is no systematic and detail report dealing with the variation of various properties of $Ba_4(La_{(1-y-z)}Sm_yBi_z)_{9.33}Ti_{18}O_{54}$, $y = 0.7$ solid solutions as a function of Bi substitution. In the present study, the structural and microwave dielectric properties of $Ba_4(La_{(1-y-z)}Sm_yBi_z)_{9.33}$ $Ti_{18}O_{54}$, $y = 0.7$, $z = 0.00$–0.20 are examined for varying Bi contents.

2. Experimental

$Ba_4(La_{1-y-z}Sm_yBi_z)_{9.33}Ti_{18}O_{54}$, $y = 0.7$ and $z = 0.00$–0.20 dielectric ceramics were synthesized by solid state reaction technique using $BaCO_3$ (99.5%), La_2O_3 (99.9%), Sm_2O_3 (99.9%), Bi_2O_3 (99.9%) and TiO_2 (99.5%). The raw materials were mixed in accordance with desired stoichiometry and ground in methanol for 12 h. All the mixtures were dried and calcined in air at 1100 °C for 2 h. The calcined powders were re-milled for 12 h in methanol and dried. A 3–5 wt% solution of polyvinyl alcohol was added as binder and pressed into pellets of cylindrical shape with 3–5 mm thickness under a load of 98 kN. These pellets were sintered at 1300 °C for 2 h in air in a linearly programmable furnace.

The crystalline phases of sintered samples were determined by X-ray powder diffraction (model PWQ 1729, Philips) using Cu Kα radiation for 2θ range from 20° to 80°. Microstructure of the freshly fractured surface of sintered samples was observed by scanning electron microscopy (model JSM 6100, JEOL Japan) and energy dispersive X-ray analysis (model INCA, Oxford). The bulk densities of compacts were measured by Archimedes method. The characterization of microwave dielectric properties namely dielectric constant and loss tangent was carried out by open-ended coaxial probe method using a network analyzer (model 8714ET, Agilent Technologies) in 0.3–3.0 GHz frequency range at room temperature. The temperature coefficient of relative permittivity (τ_ε) was determined at 100 kHz using an impedance analyzer (model 4192A, Agilent Technologies) equipped with thermostat in the temperature range 25–90 °C. The temperature coefficient of resonant frequency (τ_f) was estimated from the relation [17]:

$$\tau_f = -\left(\left(\frac{\tau_\varepsilon}{2}\right) + \alpha\right) \quad (1)$$

where τ_ε is temperature coefficient of dielectric constant and α is thermal expansion coefficient which is about 10 ppm/°C in present ceramics.

3. Results and discussion

3.1. X-ray diffraction, XRD

The X-ray diffraction patterns of $Ba_4(La_{(1-y-z)}Sm_yBi_z)_{9.33}$ $Ti_{18}O_{54}$, $y = 0.7$ for different Bi contents are shown in Fig. 1. All the peaks in the XRD spectra could be indexed according to that of tungsten bronze phase of $Ba_{6-3x}(La_{1-y}Sm_y)_{8+2x}Ti_{18}O_{54}$ for $z \leq 0.15$. However, a secondary phase of $Bi_4Ti_3O_{12}$ was observed for $z = 0.20$. The crystal structure is found out to be orthorhombic with lattice parameters a, b and c given in Table 1 for all the samples. The increase in lattice parameters and unit cell volume with increase in Bi contents could be due to replacement of La ions present in A1 rhombic sites by Bi ions as the ionic radius of Bi ions is larger than the La ions. The ionic radius of Bi and La ions as reported by Shannon [18] are 1.45 and 1.36 Å, respectively for 12 co-ordinate.

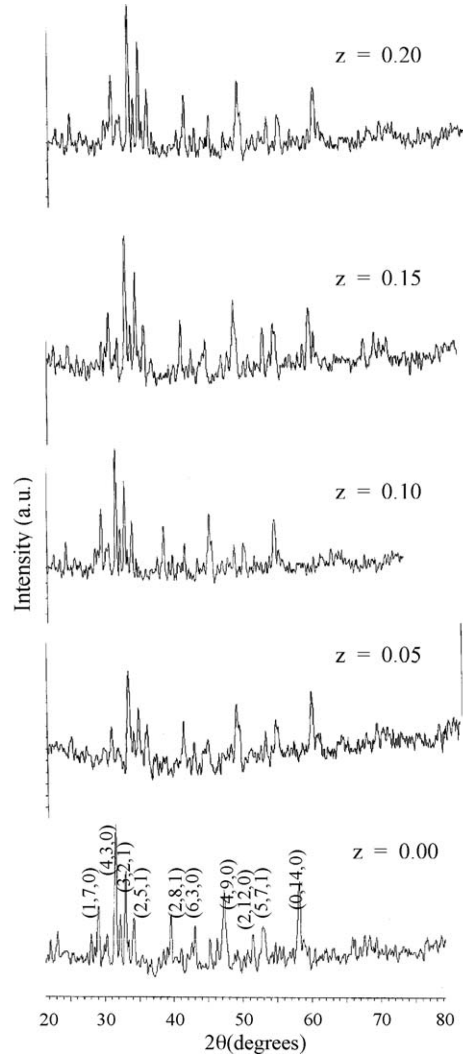

Fig. 1. X-ray diffraction patterns of $Ba_4(La_{(1-y-z)}Sm_yBi_z)_{9.33}Ti_{18}O_{54}$, $y = 0.7$ for different Bi contents.

3.2. Scanning electron microscopy, SEM

Fig. 2 shows the SEM micrographs obtained for all the freshly fractured sintered samples of $Ba_4(La_{(1-y-z)}Sm_yBi_z)_{9.33}Ti_{18}O_{54}$, $y = 0.7$ for different Bi contents. Closely packed uniform needle-like elongated grains are observed in the samples. It is seen that preferred grain growth occurs along orthorhombic a- or c-axis because a or c-axis is shorter than b-axis in orthorhombic structure. It shows that the average grain size increases with

Table 1
Variation of lattice parameters, unit cell volume, densities and temperature coefficient of resonant frequency of $Ba_4(La_{(1-y-z)}Sm_yBi_z)_{9.33}Ti_{18}O_{54}$, $y = 0.7$ for different Bi contents.

Composition z	Lattice parameters			Volume (Å^3)	Bulk density (g/cm^3)	Relative density (%)	Temperature coefficient τ_f (ppm/°C)
	a (Å)	b (Å)	c (Å)				
0.00	12.19	22.12	3.78	1019.25	5.41	91.1	48.5
0.05	12.27	22.12	3.78	1025.94	5.40	91.6	–
0.10	12.44	22.13	3.80	1046.13	5.45	92.9	−5.0
0.15	12.45	22.12	3.81	1049.25	5.47	93.4	–
0.20	12.56	22.15	3.82	1062.74	5.51	94.0	−34.0

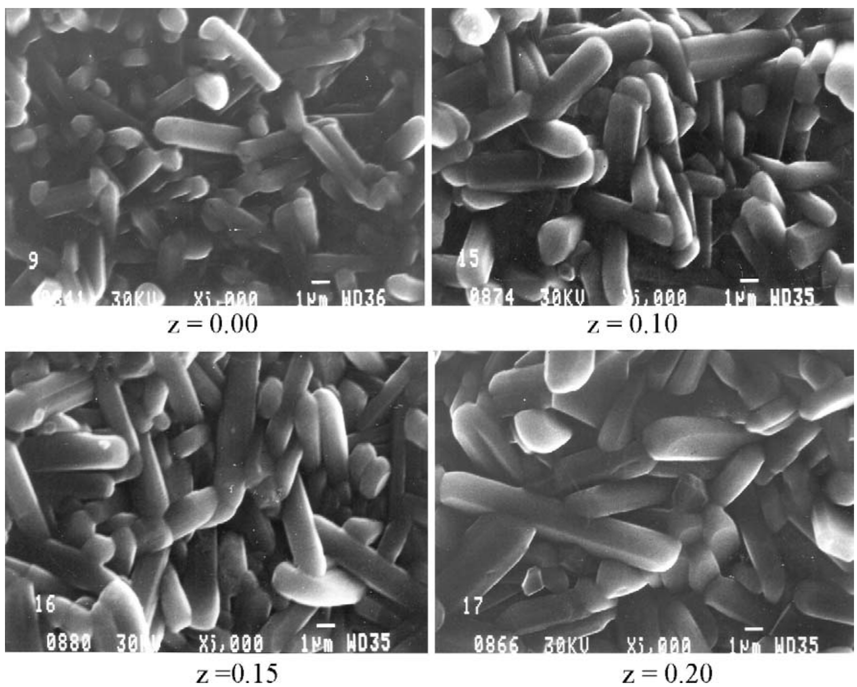

Fig. 2. SEM micrographs of $Ba_4(La_{(1-y-z)}Sm_yBi_z)_{9.33}Ti_{18}O_{54}$, $y = 0.7$ for different Bi contents.

increase in Bi contents due to the large ionic radius of substituted Bi ions as compared to La ions. The EDX analysis of two samples with $z = 0.0$ and $z = 0.20$, given in Fig. 3, clearly indicates the presence of expected elements (Ba, La, Sm, Bi, Ti and O) in desired proportion.

The bulk density and relative density for all the samples as function of Bi contents are also given in Table 1. These ceramics have high value of bulk density (>5 g/cm^3) and relative density (>90%). The maximum bulk density and relative density are measured as 5.51 g/cm^3 and 94%, respectively for $z = 0.20$ and minimum are 5.4 g/cm^3 and 91% for $z = 0.00$. The increase in calculated relative density matches with the observed grain closeness in the microstructures (Fig. 2).

3.3. Dielectric properties

The analysis of the influence of Bi substitution on $Ba_4(La_{(1-y-z)}Sm_yBi_z)_{9.33}Ti_{18}O_{54}$, $y = 0.7$ solid solutions on the microwave dielectric properties reveals clear trends in dielectric constant (Fig. 4), loss tangent (Fig. 5) and temperature coefficient of resonant frequency (Table 1).

The microwave dielectric measurements shows that ε_r increases from 81 to 84 and $\tan\delta$ from 1.2×10^{-3} to 5.1×10^{-3} at 3 GHz with increase in Bi contents from $z = 0.00$ to $z = 0.20$ at room temperature. Based on the substitution of Bi ions in place of La ions such a trend is expected. The dielectric constant depends on tilting of octahedral strings along the c-axis and polarizabilities of ions [6]. The main reason for increase in ε_r with increase in Bi contents could be an increase in average polarizability of A-site cations as the ionic polarizability of Bi^{3+} ion (6.12 Å^3) is higher than the ionic polarizability of La^{3+} ions (6.07 Å^3) as reported by Shannon [19]. Moreover, the tilting angle between the c-axis and the central axis of the octahedra is less for larger sized ions [17]. The large ionic radius of Bi ions (1.45 Å) than La ions (1.36 Å) causes decrease in the tilt of octahedra in solid solutions with higher Bi contents which results in higher ε_r. This implies that both factors contribute towards higher dielectric constant with increase in Bi contents.

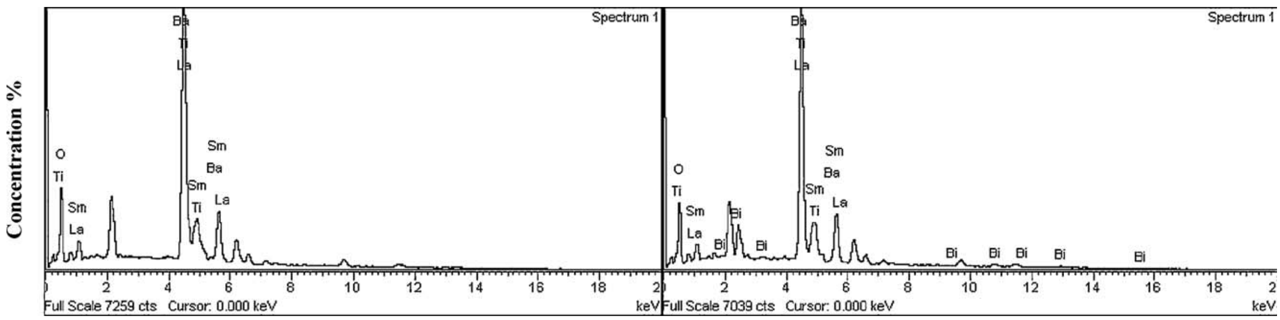

Fig. 3. EDX of $Ba_4(La_{(1-y-z)}Sm_yBi_z)_{9.33}Ti_{18}O_{54}$, $y = 0.7$ for different Bi contents.

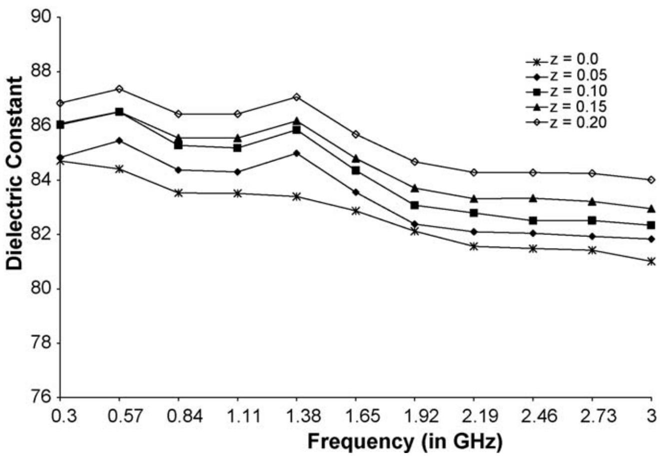

Fig. 4. Variation of dielectric constant of $Ba_4(La_{(1-y-z)}Sm_yBi_z)_{9.33}Ti_{18}O_{54}$, $y = 0.7$ with frequency for different Bi contents.

The major factors causing dielectric losses in the well processed single phase ceramics could be due to presence of compositional in-homogeneity [19] and a high concentration of structural defects. It is clear from Fig. 5 that undoped solid solution has less loss as compared to Bi-doped solid solutions. This could be attributed to the fact that compositional in-homogeneity occurs due to the presence of Sm, La and Bi ions in the rhombic A1-sites and Ba ions in the pentagonal A2-sites. Moreover, the losses are lower if the ionic radii of ions present in the A1-sites are small [20]. Thus, it can be easily concluded that the substitution of larger Bi ion in place of La results in higher loss.

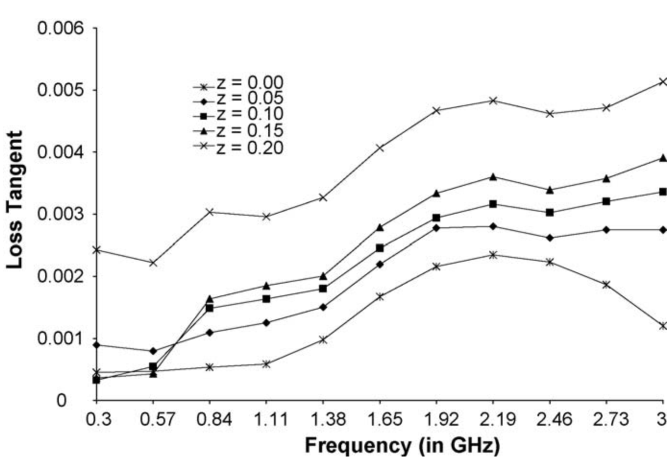

Fig. 5. Variation of loss tangent of $Ba_4(La_{(1-y-z)}Sm_yBi_z)_{9.33}Ti_{18}O_{54}$, $y = 0.7$ with frequency for different Bi contents.

The estimated values of τ_f showed a significant decrease as a result of increasing Bi concentration. From an initial value of 48.5 ppm/°C at $z = 0.00$, τ_f is suppressed to -5.0 ppm/°C at $z = 0.10$. Further substitution of Bi results in negative τ_f that reaches its minimum value of -33.96 ppm/°C at $z = 0.20$. With regard to the relations between variation in ionic radii and dielectric properties, the observed behavior can be explained by the existence of the same intrinsic mechanism that was revealed to rule the dielectric properties of undoped $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ solid solutions [17]. The extension of this study to Bi-doped $Ba_{6-3x}(La_{1-y}Sm_y)_{9.33}Ti_{18}O_{54}$, $y = 0.7$ solid solutions suggests that the increase in average size of A-site ions, originating from the substitution of Bi in place of La, changes the tilting of octahedral in the solid solution. The changes in the tilting of octahedral induce changes in the crystal field and consequently cause a decrease in τ_f.

4. Conclusion

The structural and dielectric properties of microwave dielectric ceramics with general formula $Ba_4(La_{(1-y-z)}Sm_yBi_z)_{9.33}Ti_{18}O_{54}$ where $y = 0.7$ and $z = 0.0$–0.2 have been investigated. It has been observed that combining different rare earths do not appear to alter the single phase range in tungsten bronze-type $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ ceramics. The size of the columnar grain in the microstructure increases with increase in Bi contents. The complex substitution of Sm, La and Bi significantly improves the dielectric properties of barium rare earth titanate. The dielectric constant varies from 81 to 84 and loss tangent from 1.2×10^{-3} to 5.1×10^{-3} at 3 GHz with temperature coefficient of resonant frequency changing from 48.46 to -33.96 ppm/°C as Bi contents increases from $z = 0.00$–0.20. $Ba_4(La_{(1-y-z)}Sm_yBi_z)_{9.33}Ti_{18}O_{54}$, $y = 0.7$, $z = 0.10$ solid solution has the best dielectric properties: $\varepsilon_r = 82$, $\tan\delta = 3.3 \times 10^{-3}$ at 3 GHz and $\tau_f = -5$ ppm/°C. Such materials could be suitable candidate for applications in mobile communications.

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