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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. $SrBi_{4-x}Sm_xTi_4O_{15}$ (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 content 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 dielectic 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 $Bi_2A_{m-1}B_mO_{m+3}$, where A= Bi, Pb, Na, K, Sr, Ca, Ba, rare earths; B = Ti, Nb, Ta, Fe, Mo, W; and m= 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 Ba^{3+} in $[Bi_2O_2]^{2+}$ layers by other cations such as Pb^{2+}, Sm^{3+} or Te^{4+} [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, $SrBi_2Ta_2O_9$ and SBN [6]. Takenaka et.al reported the effects of partial substitution of Nb^{5+} for Ti^{4+} as B-site ions on the formation of layer structure for ≥3 compounds and found a BLSFs series for m=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 dielectic 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 $(B'_{1/2}B''_{1/2})$ O_3 type perovskites. Later [10-11] reported the microwave dielectric properties by substituting the different rare earth elements to A $(B'_{1/2}B''_{1/2})$ O_3 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 $SrBi_4Ti_4O_{15}$ ceramic samples sintered at low temperature via microwave sintering process. The observed dielectric properties at low frequency 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 Bi_2O_3, $SrCO_3$, Sm_2O_3 and TiO_2 (Aldrich make). The powder mixture was ball milled in deionized water and then calcinated at 750^0C 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^oC 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 2θ range of 20^o-70^o at a scanning rate of 1^0/min.

The microwave dielectric properties of the $SrBi_{4-x}Sm_xTi_4O_{15}$ (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

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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 ($\varepsilon_r=\varepsilon'-j\varepsilon''$) 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 γ can be expressed as

$$\gamma = \alpha + j\beta$$

Where α is the attenuation factor and β is the phase factor. For a TE_{10} mode rectangular waveguide, we can relate the real part of the sample permittivity ε_s' to the phase constant β [13, 14] by

$$\varepsilon_s' = \frac{\beta^2 + \left(\frac{\pi}{a}\right)^2}{\omega^2 \mu_0 \varepsilon_0} \qquad (2)$$

Where a is the longer width of the wave guide, ω is the angular frequency, μ_0 and ε_0 are the free space permeability and permittivity. In the same manner, the imaginary part of the permittivity ε_s'' can be related to the attenuation α by [13, 14]

$$\varepsilon_s'' = \frac{2\alpha\varepsilon_s'}{k}\sqrt{1-\left(\frac{\lambda}{2a}\right)^2} \qquad (3)$$

Where

$$\lambda = \frac{2\pi}{k} \qquad k = \omega\sqrt{\mu_0\varepsilon_0\varepsilon_s'}$$

3. Results and Discussion

3.1 Structural

X-ray diffraction patterns of microwave sintered $SrBi_{4-x}Sm_xTi_4O_{15}$ (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].

Sm content in sample	Lattice parameters (Å)			Volume(Å)^3
	a	b	c	
Sm 0	5.425	5.436	40.95	1207.62
Sm 0.25	5.424	5.439	40.932	1207.51
Sm 0.5	5.42	5.431	40.928	1204.75
Sm 0.75	5.423	5.434	40.921	1205.88
Sm 1	5.416	5.417	40.90	1998.81
Standard	5.428	5.438	40.94	1208.88

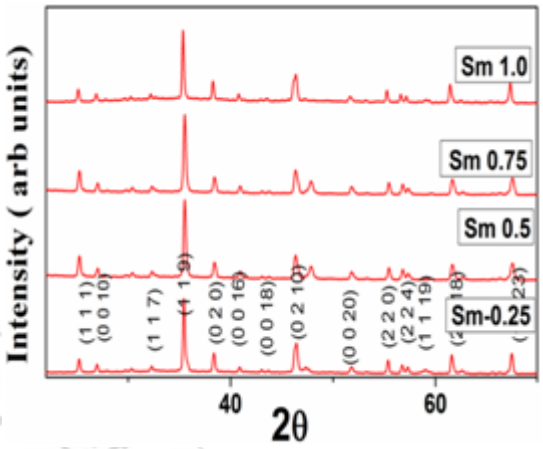

Figure 1: XRD pattern Table 1: Lattice parameter values

4. Microstructural

The microstructure of the Sm-substituted SBTi samples sintered by microwave furnaceis 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.

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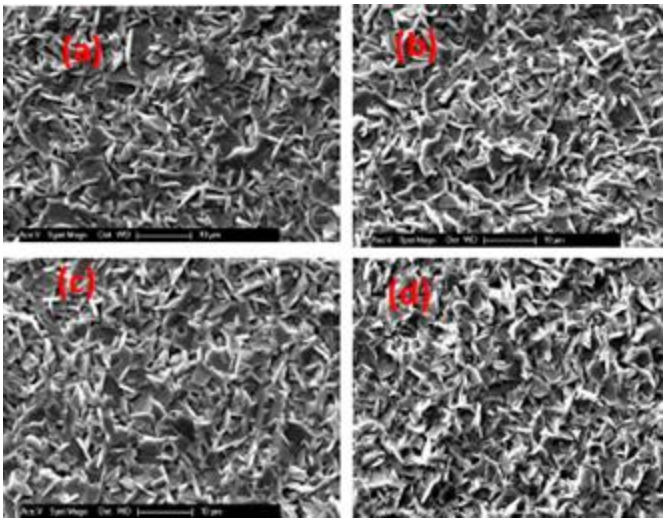

Figure 2: SEM images of the Sm-substituted SBTi ceramic samples (a) $SrBi_{3.75}Sm0.25Ti_4O_{15}$(b) $SrBi_{3.5}Sm_{0.5}Ti_4O_{15}$(c) $SrBi_{0.25}Sm_{0.75}Ti_4O_{15}$(d) $SrBi_3Sm_1Ti_4O_{15}$

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

Samples	Sm 0.25	Sm 0.5	Sm 0.75	Sm 1
Relative density (%)	92.5	96.2	97.5	88.4

5. Microwave Dielectric Properties

The microwave measurements were accomplished for the SBTi samples, obtained in the microwave sintering process at temperature 1075°C for 40min, with substitutions of Sm_2O_3 (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) and3(b), we have shown the dielectric permittivity (ε') and dielectric loss of SBTi ceramics with according to the percentage of different Smsubstitutions. 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 ofthe addition level, are associated with ionic and atomic polarization. Since the ionic radii of the addition ions Sm^{3+} are different from the original site ions (Bi^{3+}), increasing the amount of additional ions would lead to a change of 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 Sm^{3+} 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.

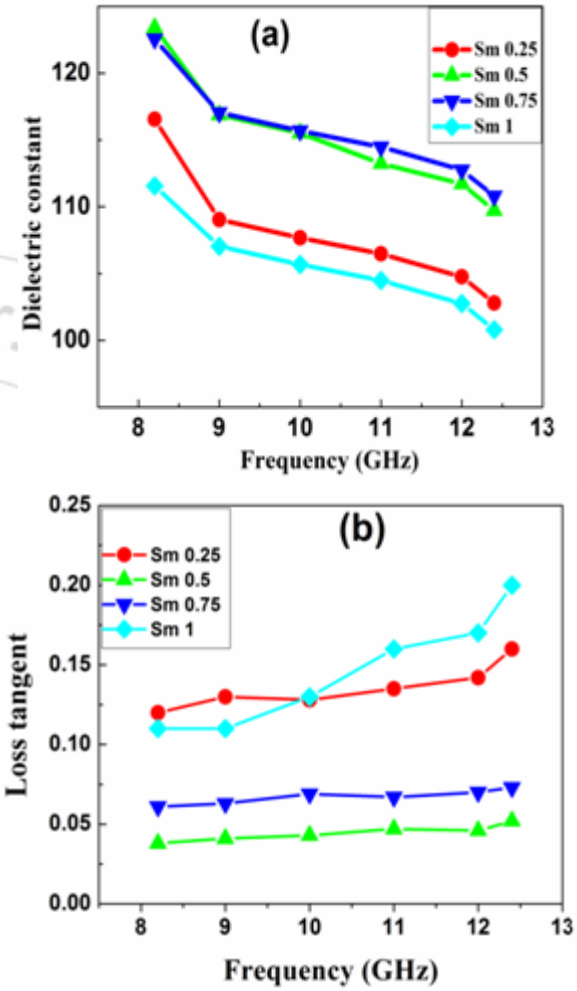

Figure 3 (a-b): (a) Microwave dielectric constant (b) loss tangent of Sm-substituted SBTi ceramics in the frequency range 8-12.4GHz.

6. Conclusions

Sm^{3+} substituted SBTi ceramics were prepared by solid state reaction method and samples sintered by microwave sintering method. Though the ionic radius of sm^{3+} is smaller than Bi^{3+}, there was no observable change in the diffraction angle till x=1 concentration of Sm^{3+}. 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 constantsdecreased 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

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Waveguide technique. 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.

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References

[1] Yen-Nien Wang, Yih-Chien Chen, Ya-Dung Pan, Wei-Chen Lee, J.CersInt 38,3097-3103,(2012).
[2] Yun Wu, Mike J, Forbess, SeanaSeraji, Steven J.Limmer, Tammy P Chou, J. Appl.Phy 90 [10],5296-5302,(2001).
[3] J.F Scott and C.A P de Araujo, Science 246, 1400 (1989).
[4] P.Millan, A Ramirez and A Castro, J. Mat.SciLett., 14, 584,(1996).
[5] P Sarah, J.Proce.Engg., 10, 2684-2689, (2011).
[6] Indranicoondoo, A.K Jha, S.K Agrwal, J. Euro.Cer Soc., 27, 253-260, (2006).
[7] Y.Wu and G.Z Cao, J. Matt. Res., 15, 1583, (2000).
[8] Irie H, Miyayana M and Kudo T, J. Appl. Phys., 91 4089-4094, (2001).
[9] M.Takata, K.Kageyama., J.Ame.Cer. Soc.,72 ,1955, (1989).
[10] LAbdulKhalam, H Sreemoolanathan, R Ratheesh, P Mohan and M.T Sebastian., J. Mat.Sci and Engg B., 107, 264-270, (2004).
[11] Feng Qiang, Jun-Hui He, Jun Zhu, Xiao-Bing Chen, J. Sol State Chem, 179, 1768-1774, (2006).
[12] Rambabu A and K C James Raju, TransIndCer Soc., 70(3) 135-141, (2011).
[13] R.Marks, *IEEE Trans.Microwave Theory Tech*. **39,** 1205 (1991).
[14] S.Ramo, etc "Fields and waves in communication electronics" *New York:Wiley* (1984).
[15] Chris Y Fang, Clive A Randal, Michael T Lanagan, *J. Electro cer*,**22**, 125-130(2009)
[16] Shannon R D and Prewitt C T,*ActaCrystallogr*. B **25,**925 (1969).
[17] P Sarah, jour Proceengg.,**10,** 2684-2689 (2011).
[18] Piagai R, Kim I-T, Park J-G and Kim Y *J. Korean Phys.Soc*. **32,**S367 (1998).
[19] Yang A-K, Wang C-A, Guo R and Huang Y,*Appl. Phys.Lett.* **98,**152902, (2011).
[20] Shannon R D and Prewitt C T,*ActaCrystallogr*. B **25 ,**925, (1969).
[21] Wu Y, Forbess M J, Seraji S, Limmer S J, Chou T P, Nguyen C P and Cao G,*J. Appl. Phys.* **90,**5296, (2001)
[22] Rocha M J S, Filho M C C, Theophilo K R B, Denardin J C,Vasconcelos I F, Ara´ujo E B and Sombra A S B, *Mater.Sci. Appl.* **3** 6.2012
[23] Silva C C and Sombra A S B, *Mater. Sci. Appl.* **2 ,**1349 (2011)
[24] Yi Li, Xiang Ming Chen, J. Euro.Cer Soc., 22, 715-719, (2002).
[25] K Stanly Jacob, R Satheesh, R Ratheesh, J. Mat. Rea. Bull., 44, 2022-2026, (2009).

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