CHAPTER 3

Influence of oxide glass addition on the elastic and structural properties of Ba$_{6-x}$R$_{8+2x}$Ti$_{18}$O$_{54}$ ceramics

3.1. Introduction

The revolution in wireless communication and information access is one of the most dramatic changes in technology during the past decade. This revolution is apparent on a daily basis in the ever-increasing number of cellular phone users. As in all technological systems, the basis of these revolutionary changes is advances in materials, which have their own specialized requirements and functions [1]. High quality microwave dielectric ceramics have been extensively used in mobile communication as well as satellite broadcasting systems, for the purpose of miniaturization of dimensions of circuit components such as filters and resonators [2]. The materials for microwave resonators are required to excel in the following three dielectric characteristics. The first one is high dielectric constant ($\varepsilon_r$), because microwave wavelength ($\lambda$) is inversely proportional to $\sqrt{\varepsilon_r}$ of the dielectric materials ($\lambda = \lambda_0 / \sqrt{\varepsilon_r}$, $\lambda_0$ is the initial wavelength). The second characteristics is the quality factor $Q$, which is the inverse of dielectric loss tangent ($Q = 1/\tan \delta$), is required to be high for achieving prominent frequency selectivity and stability in microwave transmitter and receiver components. As the third characteristic, the temperature coefficient of resonant frequency ($\tau_r$) is required to be as close to
0 ppm/°C for the system to be stable [3] as temperature changes. Presently, high $\varepsilon_r$ dielectric systems replaced SiO₂ for use as the basis of advanced capacitance components in microelectronic memory and other applications in thin film rather than in bulk form [1].

One of the first materials utilized for this application was TiO₂, which was inexpensive, displayed excellent $Q$ ($= 15,000$ at 3 GHz) and high $\varepsilon_r$ ($= 100$), but it possesses a large $\tau$ of about 400 ppm/°C [4]. The binary barium titanates were the first dielectric materials described as having practical application in modern microwave resonators [5-6] and remain in commercial use. Since 1970s, microwave dielectric ceramics with dielectric constant in the range 20 – 40, such as Ba(Mg, Ta)O₃, Ba(Zn,Ta)O₃, BaTi₄O₉ and Ba₂Ti₉O₂₀ systems, have been developed and applied successfully to many commercial units [7-8]. O'Bryan and coworkers developed Ba₂Ti₉O₂₀ based ceramics as filters for the base stations of the infant cellular industry and for conventional telephone microwave relays. The dielectric behaviour of Ba₂Ti₉O₂₀ and BaTi₄O₉ can be improved by forming composites with additives like ZnO, SnO₂, Ta₂O₅ etc [9-10]. An excellent description of many considerations involved in developing new materials for commercialization can be found in reference 9. This family of materials is quite sensitive to firing conditions and defect chemistry. This is due to the reduction of Ti⁴⁺ to Ti³⁺, which can be reduced by substituting Mn for Ti in small proportions. The detailed study of the factors affecting the formation of Ba₂Ti₉O₂₀ is done by J. Wu and Wang [11].

Other important members of barium titanate family are complex ternary materials in BaO-R₂O₃-kTiO₂ chemical systems with a bronze structure, where R =
Sm, Nd, Pr, La, are rare earth elements, with \( k = 3 - 5 \) \([12-14]\). The main phases of BaO-R_2O_3-kTiO_2 were reported as BaO-R_2O_3-4TiO_2 with a conventional formula Ba_{6-x}R_{8+2x}Ti_{18}O_{54} and BaO-R_2O_3-5TiO_2 having conventional formula Ba_{1-x}R_{2+x}Ti_5O_{14} in different studies \([2, 4, 15-17]\). The possible existence of solid solutions on the tie line of BaO-R_2O_3-3TiO_2 and BaO-R_2O_3-5TiO_2 were also suggested \([18]\). Nishigaki \textit{et al.} \([19]\) had studied the microwave dielectric properties of BaO-Sm_2O_3-4.7TiO_2 and BaO-Sm_2O_3-4.8TiO_2 systems. Y. C. Chen \textit{et al.} \([18]\) reported the zero temperature coefficient (\( \tau_T \)) compounds Ba_{2-x}Sm_{4+2x}Ti_{9}O_{26} belonging to the BaO-Sm_2O_3-4.5TiO_2 system. The phase development and microwave dielectric properties of BaO-xSm_2O_3-4.5TiO_2 (\( x = 0 - 1.25 \)) were described by S. W. Jung \textit{et al.} \([20]\). C. L. Huang \textit{et al.} \([21]\) investigated the microstructure and dielectric properties of Ba_{2-x}Sm_{4+2x/3}Ti_{8-y}O_{24+y} ceramics, belonging to the \((1-x/2)\) BaO: \((1+x/3)x\) Sm_2O_3: kTiO_2, with \( x = 0.1 \) and \( y = 0 - 2 \).

BaR_2Ti_4O_{12} and BaR_2Ti_5O_{14} are important members belonging to the BaO-R_2O_3-4TiO_2 family. The reaction sequence and dielectric properties of BaSm_2Ti_4O_{12} in different calcining temperatures were studied by P. S. Cheng \textit{et al.} \([22]\). Different intermediate phases like BaTiO_3, BaTi_4O_9, Sm_2Ti_2O_7 were revealed in the X-ray diffraction patterns, as the calcining temperature was increased from 850°C to 1250°C. Tailoring of microwave properties of BaR_2Ti_4O_{12} and BaR_2Ti_5O_{14} (R = Nd, Sm) ceramics, by the addition of Bi_2O_3 was reported by S. Solomon \textit{et al.} \([23]\). The effect of B_2O_3 doping on the dielectric properties of BaNd_2Ti_5O_{14} is explained by C. H. Lee \textit{et al.} \([24]\). They found that when the amount of B_2O_3 was greater than 5 wt %, BaNd_2Ti_5O_{14} get decomposed to Ba_2Ti_9O_{20} causing to decrease \( \varepsilon_r \), whereas Y.
Song et al. [25] reported as the dielectric properties of BaEu$_2$Ti$_4$O$_{12}$ were improved by mixing it with BaTi$_4$O$_9$. Addition of 5 -10% Bi$_2$Ti$_2$O$_7$ was found to improve the $\tau_f$ of BaNd$_2$Ti$_3$O$_{14}$. It has been reported that the variation of dielectric properties of BaNd$_2$Ti$_3$O$_{14}$ and BaSm$_2$Ti$_3$O$_{14}$ is due to the presence of secondary phases such as Ba$_2$Ti$_4$O$_{20}$, BaTi$_4$O$_9$, TiO$_2$, Nd$_2$Ti$_3$O$_7$, Sm$_2$Ti$_3$O$_7$ etc. The temperature coefficient of resonance frequency in the above systems can be improved by substituting Ba partially by Sr or Pb [26].

Ba$_{6-x}$Sm$_{8+2x}$Ti$_{18}$O$_{54}$ (BST) is an important microwave dielectric ceramic in the Ba$_{6-x}$R$_{8+2x}$Ti$_{18}$O$_{54}$ solid solution family, which received much scientific and commercial interest as the key material for microwave dielectric resonators and filters [27 31]. The relation of microwave dielectric properties of Ba$_{6-x}$Sm$_{8+2x}$Ti$_{18}$O$_{54}$ solid solutions with crystal structure in the range $0.3 \leq x \leq 0.7$ was reported by H. Ohsato et al. [2]. The dielectric properties as a function of composition $x$ for the Sm and Nd systems and for the Pr system were reported by Fukuda et al. [33]. Matveeva et al. [34] determined first the crystal structure of Ba$_{3.75}$Pr$_{9.5}$Ti$_{18}$O$_{54}$ (for $x = 3/4$ ) based on the fundamental unit cell by single crystal X-ray diffraction. BST has the typical microwave dielectric properties for the composition of $x = 2/3$, reported as $\varepsilon_r = 81$, $Qf = 9600$ GHz and $\tau_f = -14$ ppm/°C [32, 35]. The end members of the solid solution family are 3BaO. 2R$_2$O$_3$. 9TiO$_2$ for $x = 0$ and 3BaO.5R$_2$O$_3$.18TiO$_2$ for $x = 1$ [16]. The tungsten – bronze structure was confirmed by Roth et al., Ohsato et al. [35], Kolar et al. [37] and so on. A superlattice with two times the fundamental lattice spacing along the $c$-axis has been found in Ba$_{3.75}$R$_{9.5}$Ti$_{18}$ ($R =$ La, Nd, Sm) crystals.
To get dense ceramics with homogenous microstructure, BST ceramics has to be sintered at temperature of about 1300-1400 °C. When materials are sintered at such high temperatures, the bottom electrode (for thick film or thin film technology) or inner electrode (for MLC structure) must be of a noble metal, such as Pt, and which increases manufacturing costs. Therefore, studies of dielectric ceramics have focused on decreasing the sintering temperature and improving the dielectric properties by controlling the sintering conditions and microstructure and by adding sintering aids [38-40]. One method of decreasing the sintering temperature is to add sintering aids like glasses that have low melting points and make liquid phases below the sintering temperature. The relationship between the sintering temperature and dielectric properties are discussed in several papers [41-44] by earlier workers. However, not much effort has been made to understand the effects of adding such sintering aids on the elastic and mechanical properties of these materials.

The purpose of this study is to investigate how glass addition affects the elastic properties of BST ceramics. Since the dielectric constant, quality factor, dielectric loss and structural stability of ceramics are interconnected parameters and these are influenced by the mechanical strength and stability of the system, it is necessary to know the elastic stability of the system, which is closely related to structural stability. Elastic constants $C_{11}$ and $C_{44}$ are measured on BST samples added with different mixed oxide glasses and the results are presented in this chapter.
3.2. Sample Preparation

The pure BST ceramics were prepared by accurately weighing high purity (99.9 %) BaCO₃, Sm₂O₃ and TiO₂ in the stoichiometric proportions and wet mixed with distilled water and ball-milled with ZrO₂ balls for 24 hrs. The dried powders were calcined in platinum crucibles at 1150°C for 4 hrs. The calcined powder was again ground well in agate mortar and PVA (5%) was added and mixed well. After drying, the mixture was again ground well for half an hour. This fine powder was pressed into cylindrical compacts of 12 mm or 14 mm diameter and 6 mm length under a pressure in the range of 100 to 150 MPa. The pellets so obtained were then sintered at a temperature of 1350°C for about 4 hours.

For the glass added samples, the chemicals BaCO₃, Sm₂O₃ and TiO₂ were weighed in stoichiometric ratios. The powders were mixed well and calcined as described above. The calcined powder was then divided into five or six parts and fixed wt % of the different glasses were added to different parts. Dielectric ceramics were prepared from the powders by the conventional method as described above and the samples were then sintered at appropriate optimized temperatures.

3.3. Samples Studied

The samples selected for study are pure Ba₆₋ₓSmₓ₂₋₂ₓTi₁₈O₅₄ with x = 2/3 (BST) and BST with 0.5 wt% of different glasses added to it. The glasses added include MgO-Al₂O₃-SiO₂, ZnO-B₂O₃ (77:23), ZnO-B₂O₃ (50:50), B₂O₃ - SiO₂, ZnO-B₂O₃ - SiO₂, PbO- B₂O₃ - SiO₂, MgO-B₂O₃ - SiO₂, Al₂O₃ -SiO₂, Al₂O₃ -B₂O₃ -SiO₂, BaO-B₂O₃ -SiO₂ (30:60:10) and BaO-B₂O₃ -SiO₂ (30:40:30).
3.4. Structure by XRD

The Ba\(_{6-x}\)Sm\(_{8+2x}\)Ti\(_{18}\)O\(_{54}\) solid solutions were reported as ternary compounds existing on the tie line between BaTiO\(_3\) and R\(_2\)TiO\(_3\) composition in the BaO-R\(_2\)O\(_3\)-TiO\(_2\) ternary system [2,16, 45-46] as illustrated in Fig. 3.1.

![Diagram of BaO-R\(_2\)O\(_3\)-TiO\(_2\) ternary system](image)

**Fig.3.1:** A part of the BaO-R\(_2\)O\(_3\)-TiO\(_2\) ternary system.

The solid solution has a new tungsten bronze-type structure [4, 34-35] with perovskite columns, which have 2x2 unit cells of perovskite blocks and have pentagonal sites occupied by the large cation (Ba\(^{2+}\), Sm\(^{3+}\)), which have been shown by Matveeva *et al.* [34] and Ohsato *et al.* [35]. The formation region of the solid solutions is revealed as 0.3 \(\leq x \leq 0.7\) in the Ba\(_{6-x}\)R\(_{8+2x}\)Ti\(_{18}\)O\(_{54}\) equation in the case of R = Sm [12, 45].

The crystal structure of Ba\(_{6-x}\)Sm\(_{8+2x}\)Ti\(_{18}\)O\(_{54}\) has been reported by several authors [34-37]. The superlattice with twice fundamental lattice spacing along c-axis was pointed out by Matveeva *et al.* [34] and Kolar *et al.* [37]. The basic structural
formula for the $\text{Ba}_{6-x}\text{Sm}_{8+2x}\text{Ti}_{18}\text{O}_{54}$ tungsten bronze type structure is $[\text{Si}_{10}]_A[\text{Si}_4]_A\text{B}_{18}\text{X}_{54}$. This structure has three types of large cation sites: the largest ones are the four pentagonal sites ($A_2$), the medium ones are the ten rhombic sites ($A_1$) and finally the trigonal sites ($C$). The trigonal $C$-sites are empty in our case. Again, $B$ is a cation (Ti) in an octahedron and $X$ is an anion ($O^{2-}$). The basic crystal structure of these samples is given in Fig.3.2.

![Tungsten-bronze crystal structure of $\text{Ba}_{6-x}\text{Sm}_{8+2x}\text{Ti}_{18}\text{O}_{54}$ solid solutions](image)

Fig.3.2: Tungsten-bronze crystal structure of $\text{Ba}_{6-x}\text{Sm}_{8+2x}\text{Ti}_{18}\text{O}_{54}$ solid solutions

Here the $A_2$-sites are occupied by Ba ions, $A_1$-sites are occupied by Sm and partly by Ba according to the value of $x$ in the structural formula $[\text{Sm}_{8+2x}\text{Ba}_{2-3x}\text{V}_x]_A [\text{Ba}_4]_A\text{Ti}_{18}\text{O}_{54}$ (for $0 \leq x \leq 2/3$). Here $V$ means vacancy. Only when $x = 2/3$, the $A_1$-
sites and A2-sites are separately occupied by Sm and Ba respectively. This ordering results in the lowest internal strain. As the $x$ value decreases Ba ions with larger ionic radii start to occupy a part of the rhombic sites (A1) with their smaller size and this leads to internal strain. On the other hand, as the $x$-value increases, vacancies are produced in the pentagonal sites (A2), which might lead to unstable crystal structures. For $2/3 \leq x \leq 1$, the structural formula can be written as, 

$$[\text{R}_{9+13+2(x-2/3)}\text{V}_{2/3-2(x-2/3)}\text{A}_{1}\text{B}_{4(x-2/3)}\text{V}_{3(x-2/3)}\text{A}_{2}\text{Th}_{10} \text{O}_{54}]$$

Also it has been revealed that the crystal structure with the largest size difference between Ba and R has low internal strain, i.e., when $R = \text{Sm}$. H. Ohsato [46] reported that the tilt of TiO$_6$ octahedron along the $c$-axis is the main factor for the superlattice formation.

![Fig.3.3: Tilting of the TiO$_6$ octahedron](image)

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Fig.3.4: XRD pattern of BST added with 0.5 wt% of different glasses

The X-ray powder diffraction patterns of the samples were recorded with a Bruker D8 Advance X-ray powder diffractometer. The patterns for the pure sample and the same added with different glass are shown in Fig.3.4. As can be expected, the XRD patterns shown in Fig. 3.4 are similar, indicating that the addend is an amorphous solid such as glass.
3.5. Elastic Properties by Ultrasonic technique

Ultrasonic wave velocities in the ceramic samples have been measured by the Pulse Echo Overlap technique using Matec 7700 pulse modulator and receiver system [47] as described in Chapter 2. Pelletized samples of thickness 5-6 mm have been used for the measurements. The faces of the samples are well polished after making their faces parallel to each other. X-cut quartz transducer of frequency 10 MHz is mounted on the sample using nonaq stop-cock grease as the bond, which acts as the transmitter of the ultrasonic wave to the medium as well as receiver of echoes from the medium. The time gap between two selected echoes is measured following the pulse echo overlap method. Knowing the sample thickness and density ($\rho$), the longitudinal velocity ($V_L$) and elastic modulus ($C_{11}$) can be calculated using relation $C_{11} = \rho V_L^2$. To get the transverse velocity ($V_T$) and modulus ($C_{44}$), Y-cut quartz transducer is used for excitation and detection of ultrasonic waves. The transducer is bonded to the sample with silicon grease.

While measuring the time interval between selected echoes, the McSkimin $\Delta t$ criterion [48] is applied to correct the phase lag due to bonding medium on RF echoes. This technique helps to measure ultrasound transit time in the sample to an accuracy of the order of few ppm. The overall accuracy of the elastic constant value is of the order of 0.1%.

3.6. Results and Discussion

The measured elastic properties of pure BST and BST added with 0.5 wt % of different glasses are presented in Table 3.1.
Table 3.1 shows that the ultrasonic velocities and hence the elastic moduli decreases when glass is added to BST. Also the elastic properties are almost independent of the type of glass, which is added.

Generally, ceramics are inhomogeneous materials because they consist of matrix grains, grain boundaries, pores, inclusions, incomplete densification, second phases etc. If a glassy phase is formed, it decreases the density and the mechanical strength. The elastic properties are definitely affected by intragranular (crystallinity) and intergranular (grain boundary) properties. Therefore elastic properties are the result of combined contribution of degree of crystal structure imperfections and microstructural inhomogenity. The random distribution are considered to be kind of imperfection in the atomic ordering. So the lowering of elastic constants due to glass addition may be due to the disorder in ion distribution or the formation of second phase.

It is evident from Table 3.1 that addition of glass does not drastically reduce the values of elastic constants. Moreover, the Poisson’s ratio remains more or less the same. This means that the hardness of the specimen is not affected significantly due to the addition of glass. So one can say that if the addition of glass leads to significant advantages during sintering, one can truly accommodate a minor reduction in mechanical strength and hardness. The results presented in this chapter show that the mechanical strength of these materials decrease due to glass addition, but is not very significant. So one can take advantage of glass addition while using these materials for application.
Table 3.1. Elastic properties of Barium Samarium Titanate (Ba₄Sm₂₈/₃Ti₁₈O₅₄)

<table>
<thead>
<tr>
<th>BST with 0.5 wt % of</th>
<th>V₁ (m/s)</th>
<th>C₁₁ (GPa)</th>
<th>V₁ (m/s)</th>
<th>C₄₄ (GPa)</th>
<th>Young’s Modulus Y (GPa)</th>
<th>Bulk Modulus B (GPa)</th>
<th>Poisson’s ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>BST (pure)</td>
<td>6607 ± 33</td>
<td>244 ± 6</td>
<td>3729 ± 18</td>
<td>77 ± 2</td>
<td>196 ± 5</td>
<td>140 ± 3</td>
<td>0.266</td>
</tr>
<tr>
<td>MgO-Al₂O₃-SiO₂</td>
<td>6439 ± 32</td>
<td>228 ± 6</td>
<td>3657 ± 18</td>
<td>73 ± 2</td>
<td>185 ± 5</td>
<td>130 ± 3</td>
<td>0.262</td>
</tr>
<tr>
<td>ZnO-B₂O₃ (77:23)</td>
<td>6480 ± 32</td>
<td>233 ± 6</td>
<td>3673 ± 18</td>
<td>75 ± 2</td>
<td>189 ± 5</td>
<td>133 ± 3</td>
<td>0.263</td>
</tr>
<tr>
<td>B₂O₃ - SiO₂</td>
<td>6504 ± 33</td>
<td>234 ± 6</td>
<td>3680 ± 18</td>
<td>75 ± 2</td>
<td>189 ± 5</td>
<td>134 ± 3</td>
<td>0.265</td>
</tr>
<tr>
<td>ZnO-B₂O₃ - SiO₂</td>
<td>6541 ± 33</td>
<td>235 ± 6</td>
<td>3699 ± 18</td>
<td>75 ± 2</td>
<td>190 ± 5</td>
<td>135 ± 3</td>
<td>0.265</td>
</tr>
<tr>
<td>PbO- B₂O₃ - SiO₂</td>
<td>6505 ± 33</td>
<td>236 ± 6</td>
<td>3680 ± 18</td>
<td>75 ± 2</td>
<td>191 ± 5</td>
<td>135 ± 3</td>
<td>0.265</td>
</tr>
<tr>
<td>MgO-B₂O₃ - SiO₂</td>
<td>6512 ± 33</td>
<td>235 ± 6</td>
<td>3677 ± 18</td>
<td>75 ± 2</td>
<td>189 ± 5</td>
<td>135 ± 3</td>
<td>0.266</td>
</tr>
<tr>
<td>ZnO-B₂O₃ (50:50)</td>
<td>6587 ± 33</td>
<td>242 ± 6</td>
<td>3718 ± 18</td>
<td>77 ± 2</td>
<td>196 ± 5</td>
<td>140 ± 3</td>
<td>0.266</td>
</tr>
<tr>
<td>Al₂O₃ - SiO₂</td>
<td>6419 ± 32</td>
<td>225 ± 6</td>
<td>3649 ± 18</td>
<td>73 ± 2</td>
<td>184 ± 5</td>
<td>130 ± 3</td>
<td>0.261</td>
</tr>
<tr>
<td>Al₂O₃ - B₂O₃ - SiO₂</td>
<td>6445 ± 32</td>
<td>228 ± 6</td>
<td>3666 ± 18</td>
<td>74 ± 2</td>
<td>186 ± 5</td>
<td>130 ± 3</td>
<td>0.261</td>
</tr>
<tr>
<td>BaO-B₂O₃ - SiO₂ (30:60:10)</td>
<td>6603 ± 33</td>
<td>241 ± 6</td>
<td>3723 ± 18</td>
<td>77 ± 2</td>
<td>194 ± 5</td>
<td>139 ± 3</td>
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<td>BaO-B₂O₃ - SiO₂ (30:40:30)</td>
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<td>245 ± 6</td>
<td>3725 ± 18</td>
<td>77 ± 2</td>
<td>195 ± 5</td>
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References


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