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Effect Of Rare Earth Dope Synthesis, Structural, Ferroelectric And Dielectric Properties Of Rare Earth-Doped Basrtio$_3$ Ceramics

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Abstract-
In this research, we explore the effects of rare earth (Gd, Sm, Y) doping on the structural, microstructural, and dielectric properties of $Ba_{0.8}Sr_{0.2}TiO_3$ (BST) ceramics. X-ray diffraction (XRD) analysis confirms that the tetragonal perovskite structure is maintained across all samples, with noticeable lattice expansion due to the incorporation of rare earth ions. The FTIR spectra further validate the structural integrity, while the FESEM images reveal a more uniform grain distribution and improved densification in the doped samples. Impedance spectroscopy shows a significant reduction in the impedance of doped BST ceramics, indicating enhanced dielectric properties. These findings suggest that rare earth-doped BST ceramics exhibit superior characteristics compared to undoped BST, making them promising candidates for advanced electronic applications, such as capacitors and other devices requiring high dielectric performance.
Keywords: *$BaSrTiO_3$; dielectric properties; P-E hysteresis; Impedance.*

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I. Introduction

Barium strontium titanate ($Ba_{0.8}Sr_{0.2}TiO_3$, BST) is a solid solution that has garnered significant attention in the field of material science due to its remarkable dielectric properties, making it an excellent candidate for a variety of electronic applications. BST ceramics exhibit a tunable dielectric constant, which is particularly useful in devices such as capacitors, phase shifters, and tunable microwave devices [1-4]. The versatility of BST arises from its perovskite structure, which allows for substantial modification through doping. Doping involves introducing small amounts of foreign ions into the crystal lattice, which can significantly alter the electrical and structural properties of the material.

Rare earth elements, such as gadolinium (Gd), samarium (Sm), and yttrium (Y), are known for their ability to enhance the performance of ferroelectric and dielectric materials. These elements have larger ionic radii compared to titanium (Ti), the ion they typically replace in the BST lattice. This size difference can induce local strain, modify the crystal field, and alter the polarization behavior of the material [5,6]. Moreover, rare earth doping can influence grain growth during the sintering process, thereby affecting the microstructure and, consequently, the dielectric and impedance properties of the ceramics [7].

The impact of rare earth doping on BST ceramics is not only of scientific interest but also of practical importance. For instance, the dielectric constant of BST can be increased or decreased depending on the type and concentration of the dopant, thereby tailoring the material's properties for specific applications. Additionally, the impedance characteristics, which are crucial for energy storage and dissipation in electronic devices, can be optimized by controlling the grain boundary resistance through doping.

Despite extensive research on BST and its doped variants, the specific effects of Gd, Sm, and Y doping on the structural, dielectric, and impedance properties of $Ba_{0.8}Sr_{0.2}TiO_3$ ceramics are not fully understood. Previous studies have suggested that these dopants can improve the material's performance, but a comprehensive investigation comparing these dopants in the same host matrix is lacking. This study aims to fill this gap by synthesizing Gd, Sm, and Y-doped BST ceramics using a solid-state reaction method and systematically analyzing their properties using various characterization techniques [9-11].

This research not only seeks to elucidate the fundamental changes induced by rare earth doping in BST but also to explore the potential of these doped ceramics for use in advanced electronic applications. By understanding the relationship between the dopant type, microstructure, and electrical properties, we can provide valuable insights into the design and optimization of BST-based materials for next-generation electronic devices.

II. Experimental Details

The synthesis of Rare Earth (Gd, Sm, Y) doped $Ba_{0.8}Sr_{0.2}TiO_3$ (BST) $Ba_{0.8}Sr_{0.2}(Ti_{0.96}Gd_{0.04})O_3$ (BSTG), $Ba_{0.8}Sr_{0.2}(Ti_{0.96}Sm_{0.04})O_3$ (BSTS), and $Ba_{0.8}Sr_{0.2}(Ti_{0.96}Y_{0.04})O_3$ (BSTY) was carried out using the high-energy ball milling technique, which is effective for producing fine, homogeneously mixed powders necessary for solid-state reactions. The precursors, including $BaCO_3$, $SrCO_3$, TiO_2, and the respective rare earth oxides, were precisely weighed and mixed. This mixture was then transferred to a zirconia milling jar with zirconia balls and ethanol to facilitate the milling process. The milling was conducted at 300-400 rpm for 12-24 hours, ensuring thorough mixing and particle size reduction.

After milling, the ethanol was removed by drying the slurry at 100°C, resulting in a fine powder. The powder underwent calcination at 1100°C for 4 hours to initiate the solid-state reaction, forming the desired perovskite phase. The calcined powder was then pressed into pellets and sintered at 1350°C for 4 hours to enhance densification and crystallinity.

The synthesized BST samples were subsequently characterized using various techniques. X-ray diffraction (XRD) confirmed the phase purity, Fourier-transform infrared spectroscopy (FTIR) provided insights into chemical bonding, and field emission scanning electron microscopy (FESEM) combined with energy dispersive X-ray spectroscopy (EDX) was used to examine the microstructure and elemental composition. This method effectively produces high-quality BST ceramics with tailored electrical properties, suitable for various applications in electronic devices.

III. Results And Discussions

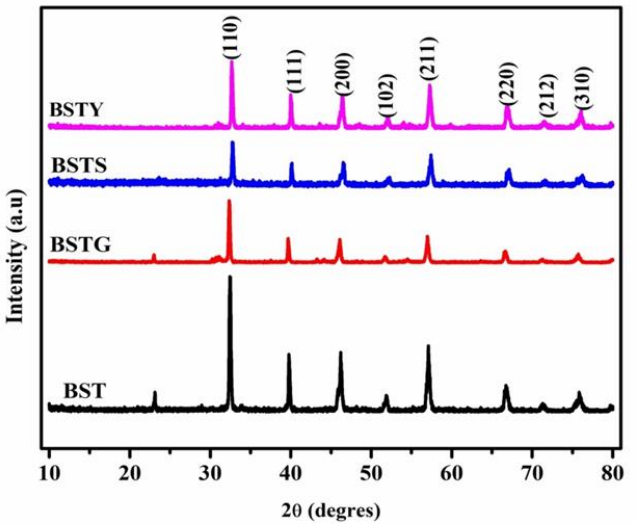

Figure 1. XRD Spectra of BST, BSTG, BSTS and BSTY.

Figure 1 shows the XRD graphs of prepared samples. The XRD analysis for the samples, including undoped $Ba_{0.8}Sr_{0.2}TiO_3$ (BST) and rare-earth-doped variants (BSTG, BSTS, BSTY), confirms the preservation of the tetragonal phase across all compositions. The X-ray diffraction (XRD) patterns of all samples exhibit distinct peaks that correspond to the tetragonal phase of $Ba_{0.8}Sr_{0.2}TiO_3$. The peaks at 2θ angles 23.56°, 33.94°, 40.50°, 46.61°, 53.99°, 57.81°, 67.01°, 71.25°, and 75.70° correspond precisely to the Miller indices (101), (110), (111), (200), (102), (211), (220), (212), and (310), respectively. The observed peaks correspond to the JCPDS card no: 08-22618, confirming the tetragonal structure of both the doped and undoped BST samples. The diffraction peaks correspond to the tetragonal perovskite structure, with slight shifts indicating successful doping without altering the crystal structure. The increase in lattice constants and cell volume with rare-earth doping suggests lattice expansion due to the incorporation of larger ionic radii dopants (Gd^{3+}, Sm^{3+}, Y^{3+}) compared to Ti^{4+} [12-14].

Table 1 The value of Lattice Parameter (a), X-ray density (ρ_x), Bulk density (ρ_B), cell volume, and Strain for $(Ba_{0.8}Sr_{0.2})TiO_3$, $(Ba_{0.8}Sr_{0.2})TiO_3$ $(Ti_{0.98}Gd_{0.02})O_3$, $(Ba_{0.8}Sr_{0.2})TiO_3$ $(Ti_{0.98}Sm_{0.02})O_3$, $(Ba_{0.8}Sr_{0.2})TiO_3$ $(Ti_{0.98}Y_{0.02})O_3$.

sample	*a*	*c*	Cell volume (Å^3)	*c/a*	ρ_x	ρ_B	% of porosity
BST	4.00	4.02	64.32	1.005	5.20	4.40	16
BSTG	4.03	4.06	65.93	1.050	5.30	4.60	14
BSTS	4.08	4.11	68.41	1.007	5.50	4.80	13
BSTY	4.06	4.08	67.25	1.004	5.40	4.90	10

It is clear from Table 1, that the lattice constants '*a*' and '*c*' increase slightly with rare-earth doping, indicating lattice expansion, which is reflected in the cell volume increase, particularly for BSTS (68.41 Å^3). The c/a ratio remains close to unity, confirming minor tetragonal distortion. Theoretical and bulk densities also rise with doping, indicating higher atomic masses of the dopants and improved packing density, respectively. A corresponding decrease in porosity is observed, suggesting enhanced material compactness and potentially improved mechanical and dielectric properties.

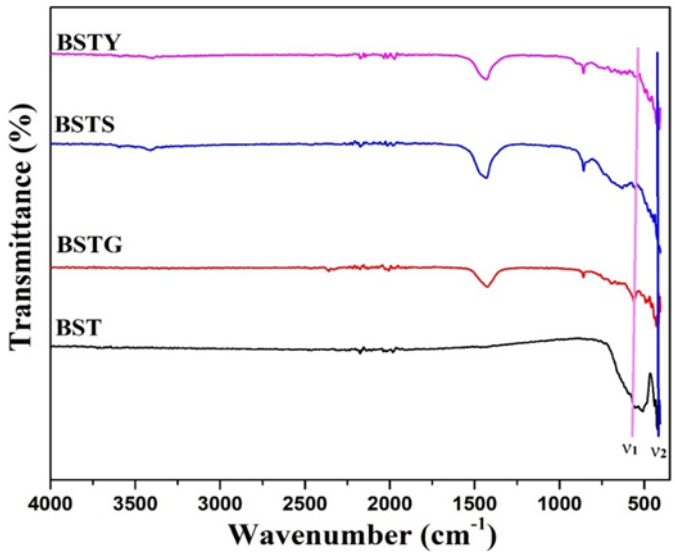

Figure 2. FTIR Spectra of Ba(SrTi)O$_3$ and Re(Gd,Sm,Y)-doped Ba(SrTi)O$_3$.

Figure 2 presents the FTIR spectra of BST, BSTG, BSTS, and BSTY, highlighting the characteristic vibrational bands associated with the Ti-O bonds within the TiO_6 octahedra of the perovskite structure. The high-frequency band (v_1), observed between 550-600 cm^{-1}, corresponds to the stretching vibrations of these bonds. In BST, this band is prominent, indicating strong Ti-O bond stretching [15, 16]. Doping with Gd^{3+}, Sm^{3+}, and Y^{3+} results in slight shifts in this band, reflecting changes in bond lengths and angles, particularly with Gd^{3+} and Sm^{3+}, which have larger ionic radii compared to Ti^{4+}.

The low-frequency band (v_2), observed between 400-450 cm^{-1}, corresponds to the bending vibrations of the Ti-O-Ti bonds within the TiO_6 octahedra. The v_2 band shifts similarly to the v_1 band with Gd^{3+} and Sm^{3+} doping, indicating consistent effects on both stretching and bending vibrations. The presence of these bands confirms the formation of a single-phase perovskite structure across all samples, consistent with the expected vibrational modes in such systems [17].

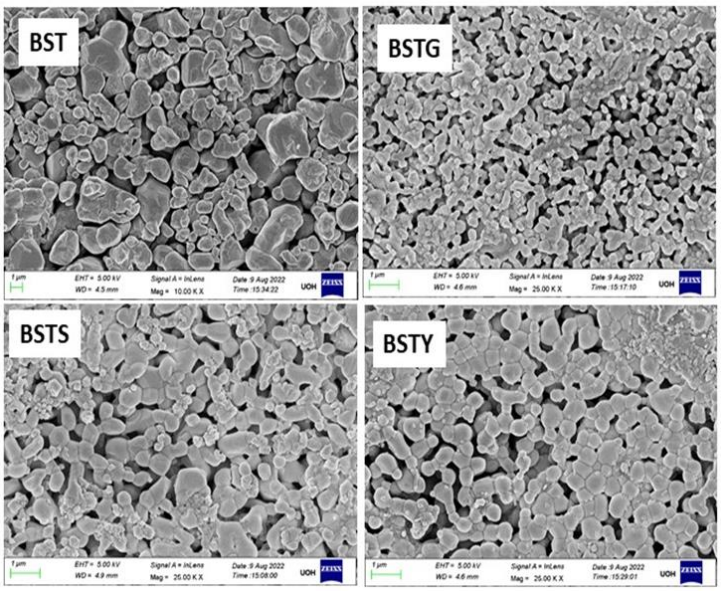

Figure 3. FESEM images of Ba(SrTi)O$_3$ and RE(Gd,SM.Y)-doped Ba(SrTi)O$_3$.

Figure 3 shows the FESEM images of BST and its doped variants (BSTG, BSTS, and BSTY), highlighting the microstructural changes due to rare earth element doping. The undoped BST sample exhibits uniformly distributed, highly crystalline submicron grains with noticeable porosity. Doping with Gd^{3+} in BSTG results in larger, more irregular grains with reduced porosity, indicating enhanced densification. Sm^{3+} doping in BSTS leads to elongated grains with clear boundaries and further reduced porosity. Y^{3+} doping in BSTY results in moderately sized grains with a compact structure and minimal porosity, reflecting improved packing and densification [18].

Figure 4 illustrates the Energy Dispersive X-ray (EDX) investigation of BST samples doped with Rare Earth elements (Gd, Sm, Y). The BST sample mostly consists of Ba, Ti, and Sr, with a small amount of O, as anticipated for $Ba_{0.8}Sr_{0.2}TiO_3$. The presence of prominent Gd peaks in the BSTG sample suggests that the doping process with Gd was effective. The BSTS analysis reveals distinct peaks of Sm, providing confirmation of Sm doping. BSTY has distinct peaks that correlate to the presence of Y, indicating Y doping. The continuous occurrence of Ba, Ti, and Sr in all samples confirms the fundamental composition, whereas the shifting peaks of rare earth elements emphasize the effectiveness of doping. The compositional details shown in this study are consistent with the anticipated outcomes of doping with Gd, Sm, and Y, as indicated by previous research.

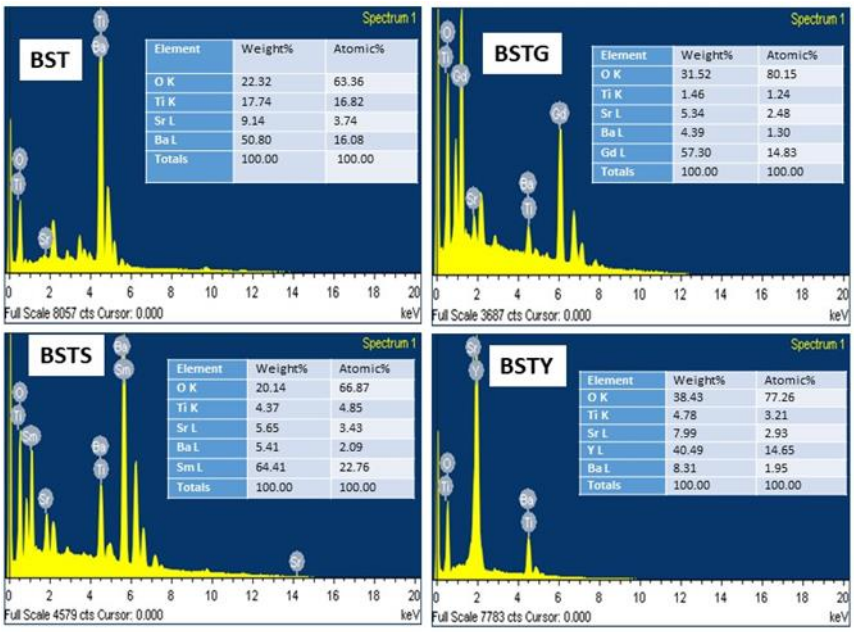

Figure 4. EDX Spectra of $Ba(SrTi)O_3$ and Re(Gd,Sm,Y)-doped $Ba(SrTi)O_3$.

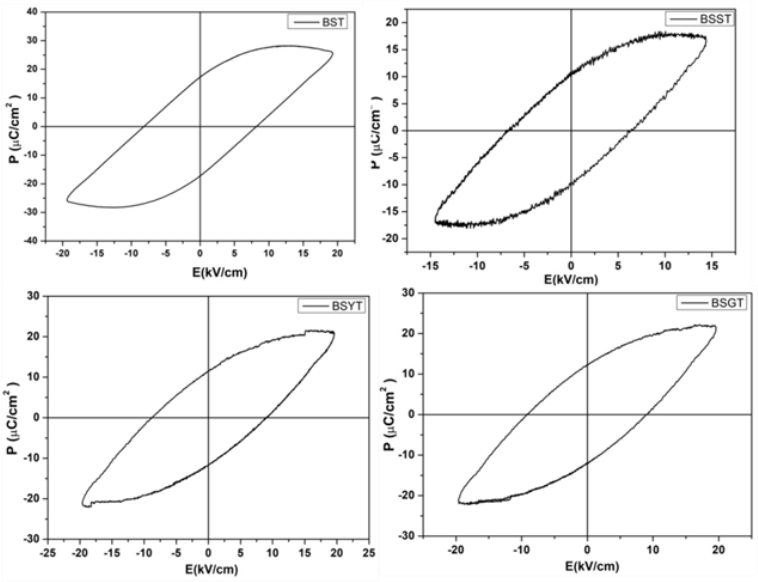

Figure 5. P-E hysteresis loops of BST, BSTG, BSTS, and BSTY ceramics at 20 kV/cm applied electric fields at room temperature.

Figure 5 shows the P-E hysteresis loops of BST and its doped variants (BSTG, BSTS, BSTY), illustrating their ferroelectric properties. Undoped BST exhibits strong ferroelectric behavior with high remanent and saturation polarization and a moderate coercive field. Doping with Gd^{3+} (BSTG) slightly reduces remanent polarization but increases coercive field, indicating enhanced stability. Sm^{3+} doping (BSTS) improves remanent and saturation polarization but at the cost of higher coercive force, while Y^{3+} doping (BSTY) maintains similar ferroelectric properties to undoped BST with minimal changes [19-21].

Table 2 Ferroelectric, Dielectric and Impedance data of prepared ceramics.

x	Psat (μC/cm²)	Pr (μC/cm²)	Ec (kV/cm)	(Ɛ′)	tan δ	Z’	Z”
BST	27.20	16.89	8.26	1720	3.25	30941	17713
BSTG	21.84	12.32	9.03	2316	4.19	43214	22334
BSTS	17.83	10.69	6.47	2798	6.22	49504	34353
BSTY	21.36	11.81	8.74	1237	2.53	20369	8362

It is clear form Table 2 the saturation polarization (Psat) and remanent polarization (Pr) are highest in undoped BST, indicating its superior ability to polarize and retain polarization. Sm-doped BST (BSTS) shows the lowest Psat and Pr, reflecting a reduction in polarization capacity. The coercive field (Ec) is highest in Gd-doped BST (BSTG), indicating the greatest resistance to depolarization and suggesting better stability, while Sm-doped BST (BSTS) has the lowest Ec, indicating easier depolarization. In summary, the introduction of rare earth elements (Gd, Sm, Y) into BST impacts its ferroelectric properties differently. Gd doping slightly decreases polarization but enhances stability, Sm doping significantly boosts polarization but increases coercive force, and Y doping maintains the strong ferroelectric characteristics of undoped BST with minimal impact. These findings highlight the varying effects of different dopants on BST's ferroelectric performance.

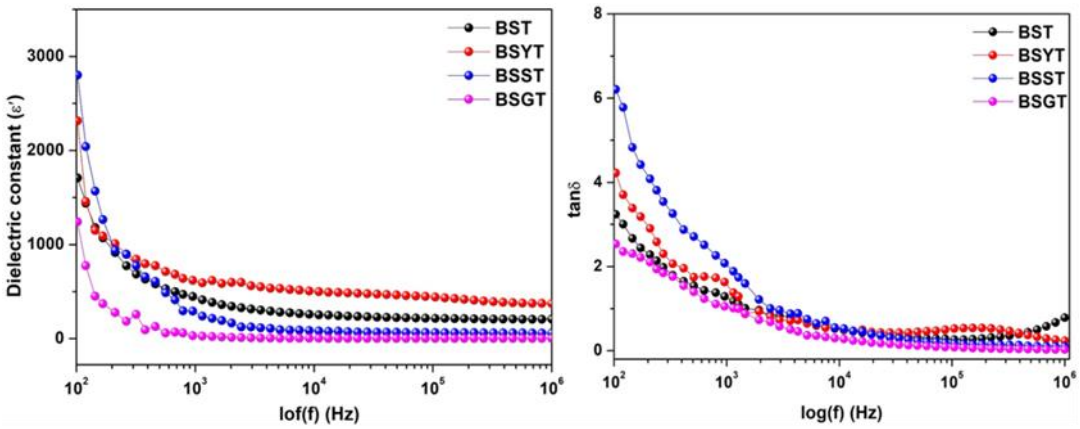

Figure 6. Dielectric constant and loss tangent of BST and Rare earth doped BST.

Figure 6 illustrates the dielectric constant spectra of BST and its rare earth-doped variants (BSTG, BSTS, BSTY) across various frequencies. At lower frequencies (~10^2 Hz), all samples show high dielectric constants, which decrease as frequency increases. This behavior, typical of ferroelectric materials, is due to space charge polarization, dipolar polarization, and interfacial polarization. Initially, BSTY and BST exhibit the highest dielectric constants, indicating better initial polarizability. As frequency rises, all samples' dielectric constants decrease, with BSTS showing the most significant reduction. At higher frequencies, doped samples have lower dielectric constants than undoped BST, suggesting that dopants restrict the dielectric response [22, 24]. Table 2 summarizes the dielectric constants, showing significant enhancement in BSTY and BSTS compared to undoped BST, likely due to reduced defects and better dipole alignment. Conversely, Gadolinium doping (BSTG) reduces the dielectric constant, possibly due to increased defects or hindered polarization. Dielectric loss is higher at lower frequencies due to enhanced dipole relaxation. Rare earth doping reduces these losses, with tan δ decreasing as frequency increases, reflecting reduced energy dissipation. Table 3.4 shows the tan δ values, with BSTS (doped with Sm) having the highest and BSGT (doped with Gd) the lowest [25].

Figure 7 shows the impedance spectra for both undoped and doped BST ceramics. The real part of impedance (Re(Z)) in undoped BST rises significantly at low frequencies, indicating high resistance. As frequency increases, Re(Z) decreases, a typical characteristic of dielectric materials due to reduced polarization effects. Among the doped samples, BSTY (Y-doped) shows the lowest Re(Z) at low frequencies, indicating enhanced conductivity [26-28]. In contrast, BSTS (Sm-doped) has the highest Re(Z), reflecting increased resistance due to Sm doping. The Re(Z) for BSTG (Gd-doped) falls between BSTY and BSTS, all showing a general decline in Re(Z) with increasing frequency.

The imaginary part of impedance (Im(Z)) is high at low frequencies in undoped BST, indicating strong capacitive effects, which decrease as frequency increases. Y-doping in BSTY reduces Im(Z) at low frequencies, indicating decreased capacitive effects. Sm-doped BSTS exhibits higher Im(Z) at low frequencies, suggesting enhanced capacitive characteristics, which significantly drop as frequency increases. BSTG shows intermediate

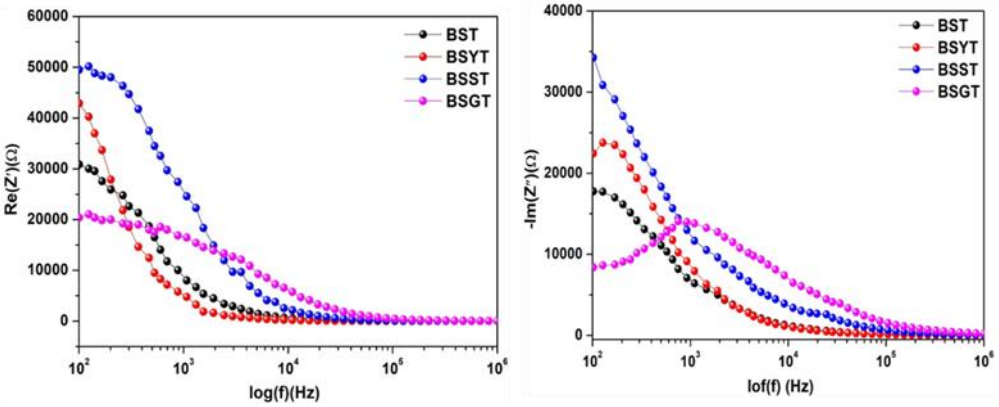

Figure 7. Real and Imaginary Part of Impedance Spectra of Ba(SrTi)O_3 and Re(Gd,Sm,Y)-doped Ba(SrTi)O_3.

Im(Z) values, similar to BSTY and BSTS, with a decline as frequency increases.

Table 2 details the impedance values for BST, BSTS, BSTG, and BSTY, including both real (Z') and imaginary (Z") components. The undoped BST sample has a Z' of 30,941 Ω and a Z" of 17,713 Ω. The Y-doped BSTY sample shows an increase in both Z' (43,214 Ω) and Z" (22,334 Ω). Sm-doped BSTS exhibits the highest impedance values, with Z' at 49,504 Ω and Z" at 34,353 Ω, indicating increased resistive and reactive components, which enhance dielectric properties. In contrast, Gd-doped BSTG has the lowest impedance values (Z' = 20,369 Ω, Z" = 8,362 Ω), suggesting better conductivity and reduced energy dissipation, making it suitable for applications requiring lower impedance.

IV. Conclusions

The Rare Earth (Gd, Sm, Y) doped $Ba_{0.8}Sr_{0.2}TiO_3$ (BST) ceramics have been prepared successfully using a solid-state mixing approach. Incorporating rare earth dopants (Gd, Sm, Y) into $Ba_{0.8}Sr_{0.2}TiO_3$ (BST) significantly alters its structural, dielectric, and impedance properties. X-ray diffraction confirms perovskite structure formation with lattice distortions. FTIR analysis reveals changes in Ti-O vibrational modes, while FESEM shows uniform microstructures with reduced grain sizes in doped samples. Dielectric studies indicate Sm and Y enhance dielectric constants and losses, while Gd reduces them, improving conductivity. Impedance spectroscopy highlights Sm and Y increase impedance, whereas Gd enhances overall conductivity, suggesting tunability for electronic applications.

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