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EFFECTS OF Sm SUBSTITUTION ON DIELECTRIC PROPERTIES OF $Ba_2(La_{(1-y)}Sm_y)_{4.66}BiTi_9O_{27}$ CERAMICS

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ABSTRACT

The effects of Sm substitution for La on the dielectric and structural properties of $Ba_2(La_{(1-y)}Sm_y)_{4.66}BiTi_9O_{27}$ ceramics are investigated in present study. Three samples with varying Sm contents are synthesized using conventional mixed oxide route and subsequently characterized for structural and dielectric properties at 0.3 GHz to 3.0 GHz. Formation of Tungsten bronze type crystal structure is confirmed from the X-ray powder diffraction results. Microstructural analysis indicated closely packed elongated grains having desired elements in required proportion. The dielectric study showed improvement in loss tangent and temperature coefficient of resonant frequency along with slight reduction in relative permittivity with increase in Sm contents.

Keywords: **Ceramics, Loss Tangent, Relative Permittivity, Temperature Coefficient Of Resonant Frequency**.

I INTRODUCTION

Due to rapid development in the field of wireless communication, requirement of new or modified dielectric ceramics with desired properties has increased tremendously. Various applications such as wireless FAX, global positioning systems (GPS), intelligent transport systems (ITS), ultra high speed local area networks, direct broadcast satellites etc. require materials with high relative permittivity (ε_r) for miniaturization; low loss tangent ($\tan\delta \approx 1/Q$) for better selectivity and nearly zero temperature coefficient of resonant frequency (τ_f) for temperature stability.

Microwave dielectric ceramics with general formula $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ in $BaO\text{-}R_2O_3\text{-}TiO_2$ ternary system (R: Sm, Nd) have been studied extensively and used in practical components due to their excellent dielectric properties [1-4]. The fundamental structural formula was reported as $[R_{8+2x}Ba_{2-3x}V_x]_{A1}[Ba_4]_{A2}[V_4]_CTi_{18}O_{54}$, where V is vacancy, A1-site, A2-site and C-site are rhombic, pentagonal and trigonal respectively. The three different size cations occupy different sites – largest Ba^{2+} ions occupy A2-sites and A1-sites; middle sized R^{3+} ions occupy A1-sites and the smallest Ti^{4+} ions alone occupy octahedral B-sites. The special composition at x = 2/3, in which R^{3+} and Ba^{2+} ions occupy the A1 and A2 sites respectively, exhibits the highest quality factor or lowest loss [5-6].

In this system, R = La based solid solutions have not been focused much due to very high temperature coefficient of resonant frequency (300 ppm/k) and high dielectric loss [7]. Various reports [8-10] are present for A-site and B-site substitution to improve the dielectric properties. In the present work $Ba_2(La_{(1-}$

$_{y)}Sm_y)_{4.66}BiTi_9O_{27}$, y = 0.0, 0.5, 0.7 solid solution with varying Sm contents are synthesized and studied in detail for dielectric and structural properties.

II EXPERIMENTAL PROCEDURE

A Series of Barium Lanthanum Bismuth Titanate dielectric ceramics with general formula $Ba_2(La_{(1-y)}Sm_y)_{4.66}BiTi_9O_{27}$ with y = 0.0, 0.5 and 0.7 was prepared by the conventional solid-state reaction method. Reagent grade high-purity (≥ 99.5%) $BaCO_3$, La_2O_3, Sm_2O_3, Bi_2O_3 and TiO_2 powders were weighed in appropriate molar proportions, mixed and ground in methanol for 12 h. These were then calcined at 1100 ºC for 2 h in air. The calcined powders were re-ground for 12 h and mixed with 3-5 wt% polyvinyl alcohol, and then pressed into circular pellets under a load of 98 kN. Subsequently, these pellets were sintered at 1300 ºC for 2 h in air in a linearly programmable furnance.

The crystalline phases of the crushed samples were identified using the X-ray powder diffraction (XRD: Model PWQ 1729, Philip) method and the lattice parameters of the sample were calculated by the least squares method. The bulk densities of the samples were determined by the Archimedes method. Micro-structural investigation was performed using scanning electron microscopy (SEM: Model JSM 6100, JEOL Japan). In order to evaluate the dielectric properties, the pellets were electrode by silver paste. The dielectric properties, namely relative permittivity and loss tangent were measured in the frequency range 0.3 GHz to 3.0 GHz by using a network analyzer (Model 4192A, Agilent Technologies) at room temperature.

III RESULTS AND DISCUSSION

The x-ray diffraction patterns of $Ba_2(La_{(1-y)}Sm_y)_{4.66}BiTi_9O_{27}$ with y = 0.0, 0.5 and 0.7 are shown in figure 1. All the major peaks are indexed and assigned to tungsten bronze type two overlapped phases [$BaSm_2Ti_4O_{12}$ having JCPDS file no 43-0235 and $Ba_4La_8Ti_{17}O_{50}$ having JCPDS file no 42-0419] along with a small amount of secondary phase $Bi_4Ti_3O_{12}$ All the synthesized sample possess perovskite structure with an orthorhombic symmetry.

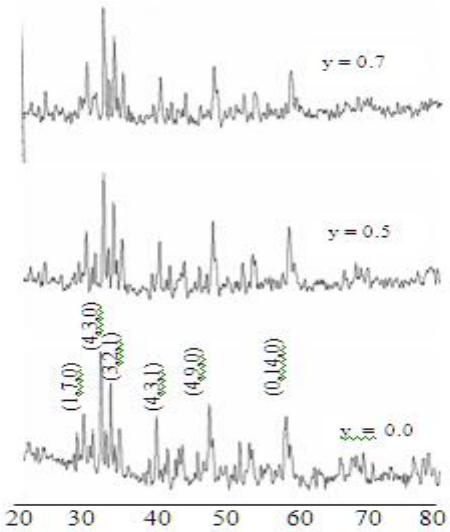

Fig 1 : XRD patterns of $Ba_2(La_{(1-y)}Sm_y)_{4.66}BiTi_9O_{27}$ for varying Sm contents

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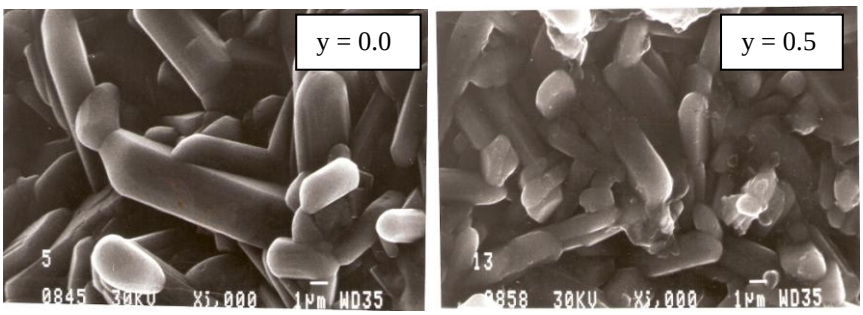
Table 1. Lattice parameters, unit cell volume, bulk density relative density and temperature coefficient of resonant frequency of $Ba_2(La_{(1-y)}Sm_y)_{4.66}BiTi_9O_{27}$ for varying Sm contents

Composition	Lattice Parameters			Volume	Bulk	Relative	Temp
y	a(Å)	b(Å)	c(Å)	(Å3)	Density (gm / cc)	Density (%)	Coeff ppm / ºC
0.0	12.35	22.39	3.90	1078.41	5.10	90.00	54.46
0.5	12.52	22.32	3.87	1076.64	5.40	94.38	-8.37
0.7	12.56	22.15	3.82	1062.74	5.51	94.01	-34.91

The lattice parameters, unit cell volume, bulk and relative density for varying Sm contents are given in table 1. It has been observed that lattice parameter of a-axis increased slightly whereas lattice parameter of b-, c-axis and unit cell volume decreased with increase in Sm contents. The change in lattice parameters is due to the replacement of larger La^{3+} ions by smaller Sm^{3+} ions. The effective ionic radii for 12-coordinate of Sm^{3+} ions and La^{3+} ions were reported as 1.24 Å and 1.36Å respectively [11]. Density measurements indicated that synthesized solid solutions have high values of relative density (> 90 %) and bulk density (> 5.0 g/cm3). High relative density for all the solid solutions matched with the low observed porosity and grain closeness in the microstructures (figure 2).

Figure 2 shows the SEM micrograph of $Ba_2(La_{(1-y)}Sm_y)_{4.66}BiTi_9O_{27}$ ceramics for varying Sm contents. It was noted that the length of closely packed uniform bar shaped grains of the order of micrometer does not change much with increase in Sm contents. The Energy Dispersive X-ray (EDX) spectra for bar shaped grains of two sample are shown in figure 3 and their predicted and measured atomic concentrations of various constituent elements are given in table 2. The expected elements (Ba, La, Sm, Bi, Ti and O) are present in required proportion indicating the formation of desired solid solution. The difference in predicted and measured concentration of different elements are within the experimental error of EDX analysis.



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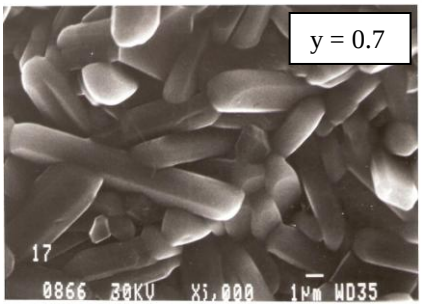

Fig. 2: SEM micrograph of $Ba_2(La_{(1-y)}Sm_y)_{4.66}BiTi_9O_{27}$ for varying Sm contents

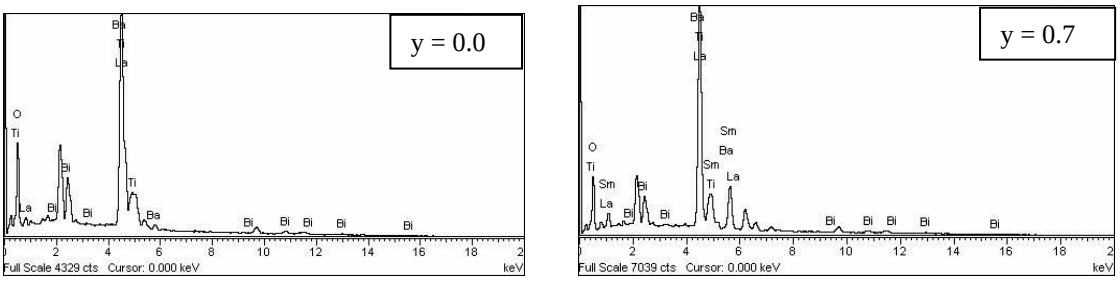

Fig. 3 EDAX spectra of of $Ba_2(La_{(1-y)}Sm_y)_{4.66}BiTi_9O_{27}$ with y = 0.0 and 0.7

Table 2 Predicted and measured atomic concentrations of $Ba_2(La_{(1-y)}Sm_y)_{4.66}BiTi_9O_{27}$ with y = 0.0 and 0.7

Element	Atomic Concentration (%)			
	For y = 0.0		For y = 0.7	
	Predicted	Measured	Predicted	Measured
Ba	4.69	4.26	4.69	4.45
La	8.75	8.00	1.09	0.99
Sm	-	-	7.65	7.01
Bi	2.19	2.09	2.19	1.97
Ti	21.09	20.03	21.09	20.41
O	63.28	65.62	63.28	65.17

The effect of Sm substitution on dielectric properties namely relative permittivity and loss tangent with respect to frequency are shown in figure 4 and 5 respectively. A high value of relative permittivity of 91.26 for y=0.0; 88.53 for y = 0.5 and 84.28 for y = 0.7 is obtained at 2.4 GHz frequency. It has been noted that relative permittivity decreased with increase in substitution of Sm^{3+} ions in place of La^{3+} ions. This decrease could be due to direct dependence of relative permittivity on the ionic polarizability of the ions and lower ionic polarizability of Sm^{3+} ions (4.74Å) as compared to La^{3+} ions (6.07Å) [12]. The relative permittivity also decreased with increase in frequency for all the studied samples. This is because at higher frequencies, the hopping of ions could not follow the applied field frequency and lags behind it [5].

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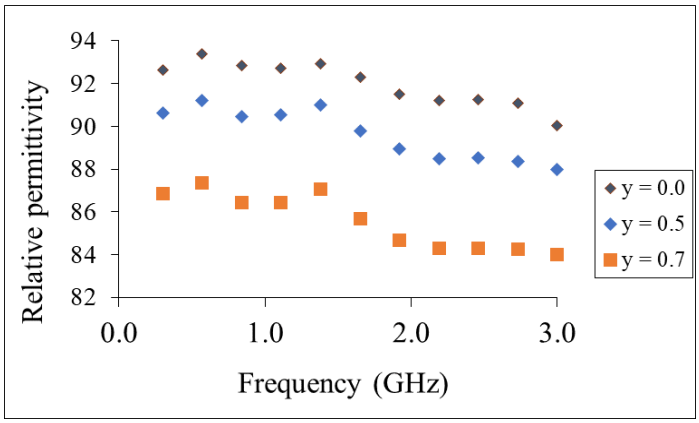

Fig. 4 Variation of relative permittivity of $Ba_2(La_{(1-y)}Sm_y)_{4.66}BiTi_9O_{27}$ with frequency for varying Sm contents Sm contents at room temperature.

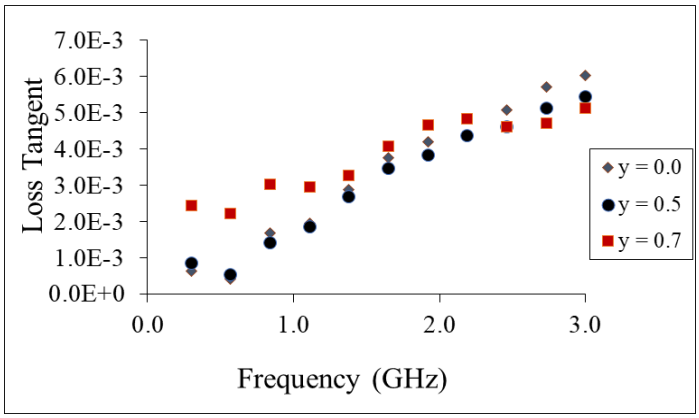

Fig. 5 Variation of loss tangent of $Ba_2(La_{(1-y)}Sm_y)_{4.66}BiTi_9O_{27}$ with frequency for varying Sm contents at room temperature.

Dielectric losses are mainly determined by compositional inhomogeneity and structural defects as more energy is consumed to align dipole in a changing field [13]. From figure 5, it is observed that the loss tangent decreased with increase in Sm substitution. It is found out to be 5.08 x 10^{-3} for y = 0.0; 4.62 x 10^{-3} for y = 0.5 and 4.61 x 10^{-3} for y = 0.7 at 2.4 GHz. Loss tangent has similar variation with respect to composition as shown by relative permittivity so can be explained in similar way. Third and important dielectric performance parameter i.e. temperature coefficient of resonant frequency (table 1) also decreased with increase in Sm substitution in place of La. It changed from 54.46 ppm/K for y = 0.0 to -8.37 ppm/K for y = 0.5 and finally -34.91 ppm/K for y = 0.7. This variation in temperature coefficient with respect to composition is due to change in crystal field obtained as a result of change in the tilt of octahedral originated from reduction of average ionic size of A-site ions [14].

IV CONCLUSIONS

The effects of Sm substitution in place of La in $Ba_2(La_{(1-y)}Sm_y)_{4.66}BiTi_9O_{27}$ solid solution with y = 0.0, 0.5, 0.7 have been studied and analyzed. X-ray diffraction patterns confirmed the formation of tungsten bronze type structure with orthorhombic symmetry. Scanning electron microscopic images and density measurements indicated the formation of closely packed elongated bar shaped grains with low porosity. It can be concluded

that Sm substitution improved the dielectric properties. Composition $Ba_2(La_{(1-y)}Sm_y)_{4.66}BiTi_9O_{27}$, y = 0.5 has got excellent properties having relative permittivity of 88.53 and loss tangent of 4.62 x 10-3 at 2.4 GHz with temperature coefficient of -8.37 ppm/K. The studied compositions have great potential to be used as resonators and filters in advanced wireless communication systems.

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