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# Influence of frequency variations on the dielectric properties of Sm doped $Ba_4La_{9.33}Ti_{18}O_{54}$ dielectric ceramics at various temperatures

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The dependence of frequency variations on the dielectric properties of Sm substituted barium lanthanum titanate was investigated. Dielectric ceramics based on the $Ba_4(La_{1-y}Sm_y)_{9.33}Ti_{18}O_{54}$ system, where $y$ = 0.0, 0.3, 0.5, 0.7, were synthesized and subsequently characterized for their structural and dielectric properties. The temperature dependences of the relative permittivity and the dielectric losses were measured in the frequency range from 10 kHz to 10 MHz, for temperatures ranging from 25 °C to 150 °C. The measurement system consisted of an impedance analyzer and a temperature chamber. Substituting Sm for La was an effective way to stabilize the variations in relative permittivity, within the temperature range of interest. No dielectric anomaly was observed in this temperature range. The temperature coefficient of the resonant frequency improved from 273.9 ppm/°C at $y$ = 0.0 to 53.8 ppm/°C at $y$ = 0.7. The relative permittivity of 90.33 and a dielectric loss of 0.09 were obtained at 25 °C for $y$ = 0.5 at 10 MHz; the temperature coefficient of the resonant frequency was 106.8 ppm/°C. The materials under investigation have high relative permittivities, remaining constant under temperature variation, which therefore makes them suitable for applications in communication devices.

Keywords: *ceramics; relative permittivity; dielectric loss; temperature coefficient of resonant frequency*

## 1. Introduction

The revolution in microwave telecommunication and satellite broadcasting systems has created the need for good quality dielectric ceramics. The important properties required for these materials are a high electric permittivity ($\varepsilon_r > 70$) for miniaturization, low loss or a high quality factor ($Q > 2000$) for selectivity, and a low temperature coefficient of the resonant frequency ($\tau_f$) for stability. The unique dielectric properties, namely high relative permittivity (70–100), low dielectric losses and low temperature coefficient of resonant frequency, of $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R is a rare earth atom such as La, Nd, Sm or Gd) solid solutions [1–3] make them very important

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for applications in communication devices. However, the requirements of modern communication technologies demand even greater improvements in the performance of the materials. Ohsato et al. [4–7] have extensively studied the structural and dielectric properties of $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ and found that the ordering of $Ba^{2+}$ and $R^{3+}$ ions at $x = 2/3$ leads to the lowest internal strain, which in turn results in a maximum quality factor. In this system, La based solid solutions [5, 7, 8] have the highest relative permittivity, but dielectric loss and the temperature coefficient of the resonant frequency (~300 ppm/°C) are also high. Some reports have been published on the improvement of dielectric properties of $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ solid solutions by A and/or B site substitution [9, 10]. In our previous paper [11], we have reported the required reduction in dielectric loss tangent by Sm substitution in $Ba_4La_{9.33}Ti_{18}O_{54}$ dielectric ceramic while keeping the high relative permittivity. Now, the main objective is the suppression of the temperature coefficient of the resonant frequency ($\tau_f$) while retaining low dielectric loss and a high relative permittivity ($\varepsilon_r$). The goal of this study is to investigate the effect of various Sm substitutions on $Ba_6La_{9.33}Ti_{18}O_{54}$ solid solutions over a wide temperature and frequency range.

## 2. Experimental

Ceramic samples of $Ba_4(La_{(1-y)}Sm_y)_{9.33}Ti_{18}O_{54}$, where $y$ = 0.0, 0.3, 0.5 and 0.7, were prepared using the high temperature solid state reaction technique. The stoichiometric mixtures of high purity powders of $BaCO_3$ (99.5%), $La_2O_3$ (99.9%), $Sm_2O_3$ (99.9%) and $TiO_2$ (99.5%) were weighed and ground for 12 h in methanol. The mixtures were then dried and calcined in air at 1100 °C for 2 h. The calcined powders were thoroughly re-ground, mixed with 3 wt. % of polyvinyl alcohol (PVA) as a binder and pressed into pellets of various shapes under the load of 98 kN. These pellets were then sintered at 1300 °C for 2h in air.

X-ray diffraction data were collected on a Philips, PWQ 1729 powder X-ray diffractometer using $CuK_\alpha$ radiation in the $2\theta$ range from 20° to 80°. The microstructures of freshly fractured sintered samples were examined using a JEOL, JSM 6100 scanning electron microscope and an Oxford, INCA energy dispersive X-ray analyzer. The bulk densities of the sintered samples were measured by the Archimedes method.

Flat surfaces of the pellets were polished with high purity conductive silver paste. The dielectric properties, namely the relative permittivity and the dielectric loss in function of temperature in the range from 25 °C to 150 °C and frequency in the range from 10 kHz to 10 MHz, were calculated from the data recorded from an Agilent, HP 4192A impedance analyzer and a programmable temperature chamber interfaced with a PC. The temperature coefficients of the resonant frequency ($\tau_f$) in the temperature range from 25 °C to 90 °C were estimated using the dependence [12]:

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

where $\tau_\varepsilon$ is the temperature coefficient of the relative permittivity and $\alpha$ is the thermal expansion coefficient, which is about 10 ppm/°C [9] in the ceramics under study here.

## 3. Results and discussion

The XRD patterns and SEM micrographs of $Ba_4(La_{1-y}Sm_y)_{9.33}Ti_{18}O_{54}$ ceramics having different Sm content were reported earlier [11]. Detailed structural analysis, along with lattice parameters, has already been reported.

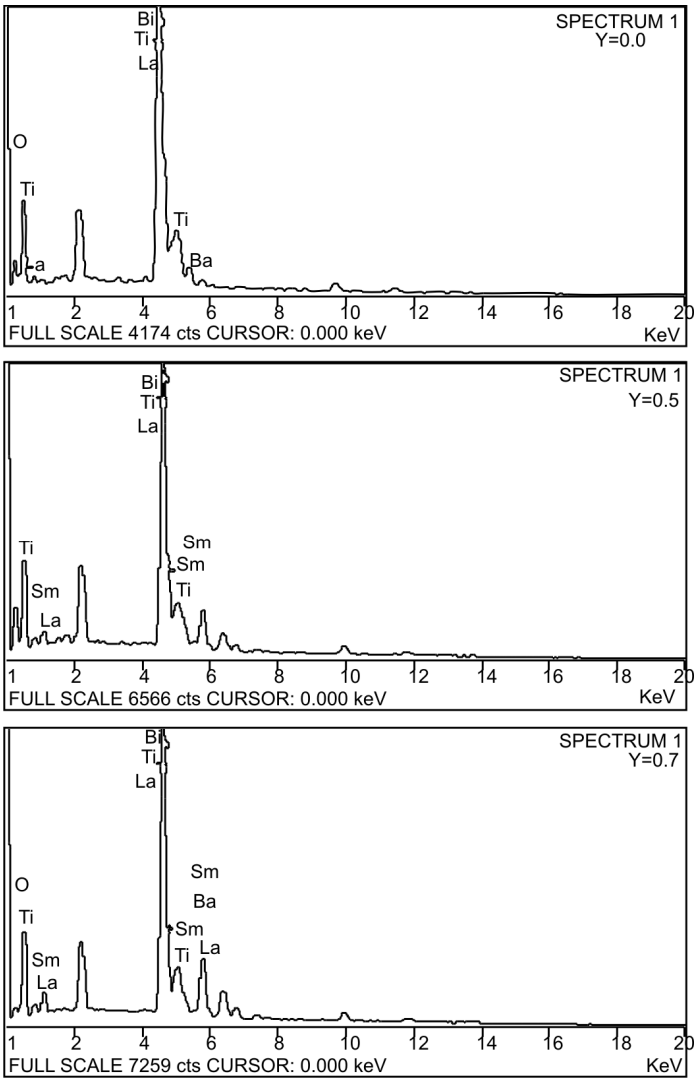


Fig. 1. Results of EDX analysis of $Ba_4(La_{(1-y)}Sm_y)_{9.33}Ti_{18}O_{54}$ for various Sm contents

It has been found that all the ceramic samples possess single phase of tungsten bronze-type compounds and have orthorhombic symmetry. Microstructural examination showed the presence of closely packed uniform hexagonal grains with low porosity. Figure 1 shows the results of the EDX analysis of three samples, with $y = 0.0$, 0.5 and y = 0.7. The observed and the calculated atomic concentration of various elements in $Ba_4(La_{(1-y)}Sm_y)_{9.33}Ti_{18}O_{54}$ solid solution are given in Table 1. This indicates the presence of expected elements (Ba, La, Sm, Ti and O) in the required proportions.

Table 1. Observed and calculated atomic concentrations [at. %] of various elements in $Ba_4(La_{(1-y)}Sm_y)_{9.33}Ti_{18}O_{54}$

| Element | $y = 0.0$ | | $y = 0.5$ | | $y = 0.7$ | |
|---|---|---|---|---|---|---|
| | Calculated | Observed | Calculated | Observed | Calculated | Observed |
| Ba | 4.69 | 4.52 | 4.69 | 4.85 | 4.69 | 4.59 |
| La | 10.93 | 10.29 | 5.47 | 5.07 | 3.28 | 2.98 |
| Sm | – | – | 5.47 | 5.27 | 7.65 | 7.05 |
| Ti | 21.09 | 20.13 | 21.09 | 20.22 | 21.09 | 19.42 |
| O | 63.29 | 65.06 | 63.28 | 64.59 | 63.28 | 65.96 |

The bulk density for all the samples in function of Sm content is shown in Fig. 2. These ceramics have a high bulk density (>5.0 g/cm3), with a maximum of 5.46 gm/cc for y = 0.7, confirming the observed porosity diminution in the microstructures [11] (grain closeness).

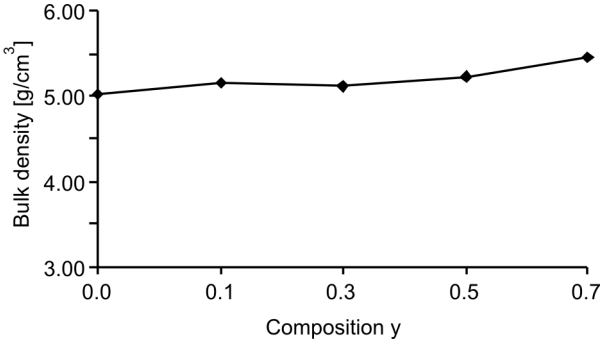


Fig. 2. Bulk densities of $Ba_4(La_{(1-y)}Sm_y)_{9.33}Ti_{18}O_{54}$ for various Sm contents

The dependences of relative permittivity and dielectric losses on frequency in the range of 10–10 MHz for various Sm contents at room temperature are shown in Figs. 3 and 4, respectively. The relative permittivity decreases from 106.44 for $y = 0.0$ to 90.33 for $y = 0.5$ and finally to 89.27 for $y = 0.7$ at 10 MHz. These results are in accordance with the variation in relative permittivity and loss at high frequencies (0.3 GHz–3.0 GHz) as previously reported [11]. The relative permittivity $\varepsilon_r$ decreases

with the increase in Sm content, due to the substitution of Sm ions for La ions. The relative permittivity depends on the unit cell volume, tilting of octahedral strings along the *c* axis and polarizabilities of ions [5]. It is evident from previously reported results that the unit cell volume decreases with increase in Sm contents thereby decreasing $\varepsilon_r$. The tilting angle between the *c* axis and the central axis of the octahedra is smaller for larger sized ions [12]. The smaller ionic radii of $Sm^{3+}$ ions (1.24 Å) than those of $La^{3+}$ ions (1.36 Å) [13] cause an increase in the tilt of octahedra in solid solutions with higher Sm content, resulting in lower $\varepsilon_r$. Moreover, the third factor, i.e. the ionic polarizability of $Sm^{3+}$ ions (4.74 $Å^3$), is lower than the ionic polarizability of $La^{3+}$ ions (6.07$Å^3$) as reported by Shannon [14] also contributes towards decrease in $\varepsilon_r$.

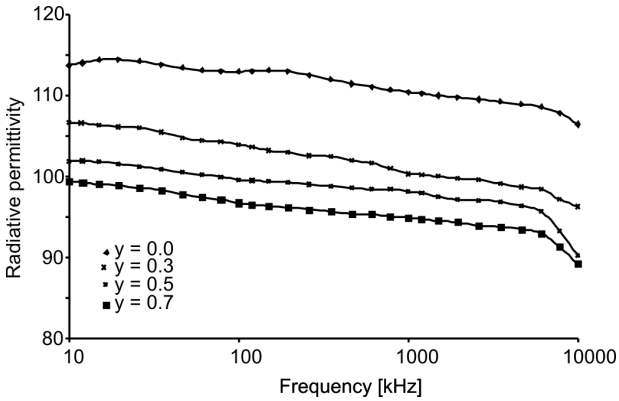


Fig. 3. Dependence of relative permittivity on frequency for various Sm contents at 25 °C

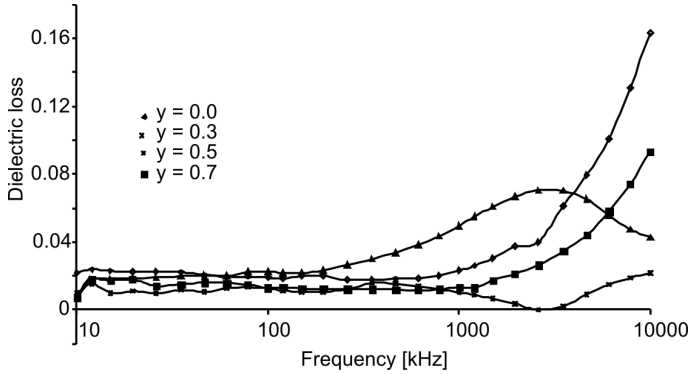


Fig. 4. Dependence of dielectric loss on frequency for various Sm contents at 25 °C

Figure 5 shows the dependence of the temperature coefficients of relative permittivity and resonant frequency on Sm contents. The estimated value of the temperature coefficient of relative permittivity decreases from –567.68 ppm/°C at $y = 0.0$, through –233.46 ppm/°C at $y = 0.5$ to –127.6 ppm/°C at $y = 0.7$. The corresponding values of $\tau_f$ also decrease from 273.9 ppm/°C at $y = 0.0$ to 106.8 ppm/°C at $y = 0.5$ and finally to 53.8 ppm/°C at $y = 0.7$.

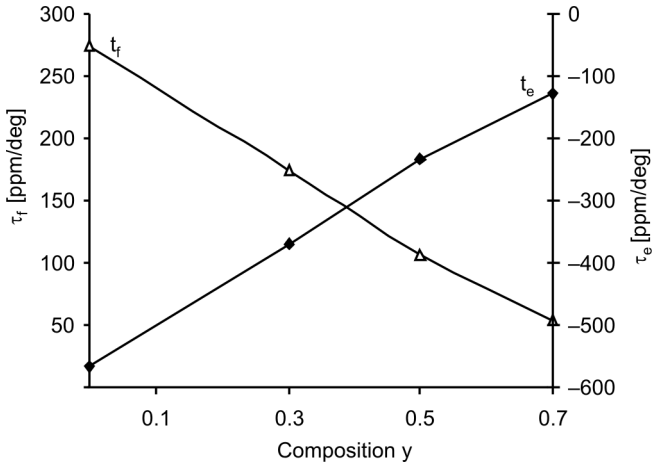


Fig. 5. Dependence of the temperature coefficient
of resonant frequency and relative permittivity for various Sm contents

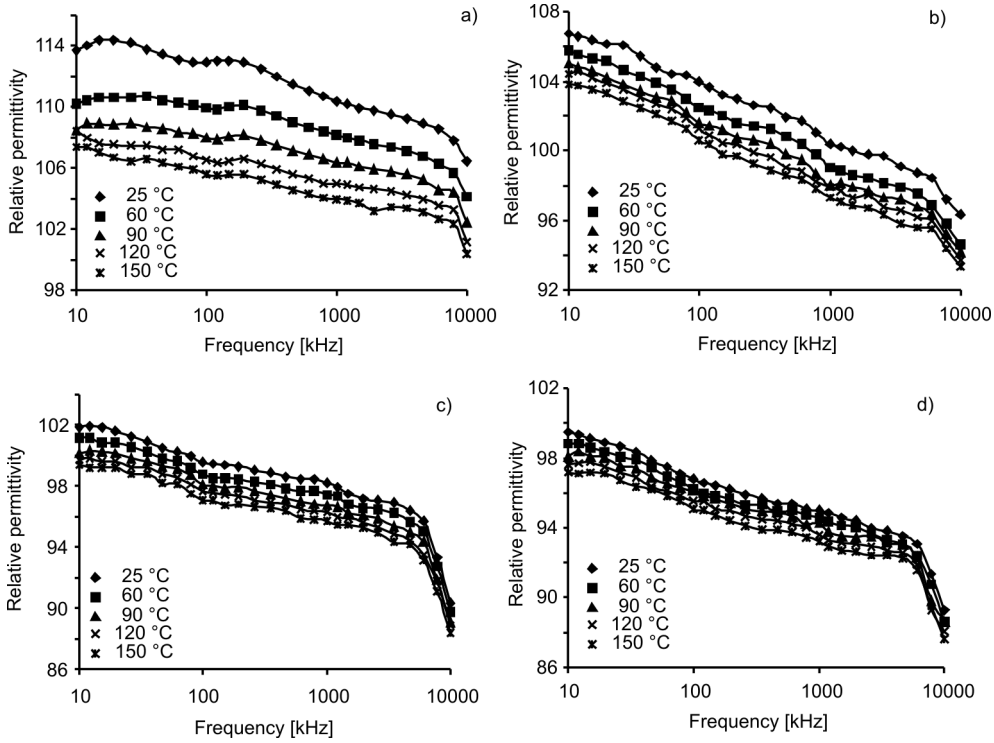


Fig. 6. Dependence of relative permittivity on frequency at various temperatures
for the following Sm contents *y*: a) 0, b) 0.3, c) 0.5, d) 0.7

With regard to the dependences of dielectric properties on ionic radii, the observed behaviour can be explained by the existence of the same intrinsic mechanism revealed

to govern the dielectric properties of undoped $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ solid solutions [12]. The extension of this study to Sm doped $Ba_{6-3x}La_{9.33}Ti_{18}O_{54}$ solid solutions suggests that the changes in the tilting of the octahedral due to substitution of small sized Sm ions for large sized La ions induce changes in the crystal field and consequently cause a decrease in $\tau_f$.

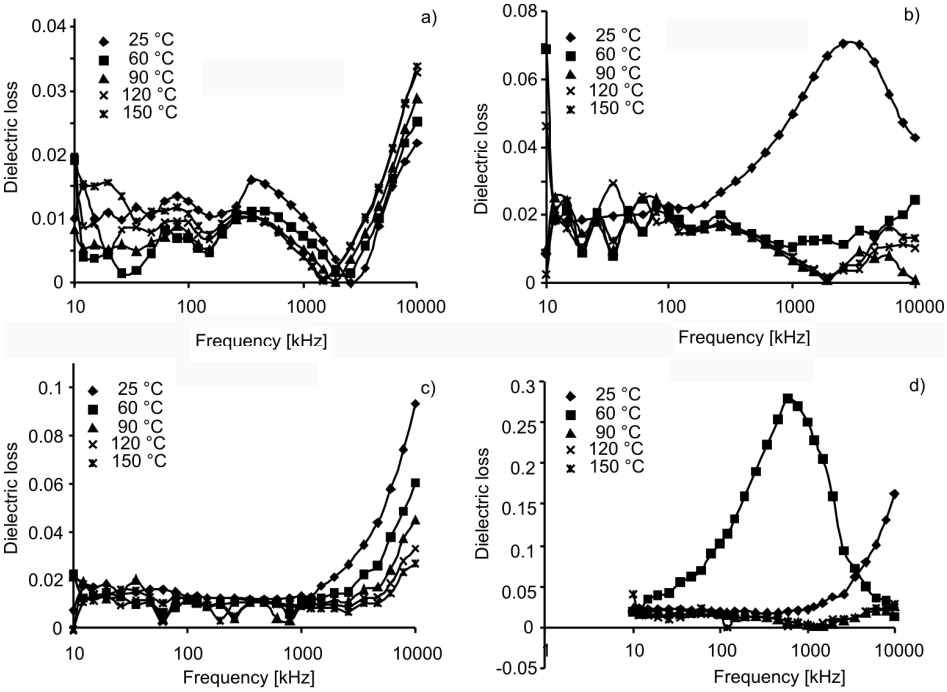


Fig. 7. Dependence of dielectric losses on frequency at various temperatures for the following Sm contents *y*: a) 0, b) 0.3, c) 0.5, d) 0.7

The dependences of the relative permittivity and dielectric losses with frequency for various temperatures and Sm contents of are shown in Figs. 6 and 7. No dielectric anomaly was observed for these materials in the temperature range 25–150 °C. It is assumed that there is no structural transition over the temperature range of interest which is in accordance with the results of other authors [15, 16]. The relative permittivity varies from 106.44 to 100.35 for $y = 0.0$ and from 89.27 to 87.62 for $y = 0.7$ as temperature increases from 25 °C to 150 °C at 10 MHz. However, it is also evident that the increase in the contents of Sm reduces the variations of relative permittivity with temperature, which is required for the thermal stability of ceramics having a high relative permittivity.

## 4. Conclusions

Dielectric ceramics of the general formula $Ba_4(La_{(1-y)}Sm_y)_{9.33}Ti_{18}O_{54}$, where $y = 0.0$, 0.3, 0.5 and 0.7 were synthesized by high temperature solid state reaction

technique and characterized for structural and dielectric properties. A detailed study related to the variation in the dielectric properties, namely the relative permittivity and the dielectric loss, as temperature increases from 25 °C to 150 °C, was carried out using an impedance analyzer in the frequency range 10 kHz–10 MHz. The relative permittivity decreased in the entire frequency range for all the three samples as the temperature increased. The variation in relative permittivity of $Ba_4(La_{(1-y)}Sm_y)_{9.33}Ti_{18}O_{54}$ solid solutions with temperature reduces as the concentration of Sm increases. The temperature coefficient of the resonant frequency was estimated to improve from 273.9 ppm/°C to 53.8 ppm/°C as the concentration of Sm increased.

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