Frequency and temperature dependence of dielectric and electric properties of $\text{Ba}_{2-x}\text{Sm}_{4+2x/3}\text{Ti}_8\text{O}_{24}$ with structural analysis

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Dielectric ceramics samples of barium titanium oxide doped with samarium, having a complex structural formula of $\text{Ba}_{2-x}\text{Sm}_{4+2x/3}\text{Ti}_8\text{O}_{24}$ (referred to as BST), were fabricated by a high temperature solid-state reaction technique with varying x (0.0, 0.2, 0.4, 0.6). X-ray diffraction technique was used to check the formation of particular phases. Scanning electron microscope technique was used to study the surface morphology of the samples. The samples were studied in a temperature range of 298 K to 623 K and frequency range of 10 KHz to 1 MHz. The dielectric constant (ϵ_r), loss tangent ($\tan\delta$), and AC conductivity (σ_{AC}) were measured on sintered disks of BST samples. The DC resistivity of different compositions was measured at room temperature. Detailed studies of dielectric and electrical properties showed that these properties are strongly dependent on composition, frequency and temperature. The compounds showed stable behavior in lower temperature range (up to 523 K), therefore, they can be used in practical applications in this temperature range.

Keywords: *barium samarium titanate (BST); dielectric constant (ϵ_r); loss tangent ($\tan\delta$); AC conductivity (σ_{AC}); DC resistivity*

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1. Introduction

Microwave dielectric materials have been a subject of interest of many researchers since 1970s. These ceramics became very popular research subject for miniaturization of microwave devices such as, resonators, duplexers, filters etc. They enabled us to design the equipment small in size, cheap, efficient, stable and portable [1]. A large number of materials have been developed and put into practical use for microwave filters, resonators and mobile-communication technology. BaTiO_3 , having a perovskite structure, has been the key material for microwave devices [2]. With time, rare earth metals have been intentionally doped in the structure with the formula of $\text{Ba}_{2-x}\text{Sm}_{4+2x/3}\text{Ti}_8\text{O}_{24}$ [3] to improve their properties. These developments include the ceramics: $\text{Ba-R}_2\text{O}_3\text{-TiO}_2$, $(\text{Zr},\text{Sn})\text{TiO}_4$ system, BaO-TiO_4

titanium rich system, $\text{Ba}(\text{B}_{1/3}\text{Ta}_{2/3})\text{O}_3$ ($\text{B} = \text{Mg}, \text{Zn}$) [4–7].

The structure of BST ceramics consists of corners sharing TiO_6^{2-} octahedra which extend in the shorter direction and form a network of rhombic and pentagonal channels. In this structure, titanium-oxygen tetrahedra are linked together at their corners in such a way that three types of openings with different sizes and shapes are yielded. Three different tunnels are made in the spaces between TiO_6^{2-} tetrahedra, i.e. tetrahedral openings (A_1 sites), pentagonal openings (A_2 sites) and triangle openings (A_3 sites). In a simplest unit of tungsten bronze material, there are seven A sites and ten octahedrals. It can be represented as:

$$[(A_1)_2(A_2)_4A_3][(B_1)_2(B_2)_8]O_{30}$$

where A_3 represents the vacancy unless small cations, like Li^+ , Mg^{2+} , are present. In general form, this structure has the chemical composition of $\text{BaO-Sm}_2\text{O}_3\text{-kTiO}_2$ ($k = 3 - 5$) [3].

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The three key properties required for these materials are: (i) high dielectric constant: to ensure a smaller size of dielectric resonator, (ii) low loss tangent: to have better selectivity of frequency, (iii) low temperature coefficient of resonant frequency which is a measure of drift in resonant frequency with temperature. Its value should be close to zero for thermal stability of device frequency [1, 8]. The AC conductivity arises due to random defect centers and impurities in the structure. It should be low for dielectrics to achieve fast response [9]. It is a well-known fact that these properties are frequency and temperature dependent [10]. Therefore, the study of these materials in temperature and frequency range should give valuable information about the quality of synthesized material.

In this research paper, we have investigated the variations in microwave properties with frequency and temperature for the ceramics samples. The dielectric ceramics $\text{BaO-Sm}_2\text{O}_3\text{-kTiO}_2$ was presented in the form of $\text{Ba}_{2-x}\text{Sm}_{4+2x/3}\text{Ti}_8\text{O}_{24}$, where the value of x was varied as 0.0, 0.2, 0.4 and 0.6. The dielectric constant, loss tangent and AC conductivity of these ceramics were studied in the frequency range of 10 KHz to 1 MHz and temperature range of 298 K to 623 K. Along with this we have studied the DC resistivity and temperature coefficient of resonant frequency for different substitutions of samarium.

2. Experimental

2.1. Samples preparation

Pervoskite compounds with nominal formula $\text{Ba}_{2-x}\text{Sm}_{4+2x/3}\text{Ti}_8\text{O}_{24}$ ($x = 0.0, 0.2, 0.4$ and 0.6) were prepared by the traditional mixed oxide complex route method. Stoichiometric amounts of commercially available oxides and carbonates: Ba_2CO_3 , Sm_2O_3 and TiO_2 were taken as raw material. All oxides were having purity better than 99.5 %. Moisture was removed from the samples by preheating them at 873 K for 12 hours before weighing. These oxides and carbonates were mixed thoroughly in an agate mortar for 12 hours to get a mixture. The mixture was dried and calcined at 1100 °C for 2 hours. The obtained powders were

re-grounded for 12 hours. Intermediate cooling and mechanical grinding was done to get an accurate homogenization and complete reaction. The fine homogenous powders were granulated using 3 % solution of polyvinyl alcohol (PVA) to reduce the brittleness. This step was followed by shaping the samples. The samples were pressed into pellets of cylindrical shape of 12 mm in diameter and 4 mm in thickness under a load of 98 kN. The pellet samples were sintered in air at 1300 °C for 6 hours in a linearly programmable furnace. Finally, cooling down of the disks to room temperature was done at the rate of 200 °C/h.

2.2. Electrical measurements

XRD analysis was made on SHIMADZU XRD-7000 X-ray diffractometer with $\text{CuK}\alpha$ radiation filtered by a Ni-filter. The data were collected in 2θ range of 20° to 80° with the step size of 0.02° and preset time of 0.6 s per step. The surface microstructure, like grain size distribution and morphology, was studied with a scanning electron microscope (ZEISS, SUPARA 5) operating at 20 kV. The BLT samples were polished with a fine emery paper to get flat, smooth and parallel surfaces for electrical measurements. Fine silver paint was applied on both sides of the pellets before electrical measurements to make a good electrical contact with the electrodes of sample holder. Capacitance, loss-factor and conductance were measured in the frequency range of 10 KHz to 1 MHz and temperature range of 298 K to 623 K using a Wayne Kerr 6500B precision impedance analyzer and a programmable induction furnace C-1000 interfaced with a PC with an AC signal (1 V).

The dielectric constant of the pellets was calculated from the formula:

$$\epsilon_r = (C \cdot d) / (\epsilon_0 \cdot A) \quad (1)$$

where C is capacitance, d is the thickness of the sample, ϵ_0 is dielectric constant of free space and A is the area of cross section of the sample. Value of C is obtained from impedance analyzer.

AC conductivity was estimated from the formula:

$$\sigma_{AC} = (C \cdot d) / A \quad (2)$$

where C is the conductance of the sample, d is the thickness and A is area of cross section of the sample. Conductance was measured with an impedance analyzer.

Temperature coefficient of resonant frequency was calculated in the temperature range of 298 K to 348 K as:

$$\tau_f = -((\tau_\epsilon/2) + \alpha_i) \quad (3)$$

where τ_ϵ represents the temperature coefficient of dielectric constant and α_i is a linear thermal expansion coefficient that is about +10 ppm/K in dielectric ceramics. τ_ϵ was calculated from the formula:

$$\tau_\epsilon = (\epsilon_{348} - \epsilon_{298}) / \epsilon_{298} \quad (4)$$

where ϵ_T is the value of dielectric constant at temperature T . Here, 348 K and 298 K temperatures were used for calculation.

X-ray density was calculated from the relation:

$$D_x = 2Mn/(3)^{1/2}(N_a abc) \quad (5)$$

where M is the molecular weight of the sample, a , b and c are lattice parameters, N_a is Avogadro's number per gram mole and n is number of molecules per unit cell. Experimental density of all the ceramics samples was determined by the Archimedes principle using deionized water.

3. Results and discussion

3.1. Structural and microstructural analysis

3.1.1. X-ray diffraction

Fig. 1 shows the XRD patterns for the synthesized samples. Powder diffraction data for this analysis were obtained using the step scan method on an X-ray diffractometer with $\text{CuK}\alpha$ radiation filtered by a Ni-filter. The sharp diffraction peaks confirm homogeneity and good crystallization of the BST samples. The X-ray analysis indicates that the compounds are of orthorhombic structure at room temperature. The unit lattice parameters (a , b and c) were calculated from the observed peak positions. The selected unit cell parameters were refined using least-squares method to minimize $\Sigma\Delta d$

($\Delta d = d_{\text{obs}} - d_{\text{cal}}$). It was observed from the calculations that as we increased the content of samarium, the values of unit cell parameters decreased. This was due to the reason that as the samarium content increased in the composition, the Sm^{3+} cations, being smaller than Ba^{2+} ions, substituted in the barium sites. This resulted in a decrease in the unit cell parameters. The values of the unit-cell parameters are given in Table 1.

3.1.2. Scanning electron micrographs

Fig. 2 shows the SEM micrographs of freshly fractured samples of $\text{Ba}_{2-x}\text{Sm}_{4+2x/3}\text{Ti}_8\text{O}_{24}$ ceramics coated with silver film. These micrographs show that the compound was formed in a number of phases. It possesses typical columnar grain morphology usually observed for tungsten bronze phase. This microstructure evolution confirms the observation of phase identification in XRD pattern.

3.2. Dielectric properties

3.2.1. Dielectric constant

Fig. 3 shows the variation of ϵ_r with frequency at different temperatures (298 K, 323 K, 423 K, 523 K and 623 K) for all four samples. The highest value of dielectric constant was observed for $x = 0.6$ sample at all frequencies at all temperatures.

Variation with frequency. The plots show that the dielectric constant of all four samples decreases with increasing frequency. This is the general behavior of the dielectrics and is termed as "frequency dispersion" [11, 12]. This behavior is attributed to the justification given in Maxwell-Wagner interfacial model [13]. According to this model, a dielectric material is composed of two layers in which well conducting grains are separated by poorly conducting grain boundaries. At the lower frequencies, under effect of field, the charge carriers easily migrate through the grains but get accumulated at the grain boundaries. This process results in high interfacial polarization [14]. The higher the polarization in the material, the higher the dielectric constant. Thus, all types of polarization – electronic, ionic, dipolar and interfacial/surface – play the major role in

Table 1. Variation of lattice constants for BST samples with $x = 0.0, 0.2, 0.4$ and 0.6 sintered at 1300°C for 6 hours.

Composition (x)	Formula	Lattice constant	Lattice constant	Lattice constant
		'a' (Å)	'b' (Å)	'c' (Å)
0.0	$\text{Ba}_2\text{Sm}_4\text{Ti}_8\text{O}_{24}$	12.656	23.265	4.001
0.2	$\text{Ba}_{1.8}\text{Sm}_{4.13}\text{Ti}_8\text{O}_{24}$	12.354	23.276	3.9276
0.4	$\text{Ba}_{1.6}\text{Sm}_{4.26}\text{Ti}_8\text{O}_{24}$	12.243	23.196	3.7569
0.6	$\text{Ba}_{1.4}\text{Sm}_{4.39}\text{Ti}_8\text{O}_{24}$	12.176	23.087	3.5428

Fig. 1. X-ray diffraction (XRD) patterns of BST samples with varying x (a) 0.0, (b) 0.2, (c) 0.4 and (d) 0.6.

determining the value of ϵ_r . Therefore, we obtain higher values of ϵ_r . But with the increase in frequency, the interfacial polarization reduces to almost negligible extent, only dipolar and electronic polarization contribute to dielectric constant [15]. Thus, the dielectric constant decreases. This almost constant behavior of dielectric constant is known as dielectric relaxation.

Fig. 4 shows the variation of ϵ_r with temperature at specific frequencies (0.1 MHz, 0.25 MHz,

0.5 MHz, 0.75 MHz and 1.0 MHz). All the four samples show almost constant behavior in low temperature range (298 K to 523 K).

Variation with temperature. The results show that the dielectric constant increases with an increase in temperature. This increase may be due to space charge polarization that arises as a result of ion mobility and ion imperfections [16]. The combined effects of these two factors give rise to higher dielectric constant. This increase in dielectric

Fig. 2. Scanning electron micrographs (SEM) of BST samples with varying x (a) 0.0, (b) 0.2, (c) 0.4 and (d) 0.6.

constant is larger at lower frequencies than at higher frequencies. At low frequencies, interfacial polarization and dipolar polarization are more dominant and both are temperature dependent. Interfacial polarization arises due to the accumulation of charges at the grain boundary. The charge carriers are not completely free but are strongly localized.

An increase in temperature results in thermal activation of the charge carriers and their drift mobility. This results in the increase in electron exchange interaction which results in an increase in dielectric constant. The fast increase in ϵ_r with an increase in temperature at low frequencies suggests that the effect of temperature is more pronounced on the interfacial polarization than on the dipolar

Fig. 3. Variation of dielectric constant of BST samples with frequency at specific temperatures (a) $x = 0.0$, (b) $x = 0.2$, (c) $x = 0.4$ and (d) $x = 0.6$.

polarization. At high frequencies, electronic and ionic polarizations start playing the major role and they depend on temperature to a very small extent [17].

3.2.2. Loss tangent

Fig. 5 shows the variation of $\tan\delta$ with frequency at different temperatures (298 K, 323 K, 423 K, 523 K and 623 K) for all four samples.

Fig. 4. Variation of dielectric constant of BST samples with temperature at specific frequencies (a) $x = 0.0$, (b) $x = 0.2$, (c) $x = 0.4$ and (d) $x = 0.6$.

The lowest value of loss tangent is observed in the sample with $x = 0.6$ for all frequencies at room temperature. It shows the fall in dielectric loss with frequency in accordance with formula:

$$\tan \delta = \epsilon'' / \epsilon'$$

where ϵ'' represents the dielectric loss and ϵ' represents dielectric constant.

Variation with frequency. It is observed in the plots that the loss tangent decreases with an increase in frequency. The trend followed by the loss tangent is similar to that of dielectric constant. Similar trends of ϵ_r and $\tan\delta$ were observed in other ceramics too [16]. This may be due to dielectric lagging taking place in ceramics [8]. At lower frequencies, conduction losses or ion migration losses become more dominant, resulting in high loss tangent. This process can be attributed to ion hopping frequency between two ion positions. The maximum energy loss occurs for a frequency equal to hopping frequency. When the applied AC frequency becomes greater than hopping frequency, the atoms do not have an opportunity to hop at all, so the losses become low [17].

Fig. 6 demonstrates how the loss tangent varies with respect to temperature at specific frequencies for all four samples. For dielectric ceramics, loss tangent should be as low as possible.

Variation with temperature. Fig. 6 shows the variation of $\tan\delta$ with temperature at specific frequencies (0.1 MHz, 0.25 MHz, 0.5 MHz, 0.75 MHz and 1.0 MHz). The plots show that at low temperatures the variation in tangent loss is very low and increases rapidly at higher temperatures.

This behavior can be justified on the basis of Debye's equation for loss:

$$\tan \delta = (\epsilon_s - \epsilon_\infty)\omega\tau/\epsilon_s + \epsilon_\infty\omega^2\tau^2 \quad (6)$$

As temperature increases, relaxation time decreases and $\tan\delta$ would increase according to the equation of Debye. At higher temperatures, an increase in loss tangent may be due to the increased conduction [20]. Thus, it is clear that the electric conductivity of materials and relaxation effect influence the losses in materials. With the increase in temperature, the losses that arise due to dipole orientations (τ) decrease, while the losses resulting from electric conductivity increase. Since in our research, an increase in the dielectric loss with an increase in temperature has been observed, therefore, it seems that the losses due to electrical conductivity are more dominant than those due to the relaxation effects [8, 10].

Fig. 5. Variation of loss tangent of BST samples with frequency at specific temperatures (a) $x = 0.0$, (b) $x = 0.2$, (c) $x = 0.4$ and (d) $x = 0.6$.

The observed properties and their trends are similar to the trends observed in [4, 8, 9] and [12]. Decrease with frequency and increase with temperature is a general behavior observed in this category of ceramics. Thus, their use as practical materials is possible in dielectric resonators and antennas.

Fig. 6. Variation of loss tangent of BST samples with temperature at specific frequencies (a) $x = 0.0$, (b) $x = 0.2$, (c) $x = 0.4$ and (d) $x = 0.6$.

3.3. Electrical properties

3.3.1. DC resistivity

The results of DC resistivity ($\Omega \cdot m$) are plotted in Fig. 7. As we increase the content of samarium in barium titanate, DC resistivity decreases. On the substitution of Sm^{2+} ions, vacancies are created along with reduction of Ti^{4+} and Ti^{3+} , which may result in electrons conduction in order to keep charge neutrality. This gives rise to a decrease in DC resistivity [18].

Fig. 7. Variation of DC resistivity of BST samples with composition at room temperature.

3.3.2. AC conductivity

Fig. 8 shows the variation of AC conductivity with frequency at different temperatures (298 K, 323 K, 423 K, 523 K and 623 K) for all four samples.

Variation with frequency. In the plots an increase in AC conductivity can be observed with frequency increase. This behavior is evident from the relation of AC conductivity with frequency:

$$\sigma_{AC} = \epsilon_r \epsilon_0 \omega \cdot \tan \delta \quad (7)$$

When the frequency of applied field is increased, the conductive grains become more active by promoting the hopping between ions. The frequency at which electrons start hopping between ions is called hopping frequency [19]. As the frequency increases, the hopping frequency increases. Thus, we observe a gradual increase in conductivity with frequency [20, 21].

Fig. 9 shows the variation of AC conductivity with temperature at specific frequencies (0.1 MHz, 0.25 MHz, 0.5 MHz, 0.75 MHz and 1.0 MHz).

Variation with temperature. It is observed that AC conductivity increases with an increase in temperature. In fact, AC conductivity arises due to impurities that are randomly distributed in material. Conduction is basically due to hopping mechanism of various ion species in materials. The excess electrons in narrow conduction band distort the surroundings due to their interaction with the lattice. As a result, a potential well is created that gives rise to conduction. With the rise in temperature, the number of electrons gets enhanced and they cross the well. Thus, with an increase in temperature, the AC conductivity increases [9].

Fig. 8. Variation of AC conductivity of BST samples with frequency at specific temperatures (a) $x = 0.0$, (b) $x = 0.2$, (c) $x = 0.4$ and (d) $x = 0.6$.

Similar pattern of AC conductivity were observed in other research works [8, 9, 22].

4. Conclusions

In a nutshell, dielectric ceramics with the structural formula $\text{Ba}_{2-x}\text{Sm}_{4+2x/3}\text{Ti}_8\text{O}_{24}$ with $x = 0.0, 0.2, 0.4$ and 0.6 have been synthesized and then studied at various frequencies and temperatures. The samples showed high values of dielectric constant (40 to 150) that increased with temperature, whereas decreased with frequency. Very low

Fig. 9. Variation of AC conductivity of BST samples with temperature at specific frequencies (a) $x = 0.0$, (b) $x = 0.2$, (c) $x = 0.4$ and (d) $x = 0.6$.

values of loss tangent were observed. The measured AC conductivity increased with both temperature and frequency. DC resistivity decreased with an increase in substitution. The samples showed stabilized behavior up to 523 K but above this temperature anomalies were observed in all three parameters. Such type of stable behavior makes these materials useful in numerous applications.

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