Improved Microwave Dielectric Properties of Sm-Substituted SBTi Ceramics for Resonator Applications

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Abstract: Effect of composition and sintering procedure upon the structural, microstructures and microwave dielectric characteristics of Sm-substituted SBTi ceramics were investigated. SrBi₂-xSmₓTi₄O₁₂ (x=0.25, 0.5, 0.75 and 1) ceramic samples is prepared by solid state method and sintered by microwave sintering. As the substitution constant increases, the dielectric constant values are increased up to x = 0.75. Room temperature microwave dielectric properties are measured for the same composition samples in the frequency range 8-12.4GHz. The excellent microwave dielectric constant and low loss values were achieved in the ceramics with x=0.5 and 0.75 are 102 & 110 and 0.65 & 0.35 respectively.

Keywords: Sm-substituted SBTi ceramics, Microwave sintering, Microwave dielectric properties

1. Introduction and Literature Survey

Bismuth layered structured ferroelectrics (BLSFs) have been investigated extensively, because of its promise for ferroelectric random access memories applications [1-3]. The general formula for BLSFs is Bi₃AₓBₙ₋₃O₃₃, where A= Bi, Pb, Na, K, Sr, Ca, Ba; rare earths; B= Ti, Nb, Ta, Fe, Mo, W; and n= 1, 2, 3, 4, 5, 6 [4]. This reflects the fact that there exists a good possibility for mutual doping within these various elements or with some other ions to BLSFs. Part of work has been reported on the doping effect on the improvement of physical properties in BLSFs. Millan et al reported the substitution of Ba³⁺ in [Bi₂O₅]²⁺ layers by other cations such as Pb²⁺, Sm³⁺ or Te⁶⁺ [5]. Within the pervoskite-like units, partial substitution of strontium ions by bismuth ions would increase the Curie temperature and improve the dielectric properties in both strontium bismuth tantalite, SrBi₂Ta₂O₉ and SBN [6]. Takenaka et al reported the effects of partial substitution of Nb⁵⁺ for Ti⁴⁺ as B-site ions on the formation of layer structure for ≥ 3 compounds and found a BLSFs series for n=3. Among the BLSFs, SBT and SBN have been the best candidates for non-volatile memory devices because of their fatigue-free properties [7]. Bismuth layer is reported to be paraelectric in nature while pervoskite unit cell ceramics are ferroelectric [8]. Therefore, doping in these layered ceramics to improve the properties has been matter of interest.

Recently, microwave dielectric materials with a high dielectric constant and low sintering temperature have great attention to meet the demand for the miniaturization of microwave devices. Several kinds of materials have been investigated to meet these requirements and the promising candidates are the Pb-based complex pervoskite compounds. But due to environment problems and health issues, still researchers are looking for alternative material for Pb-based materials especially microwave dielectric resonator applications. Takata and Kagyama [9] were the first to investigate the microwave dielectric properties of A (B¹/2Bº₁/2) O₃ type pervoskites. Later [10-11] reported the microwave dielectric properties by substituting the different rare earth elements to A (B¹/2Bº₁/2) O₃ type system. The improvement of dielectric and ferroelectric properties of these layered structured ferroelectrics are extensively studied at low frequency range. However, very limited studies are available on microwave dielectric properties via low temperature processing conditions.

Understanding the importance of the research problem, we have prepared and incorporated the Samarium into SrBi₂Ti₄O₁₂ ceramic samples sintered at low temperature via microwave sintering process. The observed dielectric and microwave frequency range were improved successfully.

2. Experimental Procedure

Synthesis of the material was carried out with a powder mixture containing equimolar amount of 99.9+ % pure Bi₂O₃, SrCO₃, Sm₂O₃ and TiO₂ (Aldrich make). The powder mixture was ball milled in deionized water and then calcinated at 750°C for 4 hours. Calcined powders are ball milled again for particle size reduction about 15h deionized water as mixing media. These conditions are optimized and reported in our earlier paper [12]. These powders were uniaxially pressed into circular pellets. Green pellets were sintered at 1075°C for 40min in a microwave furnace. The sintering temperature was optimized for maximum density. Density and microstructural information were obtained on microwave sintered samples by Archimedes principle and FE-SEM respectively. The formation and phase purity of the compound were checked by X-ray diffraction technique. In order to investigate the structural properties, we have used Bruker make D8 X-ray diffractometer using CuKα radiation at 1.5046 Å in a wide 20 range of 20°-70° at a scanning rate of 1°/min.

The microwave dielectric properties of the SrBi₂-xSmₓTi₄O₁₂ (x= 0.25, 0.5, 0.75 and 1) ceramic samples were characterized using PNA network analyzer (Agilent E8361C) at higher frequency (8.2GHz-12.4GHz) range. We have been used transmission/reflection method to measure...
complex permittivity. For microwave measurements the samples were prepared in rectangular disks (10.16 mm x 22.86 mm) to fit in the X-band wave-guide (test set, Agilent model E8361C, WR-90), backed.

The measurements were carried out by inserting the samples inside the X-band waveguide. In order to determine the complex permittivity at X-band frequency (8.2-12.4 GHz), the complex scattering parameters were measured using a PNA network analyzer. The real and imaginary parts of complex permittivity \( (\varepsilon = \varepsilon' - j\varepsilon'') \) was calculated from scattering parameters. Measured scattering parameters for the waveguide partially filled with the dielectric samples of two different lengths. The complex propagation constant \( \gamma \) can be expressed as

\[
\gamma = \alpha + j\beta
\]

Where \( \alpha \) is the attenuation factor and \( \beta \) is the phase factor. For a TE\(_{10}\) mode rectangular waveguide, we can relate the real part of the sample permittivity \( \varepsilon' \) to the phase constant \( \beta \) [13, 14] by

\[
\varepsilon' = \frac{\beta^2 + \left(\frac{\pi}{\alpha}\right)^2}{\omega^2 \mu_0 \varepsilon_0}
\]

Where \( \alpha \) is the longer width of the wave guide, \( \omega \) is the angular frequency, \( \mu_0 \) and \( \varepsilon_0 \) are the free space permeability and permittivity. In the same manner, the imaginary part of the permittivity \( \varepsilon'' \) can be related to the attenuation \( \alpha \) by [13, 14]

\[
\varepsilon'' = \frac{2\alpha \varepsilon_0}{\omega} \sqrt{1 - \left(\frac{\lambda}{2\alpha}\right)^2}
\]

Where

\[
\lambda = \frac{2\pi}{k}, \quad k = \frac{\omega}{\sqrt{\mu_0 \varepsilon_0}}
\]

3. Results and Discussion

3.1 Structural

X-ray diffraction patterns of microwave sintered SrBi\(_2\)O\(_3\), Sm\(_{x}\)Sr\(_{1-x}\)Ti\(_4\)O\(_{12}\) (where \( x = 0.25, 0.5, 0.75 \) and 1) ceramics were shown in figure 1. It indicates that the Samarium substitution does not change the structure of SBTi or generate new phases. No significant difference in the lattice parameters was observed in materials with various contents of Sm is shown in table 1. The position of the diffraction peaks are in good agreement with the standard orthorhombic pattern. The similarity of XRD patterns are indicative of the similarity of chemical valance involved and close values of the ionic radii between Bi\(^{3+}\) and Sm\(^{3+}\) ions. The crystalline size of the microwave sintered samples was calculated by Debye-Scherrer formula. The crystallite size of the microwave sintered samples which is 40-50nm. It is evident from the XRD pattern as each peak broadening is more in microwave sintered which we have observed in our earlier work [12].

### Table 1: Lattice parameter values

<table>
<thead>
<tr>
<th>Sm content in sample</th>
<th>Lattice parameters (Å)</th>
<th>Volume(Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>Sm 0</td>
<td>5.425</td>
<td>5.436</td>
</tr>
<tr>
<td>Sm 0.25</td>
<td>5.424</td>
<td>5.439</td>
</tr>
<tr>
<td>Sm 0.5</td>
<td>5.42</td>
<td>5.431</td>
</tr>
<tr>
<td>Sm 0.75</td>
<td>5.423</td>
<td>5.434</td>
</tr>
<tr>
<td>Sm 1</td>
<td>5.416</td>
<td>5.417</td>
</tr>
<tr>
<td>Standard</td>
<td>5.428</td>
<td>5.438</td>
</tr>
</tbody>
</table>

4. Microstructural

The microstructure of the Sm-substituted SBTi samples sintered by microwave furnace is shown in figure 2(a-d). SEM images of Sm-substituted SBTi samples showed grains in the form of platelets. This orientation is typical of Aurivillius phases and is due to the polycrystalline nature of the samples. SEM micrographs showed that the microwave sintered samples are highly densified and got uniform grain size. Similar samples were sintered in a microwave furnace at different temperatures and different time durations. It was found that there is obvious densification in the microwave field even at 1075°C for 40min heating. The maximum relative density of 97.5% is obtained at 1075°C for 40min of microwave sintering. The average grain size of the microwave sintered samples was found to range from 4-6µm respectively. The density of the Sm-substituted SBTi with \( x = 0.5 \) and 0.75 are higher than that of original SBTi ceramics for microwave sintered processed samples are shown in table 2. On the contrary, SBSmT with \( x = 1.0 \) is having lower density and this is due to structural distortion. Structural distortion in this composition is indeed evident through the shifts in XRD pattern. The rapidity of microwave sintering method could be a reason for suppression of grain growth resulting in a finer and uniform microstructure. The same phenomenon was observed by Chris Y Fang et. al also [15]. The substantially enhanced densification in the microwave sintered samples can be considered as the cause for their fairly enhanced dielectric properties.
indicates that the increase in ionic radius. An increase in ionic radius is associated with a decrease in the unit cell volume, leading to reduced dielectric permittivity [21–23]. The observed dielectric constant values are quite higher than the earlier reported values [24–25]. Interestingly, the observed dielectric loss is decreased as the Sm-content increases up to x=0.75 and increased at the higher frequencies.

Table 2: Relative density of Sm-substituted SBTi ceramics samples sintered at 1075°C

<table>
<thead>
<tr>
<th>Samples</th>
<th>Sm 0.25</th>
<th>Sm 0.5</th>
<th>Sm 0.75</th>
<th>Sm 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative density (%)</td>
<td>92.5</td>
<td>96.2</td>
<td>97.5</td>
<td>88.4</td>
</tr>
</tbody>
</table>

5. Microwave Dielectric Properties

The microwave measurements were accomplished for the SBTi samples, obtained in the microwave sintering process at temperature 1075°C for 40 min, with substitutions of Sm2O3 (0.25, 0.5, 0.75 and 1 wt %). The results were obtained, in terms of dielectric permittivity (ε') and dielectric loss for frequencies in the range of 8.2–12.4 GHz. The dielectric permittivities are related to the structural properties. In fact, the relative density, porosity and average grain sizes of sintered bodies are considered to be the key factors influencing the dielectric properties. Some authors say that the lower dielectric permittivity is due to lower density, because of pore formation.[18–19]. In figure 3(a) and 3(b), we have shown the dielectric permittivity (ε') and dielectric loss of SBTi ceramics with according to the percentage of different Sm substitutions. As the Sm content increases the dielectric constant increases up to x=0.75. There is negligible variation in values of dielectric constant for x=0.5 and 0.75. The dielectric permittivities of SBTi, regardless of the addition level, are associated with ionic and atomic polarization. Since the ionic radii of the addition ions Sm3+ are different from the original site ions (Bi3+), increasing the amount of additional ions would lead to a decrease in both the electronic and ionic polarizations. Ionic polarization is strongly dependent on the crystal structure, including density and lattice constants or unit cell volume [20]. The observed relative densities of the Sm-substituted SBTi samples are shown in table 1. These results demonstrating that the samples having more density exhibited enhanced dielectric properties. Which means the crystal structure and density are supporting to the dielectric properties. Secondly, there would be an increased ionic polarization with an increased Sm3+ concentration, due to a combination of an unchanged unit cell volume and a reduced ionic radius. An increase in the dielectric permittivity indicates that the increase in ionic polarization is predominant over the decrease in electronic polarization corresponding to a smaller ionic radius. However, a high concentration of samarium (x=1) caused a reduction in the lattice constants and the unit cell volume. Therefore, both atomic and ionic polarization would decrease with an increasing amount of samarium introduced into the system and lead to reduced dielectric permittivity [21–23]. The observed dielectric constant values are quite higher than the earlier reported values [24–25]. Interestingly, the observed dielectric loss is decreased as the Sm-content increases up to x=0.75 and increased at the higher frequencies.

6. Conclusions

Sm3+ substituted SBTi ceramics were prepared by solid state reaction method and samples sintered by microwave sintering method. Though the ionic radius of Sm3+ is smaller than Bi3+, there was no observable change in the diffraction angle till x=1 concentration of Sm3+. The dielectric constants and Curie temperature were increased as the Sm-content increased up to x=0.75. Further increasing of Sm content (x=1) the dielectric constant decreased which led to decrease the Curie temperature. It was found that a high concentration of Samarium was likely to promote space charge polarization into the system resulting in a decrease in both dielectric constants and Curie temperature. Microwave dielectric measurements were studied in X-band region by...
The composites exhibited the high dielectric constants and low loss tangents compared to the other layered structured materials. From these results, the Sm-doped SBTi ceramics are seemed to be a good candidate as lead-free piezoelectric ceramics for resonator applications.

7. Acknowledgements

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References