

Structural and dielectric investigations on BST-BZT composites

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(Received & Accepted: January 10, 2008)

ABSTRACT

Nanopowders of $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ (BST) and $\text{BaZr}_{0.3}\text{Ti}_{0.7}\text{O}_3$ (BZT) are synthesized using hydroxide co-precipitation method. The nanoparticles are used to form composites z BST + $(1-z)$ BZT for $z = 0.4, 0.5$ and 0.6 with 2 wt% Bi_2O_3 as a sintering aid. The powders of BST, BZT and composites are subjected to the investigations of XRD, complex impedance and dielectric properties. The results on variation of dielectric constant are promising and suggest usefulness of composites as a RF dielectric material, in the paraelectric region.

Key words: Dielectric study, BST-BZT composites.

INTRODUCTION

Recently there has been an increased interest in the use of ferroelectric materials just above T_c , in the paraelectric region, for applications in the tunable microwave devices. Barium Strontium Titanate (BST) system is well known for its strong response to the applied dc electric field. This property is very attractive and has been used to develop various devices operating in the microwave (MW) and millimeter wave range. The most important parameter for such thin film ferroelectric devices is the low dielectric losses ($\tan \delta$) and high tunability properties¹. Here, the BST is observed to possess higher values of dielectric losses at MW frequencies. To overcome this difficulty, composites and multilayer thin films of BST with MgO or MgTiO_3 are investigated¹. The observations on these systems have stimulated the present studies.

In the present paper, we report investigations on dielectric properties of $\text{Ba}_x\text{Sr}_{(1-x)}\text{TiO}_3$ (BST) for $x = 0.8$ formed as a composite with $\text{BaZr}_y\text{Ti}_{(1-y)}\text{O}_3$ (BZT) for $y = 0.3$. Here BZT too is a useful radio frequency (RF) and microwave (MW) dielectric material possessing higher value of dielectric tunability. Further, considering the virtues of the BZT as reported earlier, it would be interesting

to investigate the composites of BST and BZT for dielectric and other physical properties. Further, these investigations may also provide an insight into the effects of intra-grain polarization in case of composites of the dielectric materials. To achieve well dispersed BST and BZT particles nanopowders of BST and BZT is used as starting materials. To lower the temperature of formation of composites, 2 wt% Bi_2O_3 has been used as sintering aid².

Thus the paper reports investigations of structural, dielectric properties and complex impedance properties on composites of BST and BZT with an emphasis on the synthesis and dielectric properties.

EXPERIMENTAL

A Hydroxide co-precipitation route has been used to synthesize nanopowders of $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ (BST) and $\text{BaZr}_{0.3}\text{Ti}_{0.7}\text{O}_3$ (BZT) compositions.

For synthesis of BST high purity (> 99.9%) Barium nitrate [$\text{Ba}(\text{NO}_3)_2$], Strontium nitrate [$\text{Sr}(\text{NO}_3)_2$] and Pottassium Titanium Oxalate [$\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$] are used as precursors, while KOH is used as a mineralizer. Considering earlier

reports, the molar ratio of $\text{KOH}:\text{Ba}(\text{NO}_3)_2$ of greater than 1:6 is used for complete mineralization of BST³. Further it has been observed that the $\text{Ba}(\text{OH})_2$ is fractionally soluble in water but insoluble in alkaline medium⁴. Therefore the precipitates are washed in weak solution of NH_4OH . The precipitates were subjected to the DTA/TG analysis. The observed weight loss and the loss predicted from the reaction are observed to tally quantitatively and confirm the correctness of the precipitation reaction. Considering the TG analysis, the precipitate is filtered, dried and presintered at 600°C for 6 hours. The final sintering is carried out at 1100°C for 12 hours.

For synthesis of BZT, high purity Barium nitrate, Zirconyl nitrate [$\text{ZrO}(\text{NO}_3)_2$] and Potassium Titanium Oxalate are used as starting materials. The remaining procedure of co-precipitation is similar to that of the synthesis of BST. In this case also, the precipitates are subjected to DTG/TG analysis to determine the minimum required sintering temperature for formation of the product. The powders of BST and BZT are subjected to the structural investigations using XRD. The XRD is observed to indicate the formation of single phase composition with cubic crystal structure as reported earlier. The XRDs are also used for determination of particle size using Williamsons-Hall method. It is observed that the particle size of BST and BZT determined from the XRD is ~ 35 nm in both the cases. The SEM pictures of the powders also show the formation of nanocrystalline powder with average grain diameter of nearly the same size.

The nano powders of BST and BZT are used to form composites using the formula z BST + $(1-z)$ BZT + 2 wt% Bi_2O_3 , for $z = 0.6$ (COMP 1), 0.5 (COMP 2) and 0.4 (COMP 3). The Bi_2O_3 is used as sintering aid to lower the temperature of sintering and achieve higher levels of densification². In addition to the composites above, a composition 0.5 BST + 0.5 BZT has been prepared without addition of Bi_2O_3 . This composition is used to understand the effect of Bi_2O_3 on modification of the electronic state of the material. The composites in the pellet formed are sintered at 1200°C for 4 hours for measurements of dielectric constants and complex impedance using HP 4284A LCR-Q meter.

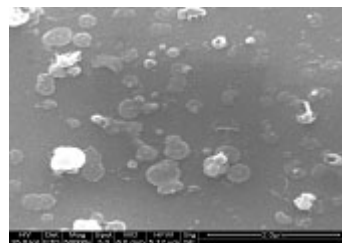


Fig. 1(a): SEM picture of BST

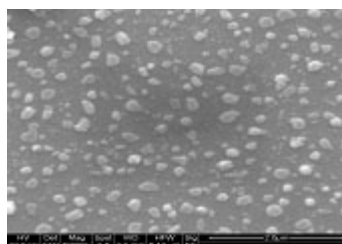


Fig. 1(b): SEM picture of BZT

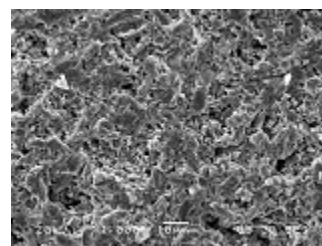


Fig. 1(c): SEM picture of COMP2

RESULTS AND DISCUSSION

Figure 2 shows variation of relative permittivity ' ϵ_r ' at an excitation frequency ' f ' of 1 KHz as a function of temperature T for COMP 1, COMP 2, COMP 3, BST and BZT systems. The compositions of the BST ($\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$) and BZT ($\text{BaZr}_{0.3}\text{Ti}_{0.7}\text{O}_3$) are so selected that the BST possesses the ferroelectric to paraelectric transition (T_c) at $\sim 30^\circ\text{C}$, while the BZT shows the paraelectric region for $T > -50^\circ\text{C}$ for this composition⁵. Here the present observations of ϵ_r on BST and BZT (figure 1) are in confirmation with these reports. It is also observed that ϵ_r for BZT is greater than for that BST, while the Q follows inverse relationship. These observations are in confirmation with the earlier reports⁵⁻⁷.

The present observations show that dielectric anomaly in case of composites is observed

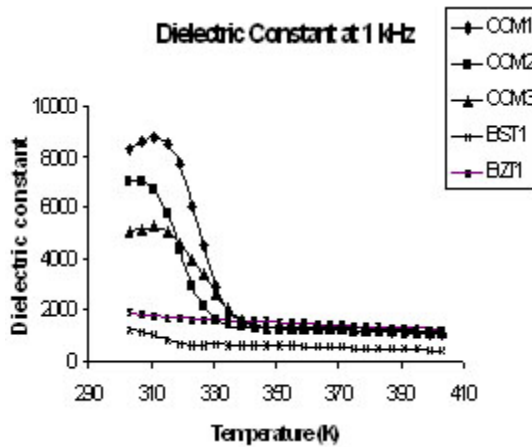


Fig. 1: Temperature dependence of Dielectric constant (ϵ_r) at 1 KHz for Composite

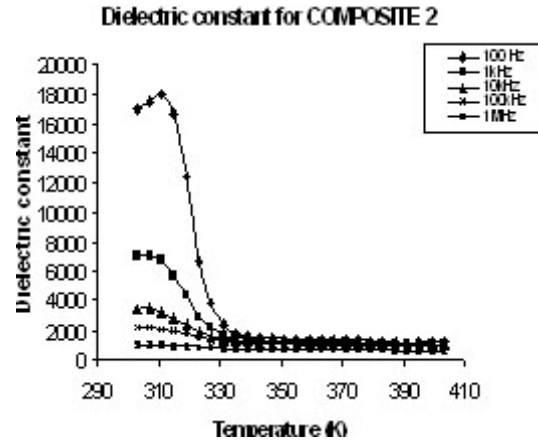


Fig. 2: Temperature dependence of Dielectric constant (ϵ_r) at various f for BST-BZT composite 2.

far more pronounced as compared to the individual BST composition. The high value of dielectric constant at T_c of the BST is believed to be due to the grain-grain boundary (g-gb) effects⁹. This causes a highly resistive grain boundary, while the bulk of grain remains semiconducting. The difference in the resistivities of grain and grain boundaries cause a barrier layer at the (g-gb) interface and leads to very high ϵ_r at $T=T_c$.

In case of BST-BZT composites the enhanced values of the ϵ_r at T_c could be attributed to the grain-grain boundary effects in BST and the contribution to the dielectric constant due to interfacial polarization at interfaces between BST and BZT grains. The interfacial polarization is expected to be predominant at lower frequencies. Figure 3 shows variation of ϵ_r at various frequencies for COMP 2. From fig. 3 it could be seen that ϵ_{rmax} for COMP 2 decreases sharply as the frequency is increased. This feature indicates contribution of the inter-grain interfacial polarization to the ϵ_r in case of the composites. Further it is observed that the T_c for all the composites increases slightly for increasing frequencies. To determine whether any relaxor behavior exists in these composites, the ϵ_r for $T > T_c$ is fitted to the equation $\epsilon_r^{-1} = \epsilon_{rmax}^{-1} + A (T-T_c)^{\gamma}$ [9]. From log-log plots of $\epsilon_r^{-1} - \epsilon_{rmax}^{-1}$ and $T-T_c$ the γ is observed to be nearly equal to 2 for all the composites.

To understand the effect of Bi_2O_3 on modification of dielectric properties, the dielectric properties of COMP 2 sintered in the same schedule but without addition of Bi_2O_3 are also investigated. The observations have shown that the effect of inter-grain interfacial polarization is increased because of addition of the Bi_2O_3 . Therefore, the increase in the ϵ_{rmax} is significant at lower frequencies than those at higher frequencies. Further, the Q for composites with sintering aid is less than that for the composites without the sintering aid. These features may occur because of the Bi_2O_3 forming a very thin conducting layer over the grain surfaces of the BST and BZT. The presence of these conducting layer may cause increase in the ϵ_r and reduction in Q of the composites, as the interfacial/ space charge polarization occurs due to the migrating charges¹⁰.

The effect of interfacial polarization is not dependent on the ferroelectric to paraelectric transition. In the paraelectric region the contribution of the interfacial effects would be significant and therefore to determine the presence of interfacial polarization in these composites, the complex impedance spectra are analyzed in the paraelectric region. The observed variation of z'' as z' could be fitted to a model, where a parallel R-C circuit representing grains (R_p - C_p) occurs in series with a interfacial capacitance C_i . Here C_p , R_p represents a grain, while the C_i represents effect of interfacial

polarization. The values of C_p , R_p and C_i for COMP 2 with and without sintering aid are shown in Table 1.

Table 1: The values of C_p , R_p , and C_i for composite 2.

Description	R_p kohm	C_p nF	C_i nF
With Bi_2O_3	348	2.28	0.505
Without Bi_2O_3	374	0.106	0.256

The C_i is observed to increase because of addition of the Bi_2O_3 . These observations therefore are in confirmation with the predictions of occurrence of inter-grain interfacial polarization based on the observations of variation of the dielectric constant with frequency and temperature.

CONCLUSIONS

The nano powders of BST and BZT have been synthesized successfully using hydroxide co-precipitation route. These powders are used to form the composites of BST-BZT and are subjected to the investigations of various physics properties. The paper emphasizes mainly on synthesis and dielectric properties.

The results on variation of ϵ_r as a function of T and f indicate that the BST-BZT composites may provide a useful range of dielectric properties at RF and MW frequencies. The present study suggests that further investigations on these composites in the thin film form may provide a vary interesting and useful range of tunable dielectrics.

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