DIELECTRIC RESPONSE OF LA MODIFIED 95BFO - 5BT COMPOSITE PREPARED BY SOL-GEL METHOD

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Abstract. Lanthanum doped 95BiFeO$_3$–5BaTiO$_3$ (95BLFO–5BT) multiferroic ceramic was prepared under extreme conditions by a PVA Sol-Gel method. A deep study of dielectric properties of La doped 95BiFeO$_3$–5BaTiO$_3$ (95BFO–5BT) ceramics with the help of comprehensive analysis of temperature and frequency dependent dielectric behavior is reported in this paper. Dielectric properties of 95BLFO–5BT ceramics were studied at various temperature and frequency. It was also found that doping of 95BiFeO$_3$–5BaTiO$_3$ by Lanthanum improved dielectric properties. The dielectric constant of a 95BiFeO$_3$–5BaTiO$_3$ (95BLFO–5BT) increased after Lanthanum doping for both low and high frequency. The dielectric constant was found to be very high ($\varepsilon' > 10^3$, for $T > 150°C$). This enhancement in the dielectric properties is possible due to the changes in structure of as prepared sample of 95BiFeO$_3$– 5BaTiO$_3$ (95BLFO– 5BT) by the addition of Lanthanum.

Keywords: Ceramic Material, Sol-Gel, Dielectric Constant, Dielectric Loss.

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Introduction

From many years researchers are very much focused on the preparation and studies on single phase multiferroic materials such as $BiMnO_3$, $TbMnO_3$, $BiFeO_3$ and $YMnO_3$ [1-4]. Due to the existence of numerous ferroic orders in the same phase, multiferroics exhibit considerable potential for use in multifunctional devices and have been thoroughly studied [5,6]. $BiFeO_3$, a type of bismuth ferrite, exhibits the coexistence of magnetic and ferroelectric orders at room temperature, making it an ideal choice for use in ferroelectric non-volatile memories and also for high performance application in electronics. These substances are also referred to as multiferroic [7-9]. Also, $BiFeO_3$ (BFO) has a high potential for practical applications as it shows ferroelectric and antiferromagnetic ordering at ambient temperature as well as elevated Curie, TC 820 °C, and N' eel temperature T_N 370°C [10,11]. $BiFeO_3$ is one of the few single-phase multiferroic magnetoelectric materials currently in existence.

The macroscopic magnetism is, however, cancelled by a superimposed spiral spin structure with a 62 nm inconsistent long-wavelength period, which also prevents the discovery of the linear magnetoelectric impact in bulk $BiFeO_3$ [12]. Additionally, it has been noted that the easily formed undesirable phases, such as $Bi_{25}FeO_{39}$ and $Bi_2Fe_4O_9$, during the manufacturing of polycrystalline BFO samples can affect their electric, ferroelectric, and magnetoelectric properties [13–15]. Sol-gel approaches [16], polymeric [17], co-precipitation [18], and high-energy ball milling are just a few of the methods that have been successfully used to create single-phased BFO powders to far. Additionally, a number of processes, including hot pressing [23], sinter forging [24], high pressure sintering [25] reported pure and dense ceramic formation. Also, shock wave compaction [26], magnetic dynamic compaction [27], and spark plasma sintering [28], have been utilized to create dense ceramics.

Additionally, the bulk $BiFeO_3$ exhibits significant current leakage issues, making it challenging to achieve high resistivity. This is owing to the existence of a large number of charge centers brought on by oxygen deprivation and bismuth evaporation during the typical solid-state manufacturing procedure [29]. Numerous attempts have been made recently to address these issues, such as depositing rare-earth or transition metal elements into Fe or Bi sites to improve the phase stability of $BiFeO_3$ [30-33]. In order to attain ferromagnetism by destroying spiral spin structure, $BiFeO_3$ nanoparticles with grain sizes less than 62 nm were also synthesized [34,35].

It has been discovered that it is difficult to produce high resistive composite BFO ceramics because of the existence of a large number of charge centre defects caused primarily by oxygen deficiency, leading to enormous leakage currents [36]. Very thin $BiFeO_3$ multi-layer films are also deposited to improve the ferroelectric properties. [37, 38]. It has been demonstrated that lanthanum substitution is an effective method for enhancing the ferroelectric and ferromagnetic properties of $BiFeO_3$. [30,31,37]. It is also found that that the bulk samples and thin films have typically been the focus of much of the research on the La doping impact in bismuth ferrite. Since the thin film's functionality is heavily influenced by the thickness of the thin film and the strain. It is frequently difficult to distinguish between the true effect of element substitution and the strain effect. Also, impurities and non-stoichiometry are still issues with bulk La doped $BiFeO_3$ material produced via solid-state reaction.

Out of all the materials reported single phase $BiFeO_3$-$BaTiO_3$ material which shows unique properties at room temperature. This single phase composite attracted a lot of attention due to its curies temperature 619°C which is considerable high [39]. Along with good improvement in all other properties such as dielectric, ferroelectric BFO–BT shows weak magnetism [40]. However, Zhou [41] and Leontsev [42] have reported the doping effect on $BiFeO_3$–$BaTiO_3$ with good piezoelectricity. It is also reported that ferroelectricity and ferromagnetism of the BiFeO3 can be improved by the addition of rare earth elements such as La, Sm, Nd, etc.[43-46]. So it is more likely that the doping of this rare earth element will modify the multiferroic properties of lanthanum modified 95$BiFeO_3$ - 5$BaTiO_3$ composite. In the present work, we have studied the dielectric behavior of lanthanum modified 95$BiFeO_3$–5$BaTiO_3$ composite synthesized by Sol Gel method.

In face of the above-mentioned issues, in this work we applied Sol Gel method and processes such as high-energy ball cryomilling and sintering in order to obtain phase pure, nanostructured La substituted $BiFeO_3$-$BaTiO_3$ powders and ceramics. The purpose is to provide further experimental evidence to examine the La doping effect in bismuth ferrite.

Experimental

The Synthesis of multiferroic material with the active content of bismuth ferrite ($BiFeO_3$) and barium titanate ($BaTiO_3$) was carried out. It is considering that it was difficult to obtain single phase of $BiFeO_3$ as a base material for multiferroic materials. It is expected that the addition of $BaTiO_3$ on ceramic alloys consist of $BiFeO_3$ and $BaTiO_3$ can improve the electrical properties of the ceramics and finally it improves the multiferroic properties of the material. Bismuth nitrate $Bi(NO_3)_3.5H_2O$ and iron nitrate $Fe(NO_3)_39H_2O$ in stoichiometric proportions were dissolved in diluted nitric acid HNO_3 solution with citric acid $C_6H_8O_7$) in a molar ratio of 6:1 with $Bi(NO_3)_3.5H_2O$. Concentrated nitric acid is also used to form the complex. While mixing above material constant stirring was done with the help of magnetic stirrer at 65°C temperature. The pH value was adjusted to 5–6 by adding ammonia ($NH_3.H_2O$), followed by stirring for about 6 to 7 hours at 80°C. The mixed solution was taken out when it was converted to floppy gel. In order to obtain powder this floppy gel solution is kept in oven at 90°C for 02 to 03 hour. This floppy gel was then crushed in to fine powder which is placed in furnace at 600°C for 2 hours. The composite of this powder was then mixed with Bismuth titanate in stoichiometric ratio. The ball milling is done for 12 hours to get well mixed material in powder form. The powder formed was then placed in furnace for calcination at 600°C for 4 hour in air. Finally, the pellets of La doped 95BFO-5BT ceramics were prepared using polyvinyl acetate as a binding agent. The pallets were then sintered at 870°C for 4 hour.

Results and Discussion

Frequency dependence of dielectric constant for La doped 95BFO–5BT ceramics

The frequency dependent plot of real part of real part of dielectric constant (ε′), imaginary part of dielectric constant (ε′′) and tangent loss (tan δ) measured at different temperature is shown in Fig. 1, Fig. 2 and Fig. 3 respectively. The as prepared sample shows a high ε′ at a low frequency range for all temperature but goes on decreasing rapidly (10^2–10^3) with increase in frequency. This decrease in ε′ is reliable with the dielectric loss peak shown in figure 3. This may be because of the dipole relaxation process of $BiFeO_3$ [47, 48]. The step line decrease in dielectric constant and the peak in dielectric loss indicate that replacement of Bi^{3+} ions by La^{3+} ions has significant effect on the dielectric properties of La doped 95BFO-5BT ceramics [49-51]. The dielectric constants for the samples decrease as the frequency increases from 1 Hz to 10MHz which can be explained by a conventional dielectric relaxation process. The dielectric relaxation is quite small and stable in fields with frequency larger than 1 MHz. The value of the real part of the dielectric constant increases after doping with Lanthanum. The improvement in the dielectric constant is possibly caused by the change of structure after lanthanum doping. The Fe-O bond length ratio increases after La substitution. This further distortion of the Fe-O octahedra might lead to an increase in polarization ability in the form of dielectric constant. Since all the La doped samples have greater values of the Fe-O bond length ratio than the un-doped samples, the dielectric constants are larger in the doped samples.

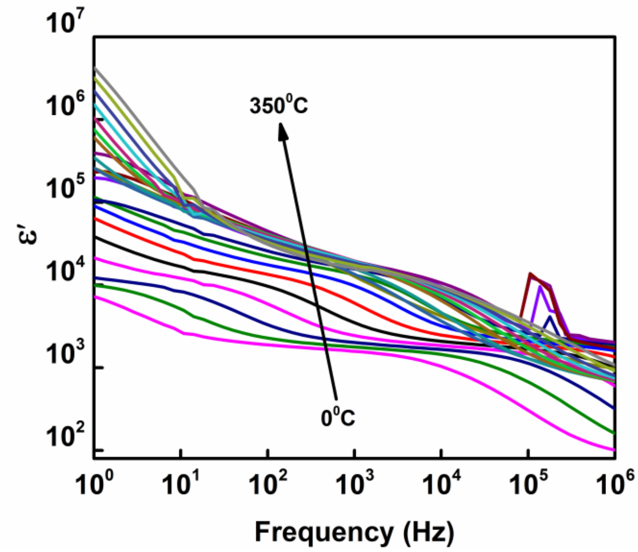

Fig.1 Real Part of Dielectric constant (ε′) as a function of frequency for La doped 95BFO–5BT

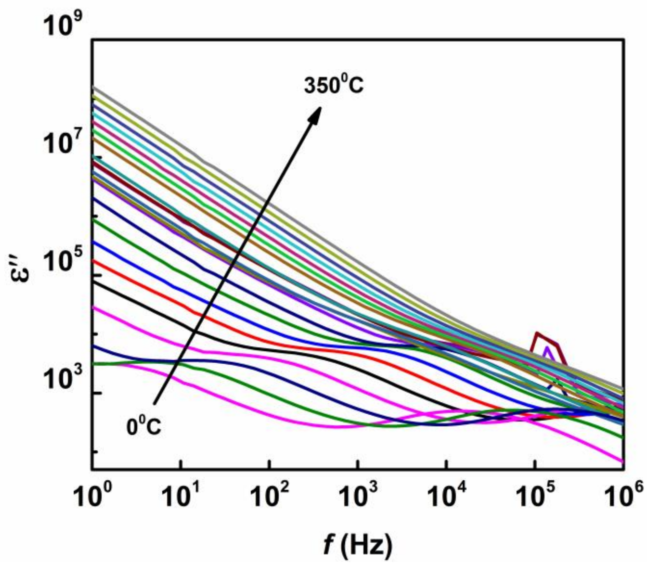

Fig.2 Imaginary part of Dielectric constant (ε″) as a function of frequency for La doped 95BFO–5BT

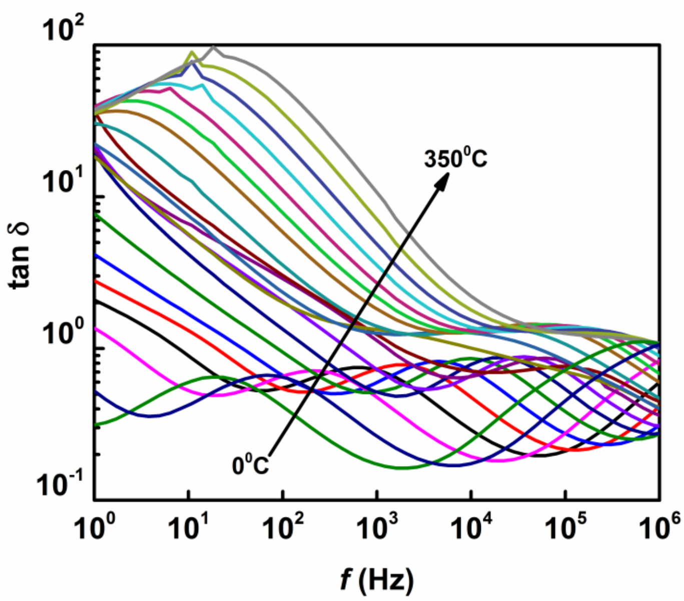

Fig.3 Dielectric loss (tan δ) as a function of frequency for La doped 95BFO–5BT

Temperature dependence of dielectric constant for La doped 95BFO–5BT ceramics
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Fig. 4, Fig.5 and Fig.6 shows the temperature dependence plot of a real part of dielectric constant
(ε′), imaginary part of dielectric constant (ε′′) and tangent loss (tan δ) measured at different frequencies.

The dielectric constant is found to be decreases with the increase in frequency which is due to the

dielectric relaxation process as stated earlier. Like dielectric constant, the dielectric loss is also found to be decreases rapidly with increasing frequency, which is same as the results mentioned by Pradhan [52]. The value of dielectric loss is ≤ 1 for all temperature below 1MHz frequency.

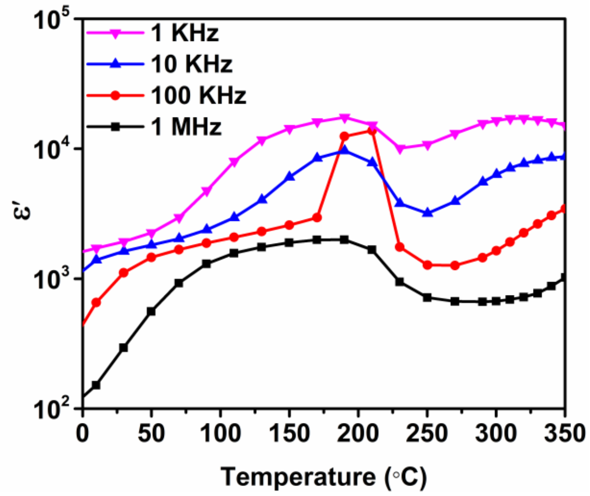

Fig.4 Real Part of dielectric constant (ε′) as a function of temperature for La doped 95BFO-5BT

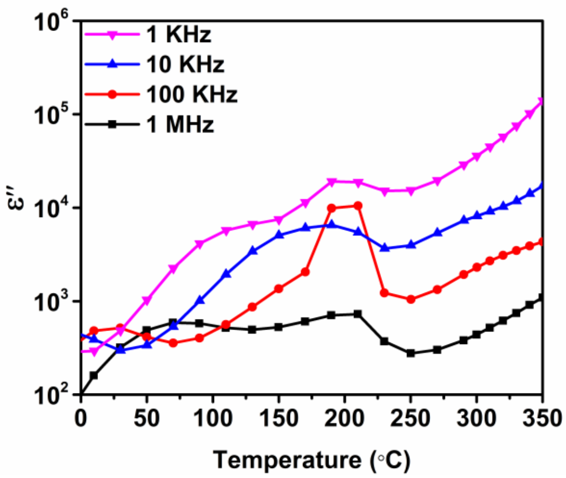

Fig. 5 Imaginary Part of dielectric constant (ε′′r) with temperature for different frequency

It can be seen that all the BFO-BTO-La-x ceramics only exhibit one dielectric peak, which is associated with the paraelectric–ferroelectric phase transition which suggests that partial substitution of La for Bi causes a diffuse phase transition. [53, 54].

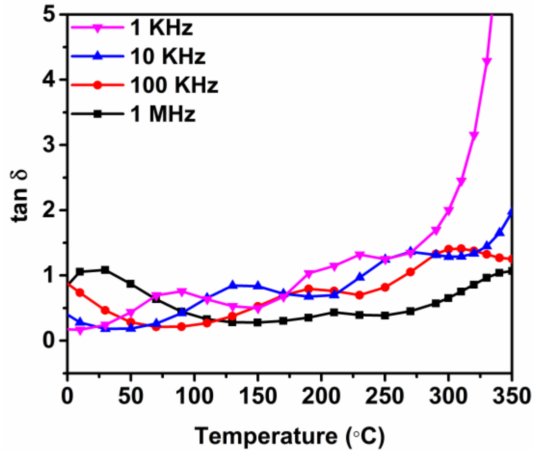

Fig. 6 dielectric loss (tan δ) with temperature for different frequency

Conclusions

In the present paper, we have prepared La doped 95 BFO- 5 BT ceramics by PVA Sol-Gel method. The highly dense and resistive ceramics obtained also presents high dielectric response and low loss tangent in a wide range of frequencies. The increase in Fe-O bond length ratio due to the addition of Lanthanum caused distortion of the Fe-O octahedra lead to an increase in polarization ability in the form of dielectric constant. The dependence of dielectric properties on frequency & temperature cleared the significant increase in dielectric constant at ε′ > 103, for T > 150°C.

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