



STRUCTURAL AND FERROELECTRIC PROPERTIES IN $(\text{Sr}_{1-1.5x}\text{Ce}_x\text{Ti}_{1-2/3y}\text{Mg}_y\text{O}_3)$ SOLID SOLUTION

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ABSTRACT

The lattice structure, grain structure and temperature dependent dielectric $\text{Sr}_{(1-x)}\text{Ce}_x\text{Ti}_{(1-2/3y)}\text{Mg}_y\text{O}_3$ ($x = 0.05, 0.10, 0.15$ and $y = 0.05$ sintered in 5% H_2 and 95% N_2 atmosphere) ceramic samples were successfully clarified. The (Sr, Ce, Ti, Mg) O_3 show a structure phase transition at SCTM1 from cubic to tetragonal. It is also obvious, that a small A/B-sites doping promoted the grain growth with relaxor ferroelectric like nature. The $\epsilon'-T$ plot, hysteresis loop along with intrinsic ferroelectricity (PUND) clarify the relaxor ferroelectric nature of the ceramics samples. Further, in the temperature span 50 °C and 200 °C, the ceramic samples showed a good frequency and temperature stability, which show its potential in energy storage devices.

Keywords: Strontium Titanate, Cerium Doping, Magnesium Doping, Relaxor Ferroelectric, Dielectric Properties, Energy Storage.

I. INTRODUCTION

In recent years, SrTiO_3 has received much attention due to the fact that minor perturbation can produce notable properties. Strontium titanate (SrTiO_3) is one of the most studied dielectric materials for capacitors and fifth generation (5G) communication system [1]. As a result of these outstanding material properties, STO is a feasible option for high energy storage dielectric material used in solid state capacitors, micro wave frequency resonator, semiconductor thermistor, sensors, electrode materials, etc. [2-4]. Strontium titanate is basically paraelectric in nature with simple lattice structure and high permittivity [5, 6]. However, the quantum fluctuation which stabilizing the paraelectric state is a challenging topic and remains an open and engaging question [7-9]. Hence, a ferroelectric state (FS) may be induced under specific conditions like A/B-site doping and Sr/Ti stoichiometry variations [10]. Further, due to the large ionic polarizability, the STO is very sensitive to the doping [11]. The cubic phase is experimentally observed at high temperature, while the TiO_6 -octahedral rotating phase is observed at a temperature lower than 105K in $\text{SrTi}^{16}\text{O}_3$ (ST-16) and 110K in $\text{SrTi}^{18}\text{O}_3$ (ST-18). The characterization of the low-temperature order parameters of the perovskites is still in progress. In addition, based on the fact that there is no ferroelectric phase (FP) in ST-16 perovskite, only in ST-18 below 23K is observed. According to report, $\text{SrTi}^{16}\text{O}_3$ perovskite is incipient ferroelectric ceramic even at temperatures close to 0K in which lowest fluctuation and the tunneling action of the atomic nuclei prevent the appearance of Ferroelectric Phase. [12,13]. Therefore, partial substitution of Sr-site (A-site) or Ti-site (B-site) in STO can change the origin and temperature of the ferroelectric-paraelectric (FPT) as reported [14-16]. Due to its large dielectric constant (Table I) and polarizability, SrTiO_3 perovskite is extremely sensitive to doping and other effects [17, 18].



TABLE I
PHYSICAL PROPERTIES

S. No.	Physical Property	Value
1	Lattice parameter at room temperature (RT)	0.3905 nm
2	Density	5.12 g/cm ³
3	Melting point	2080°C
4	Molar mass	183.49 g/mol
5	Dielectric constant ϵ_r	300
6	Solubility in water	Insoluble

Table I. Physical properties of SrTiO₃ ceramics at room temperature [19].

At room temperature, SrTiO₃ has a cubic structure with a lattice parameter of 0.3905nm(space group Pm-3m) and a density of $\rho = 5.12\text{g/cm}^3$.

A. Electric polarization from paraelectric cubic state to ferroelectric tetragonal and orthorhombic state

Fig. 1, indicates the crystal structure. [8]. Therefore, SrTiO₃ has the ability of mixed ionic and covalent bonding. Due to chemical bonding, it has a unique structure, making it a model in electronic materials. The Goldschmidt criterion can predict the degree of crystallographic distortion of most perovskites that accommodate cations of different sizes. Goldschmidt using the knowledge of crystal geometry defined a tolerance factor and/or structure stability factor (t) of the perovskite ABX₃ is expressed as

$$t = \frac{r_A + r_0}{\sqrt{2}(r_B - r_0)}$$

The ideal cubic perovskite SrTiO₃ has $t = 1$, $r_{A^{2+}} = 1.44\text{\AA}$, $r_{B^{4+}} = 0.605\text{\AA}$, and $r_{O^{2-}} = 1.42\text{\AA}$.

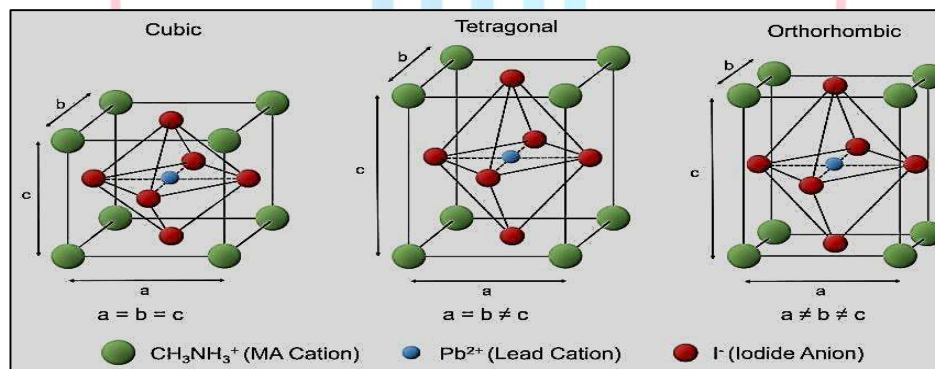


Figure 1. Electric polarization from paraelectric cubic state to ferroelectric tetragonal and orthorhombic state.

Fig. 1. Crystal structure of SrTiO₃. [8].

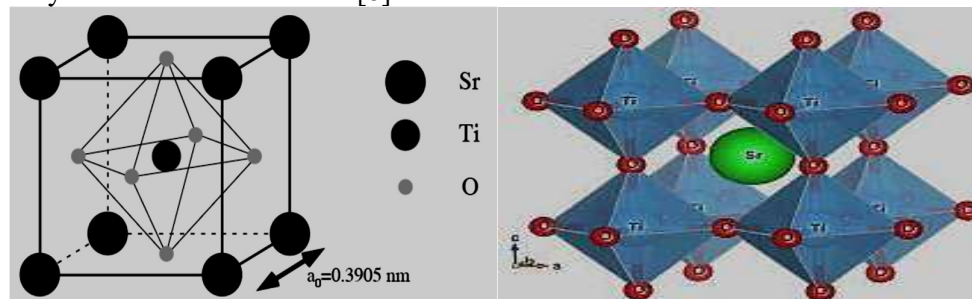


Figure 1. Atomic structure of SrTiO₃ at RT. The sizes of the spheres representing the atoms are arbitrary and are not related to atomic radii [8].

B. Crystal Structure



The simplest and highest symmetrical phase of SrTiO_3 is the cubic phase, with a space group of pm-3m , a lattice parameter of 3.905 Å, and a density of $\rho = 5.12 \text{ g/cm}^3$ at RT [20, 21]. The crystal structure is shown in Fig. 3. The Ti^{4+} ion is six folded by the O^{2-} ions, and each Sr^{2+} ion is surrounded by four TiO_6 octahedrons. Therefore, each Sr^{2+} ion is surrounded by 12 O^{2-} ions. Inside the TiO_6 octahedron, the hybridization of the O-2p state and the Ti-3d state leads to significant covalent bonding [22], and Sr^{2+} and O^{2-} ions show ionic bonding characteristics. Therefore, SrTiO_3 has mixed ionic-covalent bonding characteristics. This type and nature of chemical bonds results in a distinctive structure, making it a model electronic material. If the temperature decreases or if foreign cations/dopants are introduced into the crystal lattice, a change from cubic to lower symmetry will occur. SrTiO_3 with cubic structure at room temperature has more than three phase transitions when cooled. Similarly, STO bulk crystals are considered; tetragonal between 110 K - 65 K ($a = b \neq c$), due to the opposite rotation of the adjacent oxygen octahedrons, the orthorhombic phase is in the range of 55 K-35 K, and may be rhombohedral below 10 K, as XRD studies suggests [23,24]. In fact, there is no experimental proof to sure which structure SrTiO_3 shows below 10 K. Recently, a PAC study on this subject assure that a single low-symmetry phase is formed at 10 K, which is not specified by axial symmetry [25].

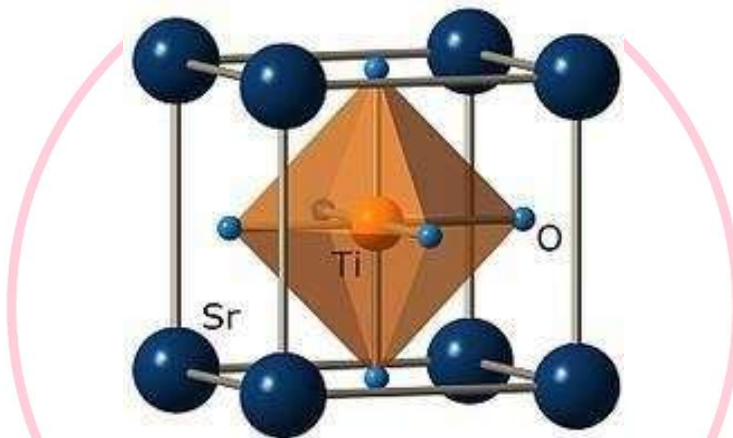


Figure 2. Schematic diagram of the crystal structure of perovskite-type SrTiO_3 at room temperature.

Fig. 3. Schematic diagram of the crystal structure of perovskite-type SrTiO_3 at room temperature.

C. Applications

SrTiO_3 has gained much attention from scientists due to its application in various applications such as energy storage, high charge storage capacity, good insulation properties, chemical stability [26], fuel cells, ultra-low temperature scanning microscopes, semiconductor ceramics, pyroelectric far-infrared detectors and sensors due to its extraordinary characteristics. One of the main applications of SrTiO_3 is a hydrogen fuel cell produced through a photocatalytic process (generation of electricity by combining hydrogen and oxygen atoms) [27]. SrTiO_3 is not only used as a high dielectric constant insulator, but also as a wide bandgap semiconductor with a bandgap of 3.2 eV, attracting much attention in the field of oxide electronics [28].

II. LITERATURE REVIEW

This chapter reviews dielectric materials, dielectric loss and strength, polarization mechanisms, ferroelectric and relaxor behavior, and the structural, microstructural, and dielectric properties of doped SrTiO_3 (STO).

A. Fundamentals of Dielectrics

Dielectrics are widely used in electronic and electrical devices [29-30]. Their performance is described by complex permittivity (ϵ^*). For high-field applications, such as insulation, materials should have high breakdown strength (E_b) and low dielectric loss.

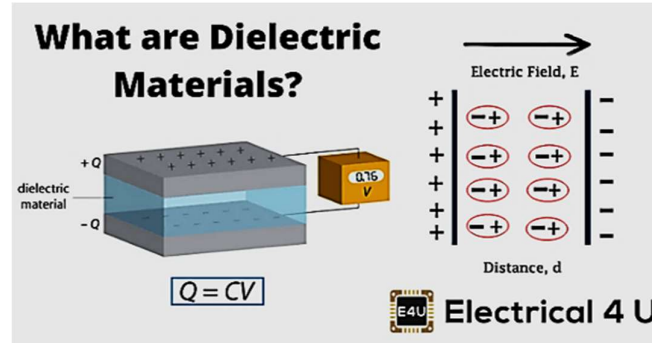


Fig. 4. Fundamentals of Dielectrics.

A dielectric is a type of electrical insulator that may respond to external stimulation, electrical field, E , with electrical polarization (P), which reflects the induced dipole moment (P) as [30, 31].

$$P = \vec{a} \sum_{i=1}^N \frac{\vec{e} \vec{p} \vec{\theta}}{\vec{\theta} \vec{d} \vec{v}_{\vec{\theta}}}$$

The permittivity is define as

$$D = e_o E + P$$

$$D = e_m E = e_r e_o E$$

where D is electric displacement, ϵ_0 is the permittivity of free space ($8.8542 \times 10^{-12} \text{ C/Jm}$), ϵ_m is the material permittivity, and ϵ is relative permittivity ($\epsilon_r = \epsilon_m / \epsilon_0 = \epsilon' - j\epsilon''$). Combining equations (1-2) and (1-3) gives [32]:

$$P = (r \cdot 1) \Omega_0 \Omega_E^0$$

B. Dielectric Constant Or Relative Permittivity (ϵ_r)

The relative permittivity or dielectric constant is the division of the permittivity ϵ' of dielectric medium by the permittivity of free space ϵ_0 is relative permittivity.

$$\epsilon_r = \frac{\epsilon_m}{\epsilon_0}$$

In terms of capacitance of capacitors, it is the ratio of capacitance of a dielectric embedded capacitor to the airfilled capacitance of capacitor.

$$\epsilon_r = C_r(\text{dielectric medium}) / C_r(\text{vacuum})$$

A substance with a high dielectric constant is particularly insulating. This property of a material determines the amount of energy that a capacitor can store compared to vacuum [39,40]. The schematic dependence of ϵ'' , ϵ' and $\tan \delta$ on the angular frequency, ω based on Debye equation is shown in Fig. 5. At the relaxation frequency, the imaginary part of the permittivity reaches its maximum, while the dielectric loss reaches its maximum at a frequency as given below,

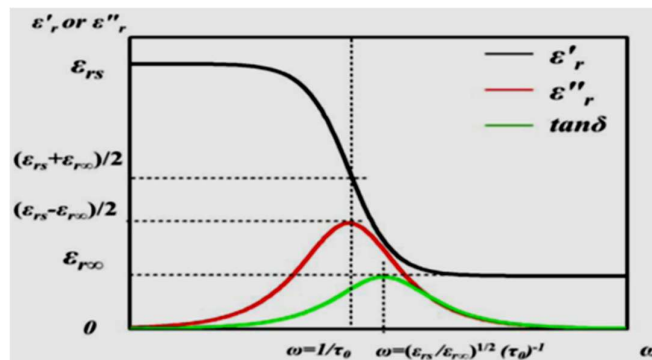


Fig. 5. Frequency dependence of ϵ' , ϵ'' and $\tan \delta$ calculated using Debye equation.



It should be mentioned that the Debye equation describes the dielectric response of the simplest case of a relaxation process. For a real material, the frequency dependence of the permittivity is usually much more complicated. In these cases, the concept of multiple relaxation times is used [41].

C. Dielectric Strength

Dielectrics are highly resistive, non-conducting materials used in electronic systems. Their permittivity (ϵ) and dissipation factor ($\tan \delta$) are important for circuit performance. Dielectric materials commonly have relative permittivity from 15 to several thousand, whereas insulators generally have higher resistivity and relative permittivity below 15. A good dielectric is also an insulator, but not every insulator is a good dielectric. Since dielectric power loss increases with frequency, low-loss materials are essential in high-frequency and high-power applications, where heating can cause breakdown. Thus, high relative permittivity combined with low loss is desirable for energy-storage capacitors [42].

D. Dielectric Loss ($\tan \delta$)

Dielectric loss is the energy dissipated as heat when a material is exposed to a varying electric field. In systems such as free space, transmission lines, microstrip lines and waveguides, dielectrics support conductors or separate regions while allowing electromagnetic energy to propagate. Maxwell's equations describe the electric and magnetic fields of waves subject to the geometry and boundary conditions of the system [43].

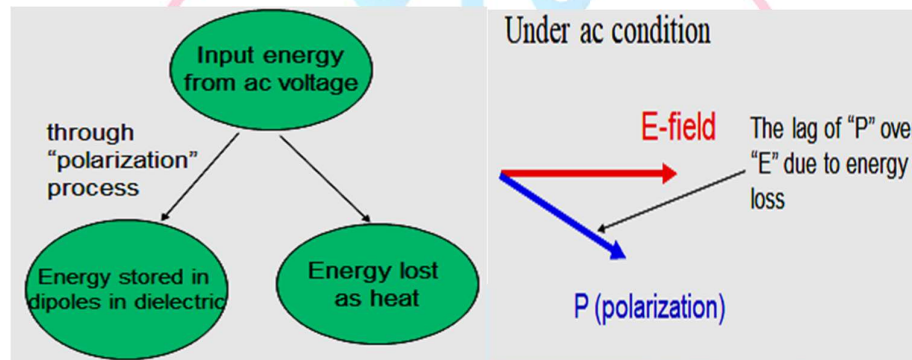


Figure 3. Diagram shows the phenomenon of dielectric loss due to dissipation of energy.

Fig. 6. Diagram shows the phenomenon of dielectric loss due to dissipation of energy.

E. Mechanism of Polarization

Physically, polarization is induced when there is electric field applied onto the materials. The electrons are uniformly dispersed around the nuclei if an electric field is not present.

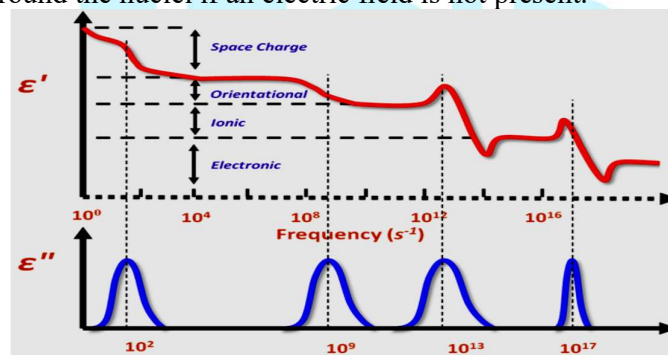


Figure 4. Frequency dependence of the permittivity for a dielectric with four different types of dielectric responses: (a) real part and (b) imaginary part.

Fig. 7. Frequency dependence of the permittivity for a dielectric with four different types of dielectric responses: (a) real part and (b) imaginary part.

The electron cloud is ejected from the nuclei in the direction opposing the applied electric field when an electric field is applied. As a result, positive and negative charges are separated, and molecules are separated [33].



F. Types of Polarization

1) Interfacial (Space Charge) Polarization. Space-charge polarization occurs when charges accumulate at grain surfaces, grain boundaries in polycrystalline materials, or electrodes (Fig. 8). Charge carriers may become trapped at grain boundaries. This mechanism is most important at low frequencies, and its contribution decreases as frequency rises; beyond 10^3 Hz, it cannot effectively follow the applied field [35].

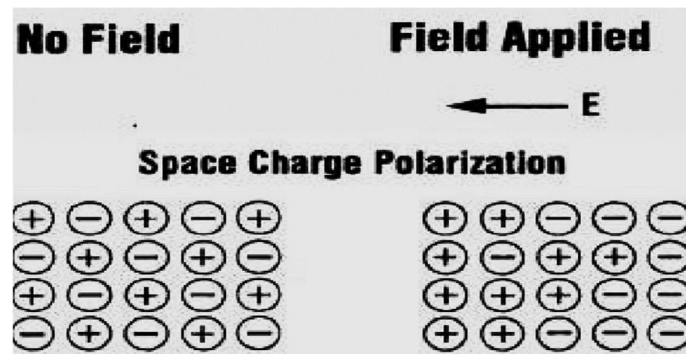


Figure 5. Space charge polarization

2) Dipolar or Orientation Polarization. A small change in orientations of dipole moment due to the applied electric field is called dipolar polarization; dipole moment in molecules of dipolar materials like H_2O , Orientation polarization is typically detected at frequency of 10^4 Hz.

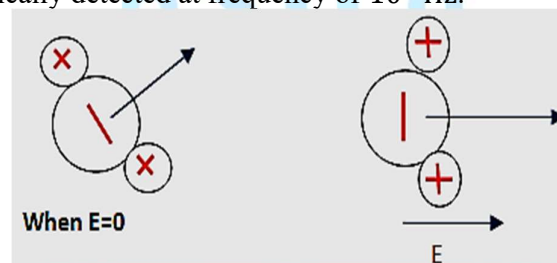


Figure 6 Dipolar polarization

During this time, it loses its ability to respond to an electric field. at the highest frequencies i.e. beyond 10^{10} Hz. However, by applying the electric field E , the dipoles arrange themselves in the field's direction, resulting in a net non-zero dipole moment and polarization. [34].

3) Ionic Polarization. By applying an electric field polarization produced in ionic material due to the relative displacement of cation (Positive charge) and an anion (Negative charge) in Fig. 10. It loses its response to applied electric field at frequency of 10^{10} Hz[15]. This kind of polarization is commonly seen in ionic crystals like NaCl and LiBr.

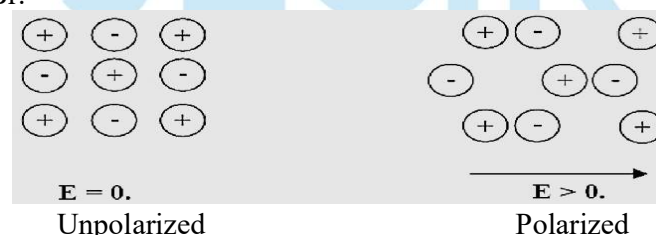


Figure 7. Ionic polarization (A.J Molson, 2003) [34].

This polarization is commonly found at frequency of 10^{12} Hz. Therefore, its response time is fast (about 10-12 s) and is almost independent of temperature [35].

4) Electronic Polarization or Atomic Polarization. This type of polarization is common in covalent bond. The electron cloud associated with the covalent bond shifts away from the positive nuclei. By applying an electric field to a sample, it generates a net dipole moment as well as polarization. Because only the movement of electrons is involved, it is referred to as instantaneous polarization, and its response time is the



fastest (10-16 s). Polarization is typically observed beyond the frequency of the visible light $\sim 10^{15}$ Hz. Usually no frequency dependency behavior is observed for this type of polarization because of the extremely fast response of the electron cloud to an applied electric field [34].

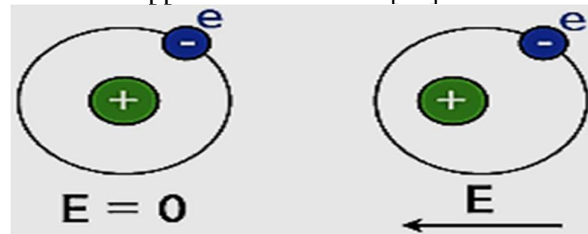


Figure 8. Electronic Polarization [34].

G. Ferroelectric Materials. Ferroelectrics exhibit spontaneous polarization without an applied field, and the polarization direction can be reversed by an external field. All ferroelectric materials are pyroelectric, although not all pyroelectric materials are ferroelectric (B Jaffe, 1971). Ferroelectricity was identified in Rochelle salt in 1921 and in BaTiO_3 in 1940; spontaneous polarization in BaTiO_3 was demonstrated in 1945 (Gene H, 1999).

Ferroelectrics generally have high relative permittivity. As temperature rises, the stability of polar and non-polar states changes, and the material may transition to a paraelectric state at the Curie-point temperature. The Curie-Weiss relationship for the dielectric constant is: $\epsilon_r - 1 = \frac{C}{T} - TC$

Here, C is the Curie constant, typically of the order of 10^3 to 10^5 . The Curie temperature is obtained by extrapolation, whereas the Curie-point temperature marks the actual transition from ferroelectric to paraelectric behavior. In second-order transitions, lattice parameters, dielectric constant and polarization vary continuously, apart from slope or peak discontinuities; in first-order transitions, these properties change discontinuously. A true ferroelectric is characterized by a dielectric-constant peak at the Curie temperature, a dielectric hysteresis loop, domain structure and finite spontaneous polarization.

H. Crystal Structure Properties of SrTiO_3 Based Perovskite

1) Structure of A-site Doped SrTiO_3 Perovskite. Room-temperature XRD patterns of A-site-doped SrTiO_3 ceramics, including $\text{Sr}(1-1.5x)\text{AxTiO}_3$ and $\text{Sr}(1-x)\text{AxTiO}_3$ ($x = \text{Ce}$ and Gd , $0.0 \leq x \leq 0.4$), indicate a single-phase solid solution without secondary phases (Fig. 12). Ce-doped samples show doublet and triplet features around the (321) and (200) peaks, suggesting deviation from cubic symmetry.

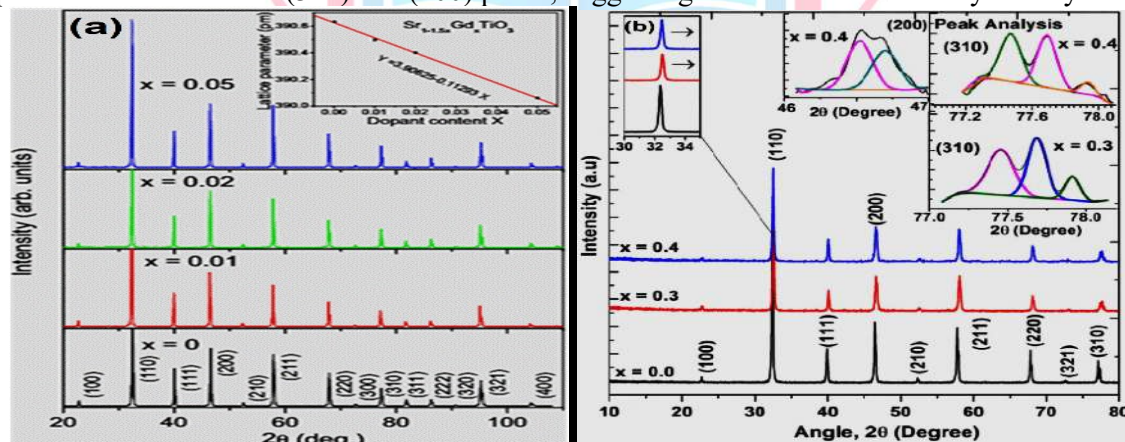
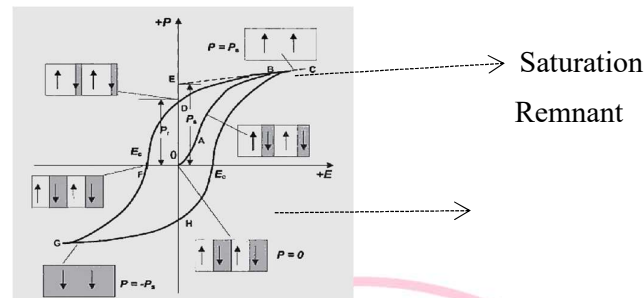




Figure 9. (a) Room temperature X-ray diffraction pattern for $\text{Sr}_{1-1.5x}\text{A}_x\text{TiO}_3$ and $\text{Sr}_{(1-x)}\text{A}_x\text{TiO}_3$ ($\text{A}_x = \text{Gd}$ and Ce for $0.0 \leq x \leq 0.4$) ceramics. (a, b) shows the shifting of the main peak towards higher angle with Gd and Ce content.

Figure 10. Ferroelectric Hysteresis loop



2) Properties of Ferroelectric Hysteresis Loop. Ferroelectric ceramics commonly have twinned domains because they can have lower free energy than a single-domain structure. Ferroelectricity is identified from a polarization-versus-electric-field hysteresis loop; its area represents energy loss, which may be reduced at low frequency ($f = 60 \text{ Hz}$). Other indicators include polar and domain structures, spontaneous polarization, high dielectric constant, and reversible piezoelectric and pyroelectric effects after poling. Applications include capacitors, ultrasonic transducers and motors, pyroelectric security sensors, and electro-optical light valves.

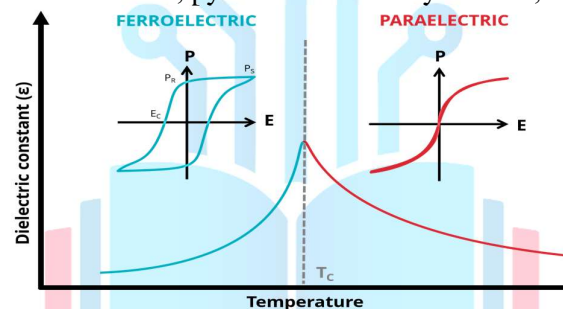


Figure 11. A transition of materials from ferroelectric to paraelectric state

3) Paraelectric Materials. Materials with intermediate properties between ferroelectric and anti-ferroelectric states are called paraelectric materials. The domains in such state of materials are haphazard and the net dipole moment is zero. It basically describes the phases that are neither ferroelectric nor anti-ferroelectric. Piezoelectric materials become paraelectric or cubic above Curie temperature (Zimbaro, Philip G., et al).

4) Relaxer-Ferroelectric Materials. In normal ferroelectrics, the temperature of maximum real permittivity (T_m) generally corresponds to the ferroelectric-paraelectric transition temperature (T_c) [44,45]. Relaxor ferroelectrics instead show a broad dielectric maximum that shifts with frequency, weak or absent macroscopic polarization, and optical anisotropy below the permittivity-peak temperature (Lu and Calvarin, 1995). Diffuse phase transitions may occur near the morphotropic phase boundary (MPB) in piezoelectric materials (G. Smolensky, 1984). Unlike the sharp peak and well-defined transition of normal ferroelectrics, relaxors show broad, frequency-dependent maxima (Kreisel et al., 2002). Many relaxors are lead-based perovskites, including $\text{Pb}(\text{Mg}_{10}\text{Nb}_9\text{Ta}_{10}\text{O}_{33})$, $\text{Pb}(\text{Sca}_{12}\text{Ta}_{12}\text{O}_{33})$ and $\text{Pb}(\text{LaZrTi})$. Disorder among ionic sites is considered a source of relaxor behavior (Huichun Yu, 2008); dielectric-maximum dispersion occurs with frequency below and above T_n (Bovtun, 2001). The three structural classes are solid solutions, dopant-induced atomic disorder, and complex perovskites containing ions of different valences. Disorder in the cation arrangement contributes to relaxor behavior (Chino, 1994 129).

The ionic radius of Ce^{3+} ($r_{\text{C, eVI}} \wedge (3+) = 1.34 \text{ \AA}$) is smaller than that of Sr^{2+} ($r_{\text{S, rXII}} \wedge (2+) = 1.44 \text{ \AA}$). Rietveld refinement shows that the lattice parameter of $\text{Sr}(1 - 1.5x)\text{A}_x\text{TiO}_3$ and



$\text{Sr}(1-x)\text{AxTiO}_3$ decreases as Gd or Ce concentration increases, likely because Sr^{2+} is replaced by Gd^{3+} and/or smaller-radius ions [46].

5) Structure of B-site Doped SrTiO_3 Perovskite. Room-temperature XRD analysis of B-site-doped $\text{SrTi}(1-x)\text{BxO}_3$ ($\text{B} = \text{Zr}$ and Nb ; $0.0 \leq x \leq 0.10$) shows that undoped and doped samples retain a cubic structure without secondary phases (PDF # 46-1235; space group pm-3m). As B-site content increases, diffraction peaks shift to lower angles, likely due to substitution at Ti sites.

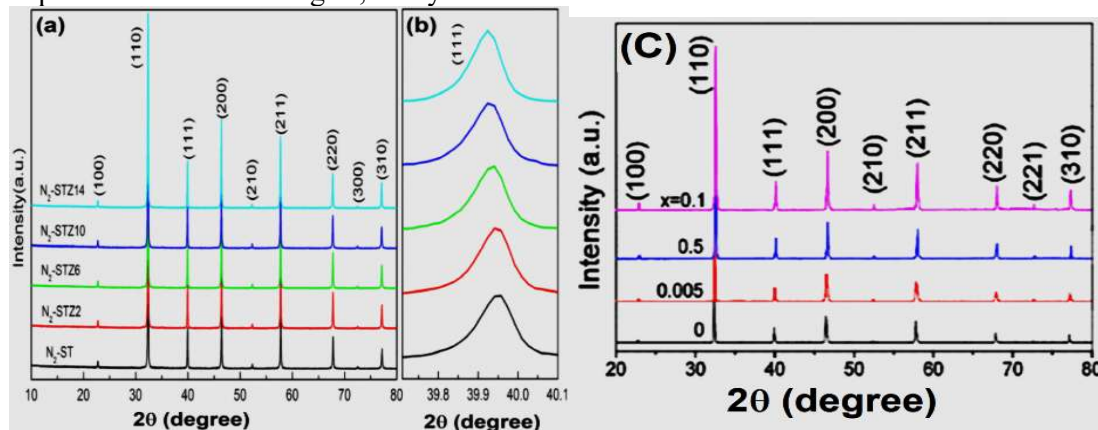


Figure 12. X-ray diffraction patterns of $\text{SrTiZr}_x\text{O}_3$ ceramics sintered in N_2 at 1500°C (a) 2h from 10° to 80° , (b) 2h from 39.7° to 40.1° (c) Sintered $\text{SrTi}_{1-x}\text{Nb}_x\text{O}_3$ ceramics with an inset whose parameters depend on the Mn content and its linear fit.

I. Microstructure Evaluations of Doped SrTiO_3 Ceramics

1) Surface Morphology of A-site doped SrTiO_3 . SEM images of pure and Gd-doped $\text{SrTiO}_3[\text{Sr}_{1-3x/2}\text{AxTiO}_3]$, $\text{Ax} = \text{Gd}, \text{Ce}$] show that pure STO grains are typically $2 - 5\mu\text{m}$. Increasing Gd content reduces grain size; this trend is also reported for Pr-doped STO ceramics [47]. For $\text{Sr}(1-1.5x)\text{CexTiO}_3$ ($x = 0.3, 0.4$), SEM indicates grain sizes of $13.6 \pm 0.2\mu\text{m}$ and $10.6 \pm 0.1\mu\text{m}$, respectively, with plate-shaped grains observed at $x = 0.4$.

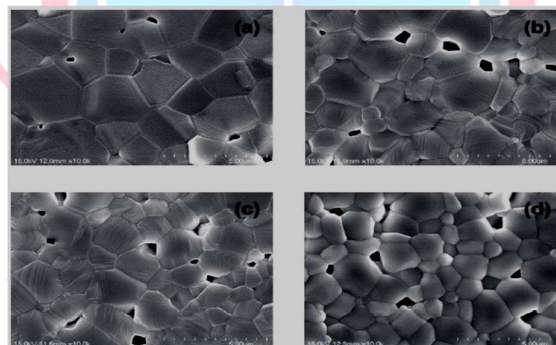


Figure 13. SEM images of (a) $\text{SGTO}_{x1/40}$, (b) $\text{SGTO}_{x1/40.01}$, (c) $\text{SGTO}_{x1/40.025}$, and (d) $\text{SGTO}_{x1/40.05}$ samples.

Ceria cations do not segregate on the grain boundary, but dissolves in the SrTiO_3 crystal lattice and promotes the grain growth. The observed trend of changes in the microstructure is related to the X-ray diffraction results. The grain size varies slightly from 3 to $6\mu\text{m}$. However, for Ce-doped $\text{SrTiO}_3[\text{Sr}_{(1-1.5x)}\text{CexTiO}_3]$ ($x \geq 0.5$, Figure 17). It can be seen that the sample presents a dense microstructure, and the grain size decreases slightly with the increase of Ce content.

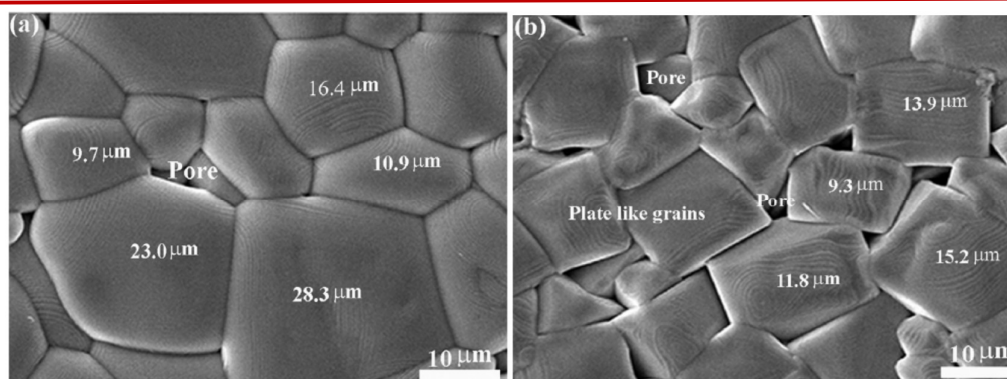


Figure 14. (a)–(b) Scanning electron microscope images of the thermally etched sample of $\text{Sr}_{1.3/2x}\text{Ce}_x\text{TiO}_3$ ($0.3 \leq x \leq 0.4$) solid solution with: (a) $x = 0.3$, and (b) $x = 0.4$.

2) Surface Morphology of B-site doped SrTiO_3 . For B-site doping, SEM micrographs of $\text{SrTiO}_3[\text{SrTi}_{(1-x)}\text{Zr}_x\text{O}_3]$ for $x = 2.5\mu\text{m}$ ceramics sintered at 1500°C are shown in Fig 18(a-e). $\text{DySr}_{1-x}\text{Ti}_{1-x/4}\text{O}_3$ ($x = 0.01 - 0.04$) is prepared by solid state reaction method. The SEM micrographs of all samples show almost dense microstructures, and show that as the Zr content increases, the crystal grains become smaller and more uniform. Figure 18(f) shows the Zr content of the $\text{SrTiZr}_x\text{O}_3$ ceramic grain size dependence.

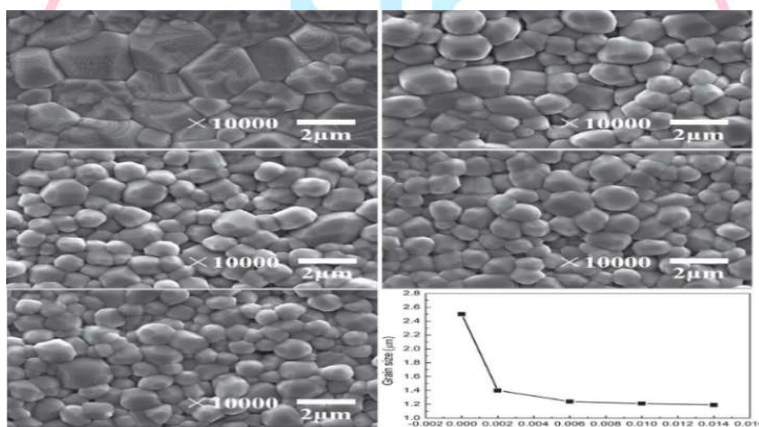


Figure 15. (a)–(f) SEM micrographs of $\text{SrTiZr}_x\text{O}_3$ ceramic sintered in N_2 at 1500°C : (a) $\text{N}_2\text{-ST}$, (b) $\text{N}_2\text{-STZ}_2$, (c) $\text{N}_2\text{-STZ}_6$, (d) $\text{N}_2\text{-STZ}_{10}$ and (e) $\text{N}_2\text{-STZ}_{14}$. (f) The dependence of the Zr content on the grain size of $\text{SrTiZr}_x\text{O}_3$ ceramics sintered in N_2 at 1500°C .

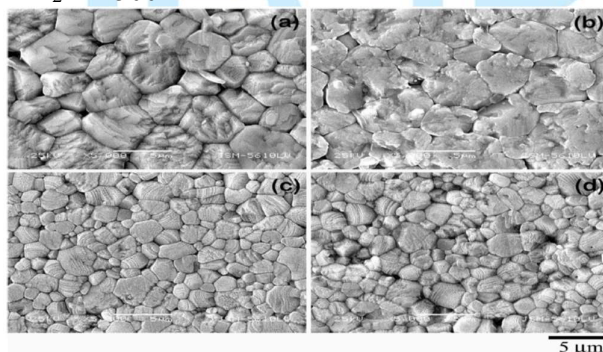


Figure 16. SEM image of $\text{N}_2\text{-ST}$

The grain size of $\text{N}_2\text{-ST}$ ceramics is about $2.5\mu\text{m}$. As the Zr content increases to $1.2\mu\text{m}$, the grain size of the sample with $1\text{mol}\%\text{ZrO}_2$ decreases. Once this value is reached, it remains unchanged. However, For $x \leq 0.02$, the grain size is determined to be $\sim 5\mu\text{m}$, and for $x \geq 0.03$ composition, the grain size is further



suppressed to $\sim 2\mu\text{m}$, as shown in Fig 19. This study shows that doping D_y ions in ceramics can inhibit grain growth comparable Inhibition of grain growth observed in other rare earth-doped fine ceramics.

J. Temperature Dependent Dielectric Property of Doped SrTiO_3

1) Dielectric Properties of A-site Doped SrTiO_3 . For high temperature ($T \geq 350^\circ\text{C}$), two dielectric variances can be identified in all samples, and their corresponding A-site tangent loss spectra [Fig. 20]. The low temperature variance (LT) is characterized by a broad peak of $\epsilon_r(T)$, which becomes smaller and shifts to a higher temperature (HT) as the application frequency increases. The LT area of the $\epsilon_r(T)$ peak shows frequency dependent behavior, while the HT area is almost independent of frequency. These behaviors are relatively similar to those of relaxation, so dielectric anomalies are characterized as relaxationlike anomalies. In addition, the composition of $x = 0.25$ seems to have an additional peak, this may be due to the uneven local distribution of Ce/Pr ions. Although the coexistence of the two peaks may be due to the contribution of a single dipole (see the enlarged image in Figure 20(c), the peak is around 150°C) and the formation of the dipole clusters (see Fig 20(c)), It peaks around $200 - 350^\circ\text{C}$. However, with the further addition of Ce/Pr content [$x \geq 0.15$, see Fig 20(a)-(d)], the interaction of dipoles becomes stronger (more dipole cluster are formed) Therefore, only the relaxation peak is about 200 to 350°C [48-50].

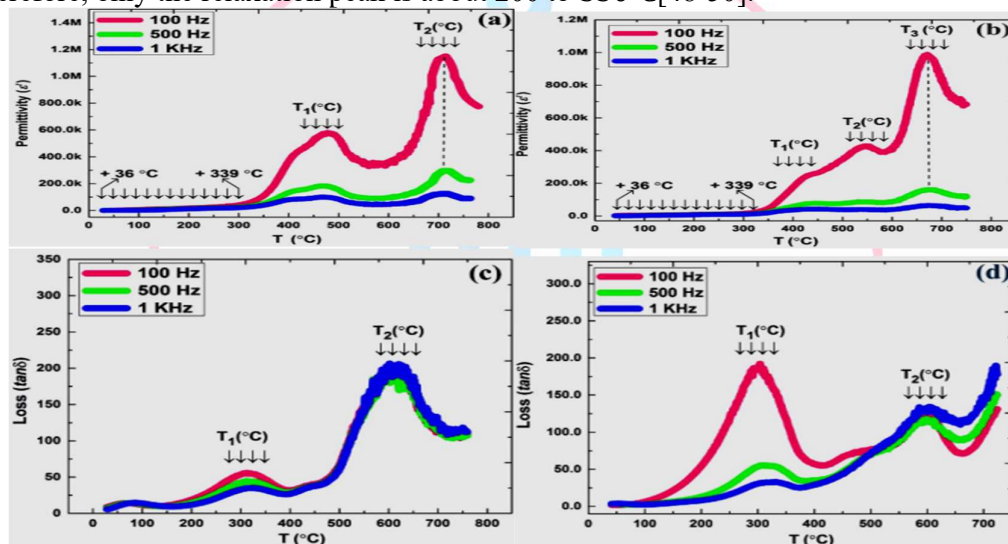


Figure 17. (a) – (d) For $\text{Sr}_{(1-1.5x)}\text{Ce}_x\text{TiO}_3$ solid solution, the temperature dependent permittivity (a) $x = 0.3$ and (b) $x = 0.4$, and the dielectric loss (c) $x = 0.3$ and (d) $x = 0.4$. The illustration shows a detailed view of the corresponding sample at low temperature.

In addition, for Fig 21, shows the temperature dependence of ϵ and $\tan \delta$ of pure and doped STO ceramics measured at the selected frequency. For pure STO, the dielectric constant increases with decreasing temperature and is stable at lower temperatures, while the two dielectric loss peaks at $\sim 40\text{K}$ (peak A) and $\sim 100\text{K}$ (peak B) are found at low temperature. These results are consistent with the results reported by STO single crystal [47].

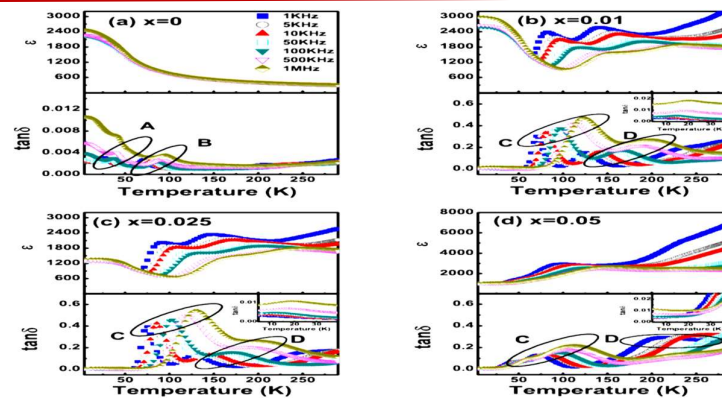


Figure 18. The temperature dependence dielectric constant and tangent loss of all sample at different frequencies (a) SGT0_x = 0, (b) SGT0_x = 0.01, (c) SGT0_x = 0.025, and (d) SGT0_x = 0.05.

This can be regarded as typical quantum paraelectric behavior. However, Gd-doped STO ceramics show some new dielectric diffusion peaks, whose amplitude and location depend on the Gd concentration. As shown in Figure 21 (b, c). SGT0_x = 0.01 and SGT0_x = 0.025 ceramics have two peaks in $\epsilon'(T)$ and $\tan\delta(T)$: the peak C in the temperature range of 70 ~ 150K and the peak D in the temperature range of 120 ~ 220K, respectively.

2) Dielectric Properties of B-site Doped SrTiO₃. Fig 22. shows the temperature dependence of the dielectric constant measured at different frequencies and the room temperature dielectric properties of SrTiZr_xO₃ ceramic sintered in N₂ measured at 1kHz. The permittivity-temperature curves of all samples showed similar changes, indicating that the permittivity decreased slowly and then increased rapidly as the temperature increased. However, the room temperature dielectric properties measured at 1kHz change significantly with the Zr doping concentration, as shown in Figure 22(f). Dielectric constant of N₂-ST ceramic is about 48,000, and the dielectric loss is about 0.005.

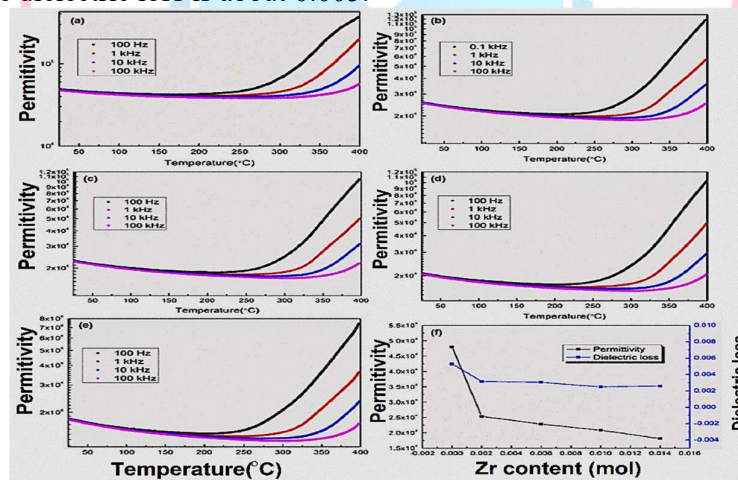


Figure 19. The temperature dependence of the dielectric constant of SrTiZr_xO₃ ceramic sintered in N₂ measured at different frequencies (a) N₂-ST, (b) N₂-STZ₂, (c) N₂-STZ₆, (d) N₂-STZ₁₀ and (e) N₂-STZ₁₄. (f) Room temperature dielectric properties of SrTiZr_xO₃ ceramic sintered in N₂ measured at 1 kHz.

When adding some ZrO₂, for the sample containing 1.4mol%ZrO₂, with the increase of Zr content, the dielectric constant drops to the minimum value of about 18,000. The dielectric loss also decreases with the addition of ZrO₂ and maintains a constant of about 0.003. In addition, Figure 23 shows the relative dielectric constant ϵ_r and dielectric loss $\tan\delta$ of D_yST ceramics, where $x = 0.02$ as a function of temperature from -60 to 200°C. It can be seen from Figure 23 that the dielectric dispersion is detected above 100°C. As the measurement frequency increases, the dielectric characteristics are strongly suppressed. This phenomenon



supports the existence of defective dipoles in DyST ceramics, and the relaxation of defective dipoles at elevated temperatures should contribute to the observed dielectric dispersion.

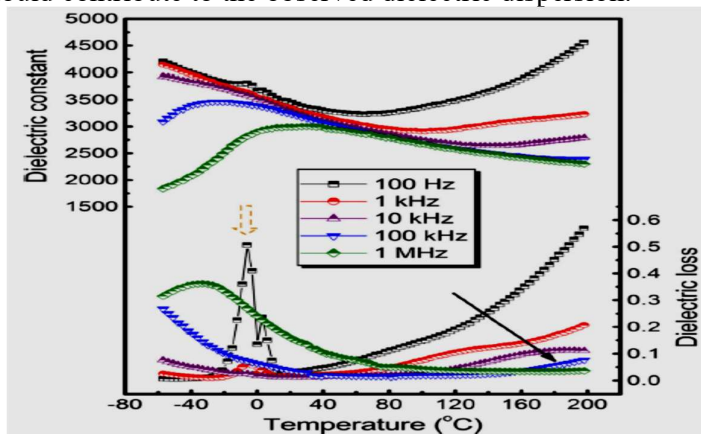


Figure 20. The relative dielectric constant and dielectric loss of DyST ceramics with $x=0.02$ as a function of temperature from -60 to 200°C .

III. METHODOLOGY

A. Ceramics Powder Processing

A process to produce small particles by mechanical process. Or, a process to prepare powders used in traditional ceramics production from natural raw materials. The process involves crushing and milling. Ceramic powder processing, as a field of materials processing, is undergoing rapid expansion.

B. Raw Powder Materials

A raw powder is a dry, bulk solid made up of many very fine particles that may flow freely when shaken or tilted. Powders are a type of granular material that comes in a variety of sizes and shapes. Although the terms powder and granular are sometimes used to distinguish individual classes of material. In particular, powders refer to those granular materials that have the finer grain sizes, and that therefore have a greater tendency to form clumps when flowing. Granular refers to the coarser granular materials that do not tend to form clumps excluding when wet.

C. Stoichiometric Mixing

Stoichiometry is the study of how to calculate the relative quantities of reactants and products in chemical reactions, as well as the methods for calculating those values. Stoichiometry can be used to calculate things like the number of things that can be made from a given number of reactants and the percent yields. A very fundamental understanding of the nature of the reaction is the interaction between products and reactants in a balanced chemical equation. This relation shows what materials are required for a reaction to proceed, for example, when oxygen and hydrogen combine to form water, two moles of water are produced when one mole of oxygen combines with two moles of hydrogen.

D. Instruments Used

In the laboratory, the following devices and equipment are used for material synthesis and characterization.

TABLE II
INSTRUMENTS AND DEVICES USED FOR PRODUCTION OF THE MATERIAL

Devices	Functions
Electronic balance	Weighing of powders
Ball mill	Milling (mixing)
Drying furnace	Drying of milled samples
200 size mesh (200 opening in one linear inch)	Sieving
Hydraulic press	Pressing powders into pellets
Chamber furnace	Calcination and sintering
Mortar	Crushing



Polisher	Polishing of pellets
Scanning Electron Microscope (SEM)	Microstructure analysis of the samples
X-ray Diffraction (XRD)	Phase and structure analysis of the sample
LCR Meter	Dielectric properties measurement

Table II. Instruments and devices used for production of the material.

E. Ball Milling

Traditional ball milling is a powder processing method that has been used for a long time. It is mostly used to minimize particle/granularity and to mix different materials. The stoichiometric starting powder was ball-milled in an ethanol along with ZrO_2 ball as grinding media in a poly-ethylene jar for 24h.

F. Calcination

Calcination is generally a one-step heating technique that decides if additional heat treatment (sintering) is needed or not. The $Sr_{(1-x)}Ce_xTi_{(1-2/3)}Mg_yO_3[(Sr, Ce)Ti,Mg)O_3, x = 0.05, 0.10, 0.15$ and $y = 0.05]$ ceramics [abbreviated as SCTM05 (for $x = 0.05$ and $y = 0.05$), SCTM10 (for $x = 0.1$ and $y = 0.05$) and SCTM15 (for $x = 0.15$ and $y = 0.05$ respectively)] will be synthesized using traditional solid-state techniques. The primary raw powders of high purity $SrCO_3$, TiO_2 , CeO_2 and MgO will be weighed according to the desire stoichiometric ratio. The raw powders will be ball milled for 24h. The mixture will be dried at $100^\circ C$ for 24h, sieved (300- μm nylon mesh) and finally calcined at $1200^\circ C$ for 24h.

G. Grinding or Addition of PVA Binder

The resultant calcined powders will be ball milled for 3h, dry at $100^\circ C$ for 24h, sieved (300- μm nylon mesh) and compact into bulk pellets using 8wt%PVA (polyvinyl alcohol) as the binder. Before sintering on ($1300^\circ C$ for 3h), the bulk samples will be heated at $600^\circ C$ for 2h (heating rate of $5^\circ C/min$) to burn out the binder.

H. Solid State Sintering

The bonding and classification of materials by heating below the material's melting point is known as solid-state sintering. During the sintering process, the free surface area of the compact is reduced. This is usually accompanied by an increase in density. In solid state, the sintering composition and firing temperature are such that no liquid is formed, all densification is achieved by reshaping the powder. This kind of reshaping is most commonly achieved through the solid-state diffusion of the atoms.

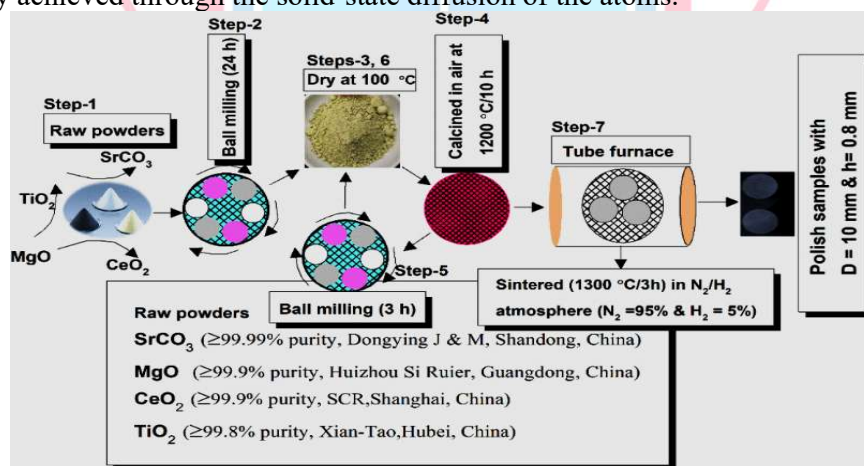


Figure 21. Models of possible synthesis reactions for polished and unpolished samples $Sr_{(1-x)}Ce_xTi_{(1-2/3)}Mg_yO_3$ ($x = 0.05, 0.10, 0.15$ and $y = 0.05$)

I. Material Characterization

X-ray diffraction was used to determine the phase analysis of the samples (XRD), then the microstructure study was examined through scanning electron microscope (SEM) and by impedance analyzer (LCR meter) the dielectric properties were studied.

1) Structure Analysis by X-Ray Diffraction (XRD). The crystal structure was examined at room temperature using X-ray diffraction (XRD) as shown in Fig 25. (Shimadzu-7000 with Cu $K\alpha$ doublet rays



(1.5406 Å, Japan). XRD is the elastic scattering of x-ray photon by periodic lattice. According to Bragg's law the X-ray is incident on the crystal surface, its angle of incidence, will reflect back with the same angle of scattering. [51].

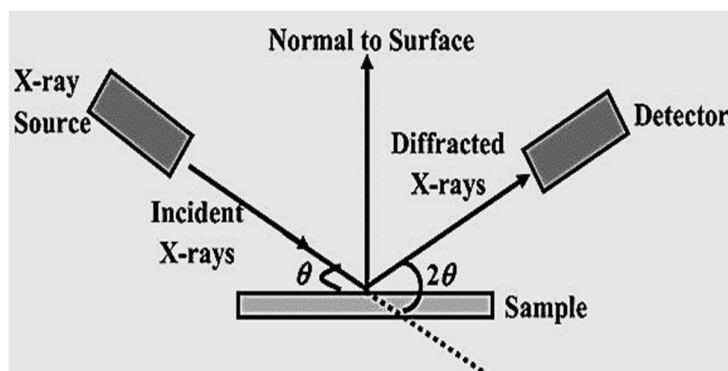


Figure 22. Schematic diagram of the XRD principle.

When X-rays were incident on the atoms, they make an electron cloud move just like an electromagnetic wave, as a result scattering of waves takes place from different atoms provide the reproducible patterns.

2) Microstructure Analysis. The microstructure of the samples was studied through scanning electron microscope (SEM) using electrons beam, sirion-200 field emission electron microscopy (Eindhoven, Netherlands) and nano SEM 450 field emission scanning electron microscope equipped with an energy dispersive X-ray spectroscopy (SEM-EDX, maps). The average size of the grains were measured through Image Pro plus (IPP) and Nano measurer 1.2 software [51,52].

3) Dielectric Analysis. For dielectric testing temperature dependent. The dielectric measurements of the samples were carried out in a temperature range from RT to 450°C as a function of frequency (at 500Hz, 1kHz, 5kHz). From the dielectric measurements, the dielectric loss ($\tan\delta$) and relative permittivity (ϵ_r) of the samples were also calculated. All these properties were measured using impedance analyzer (Agilent 4294A, Santa Clara, USA) and VDMS-2000 system (Partulab, Wuhan, China). The room temperature ferroelectric loop properties re-recorded using Sawyer-Tower circuit and RT66 B, Multiferroic devices (Radiant technologies, USA).

IV. RESULTS AND DISCUSSION

A. Structure Phase of (Sr, Ce, Ti, Mg)O₃ Ceramics

The room temperature X-ray diffraction patterns of pure and Ce/Mg-doped SrTiO₃ (for $x = 0.0, 0.05, 0.1, 0.15$ and $y = 0.5$) are shown in Fig. 1. The (Sr,Ce)Ti₂(Mg)₂O₇ compounds show cubic lattice structures with space group Pm-3m (PDF # 86-0176) for sample SCTM01, respectively. However, for SCTM15 and SCTM02 samples the prepared compound shows tetragonal symmetry with space group Pm-3m (PDF # 86-0176). Further, the shift in the [(110), $2\theta = 30^\circ$ to 35°], shows the incorporation of Ce/Mg into the ST lattice.

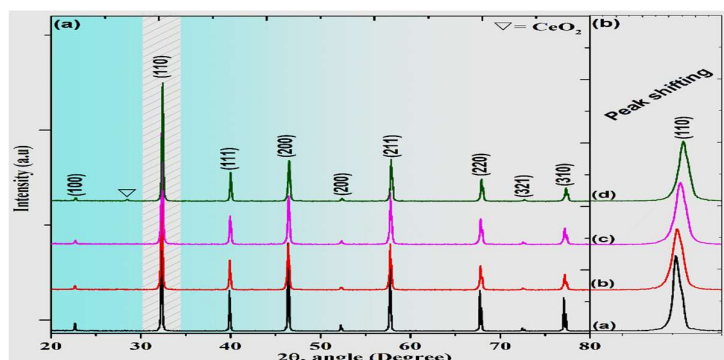




Figure 26. (a-b) Room temperature composition dependent X-ray diffraction of (Sr,Ce,Ti,Mg)O₃ (b) indicates the peak shifting of the (110) peaks with increasing the dopant concentration.

Fig. 26 shows that the existence of peaks splitting which further confirm the tetragonal nature of the samples SCTM15 and SCTM2 respectively. Besides, this to further confirm the existence of the tetragonal symmetry, Rietveld refinement was done on the SCTM15 sample. In comparison to the cubic structure symmetry [cubic space group (Pm-3m) and $\chi^2 = 5.24\%$], better fitting results were obtained for tetragonal symmetry [T-phase, space group (P4mmm) and $\chi^2 = 4.07\%$].

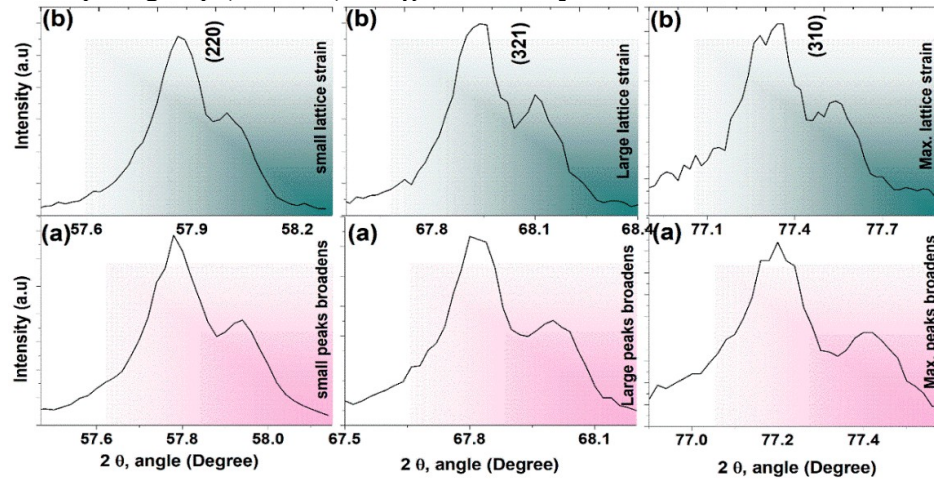


Figure 27 (a-b) X-ray diffraction peaks doublet and triplet profile associated with (220), (321) and (310) reflections for samples with (a) SCTM15 and (b) SCTM2 respectively.

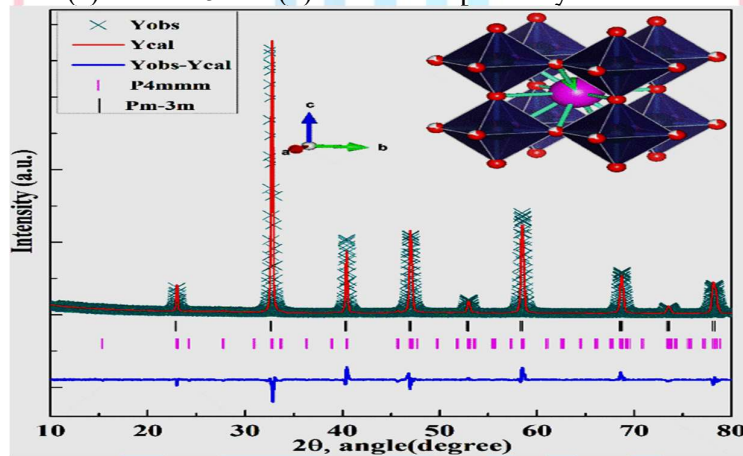


Figure 28 Refinement of room temperature X-ray diffraction for SCTM15 sample in the space group of pm-3m (cubic structure $\chi^2 = 5.24$) and P4mmm (tetragonal structure $\chi^2 = 4.07$) respectively.

Figure 29 indicates the change in the unit cell parameters and tetragonality ratio for all prepared samples. In comparison to pure ST, the decrease in lattice parameters can be attributed to the mismatch in the ionic radii of the dopants as well as the parent ions. This, decrease in the unit cell parameters indicates the solubility of dopant ions in the ST lattice. Additionally, for higher dopant concentration (SCTM15 and SCTM2) the variation of the tetragonality ratio verifies the emergence of a non-cubic symmetry.

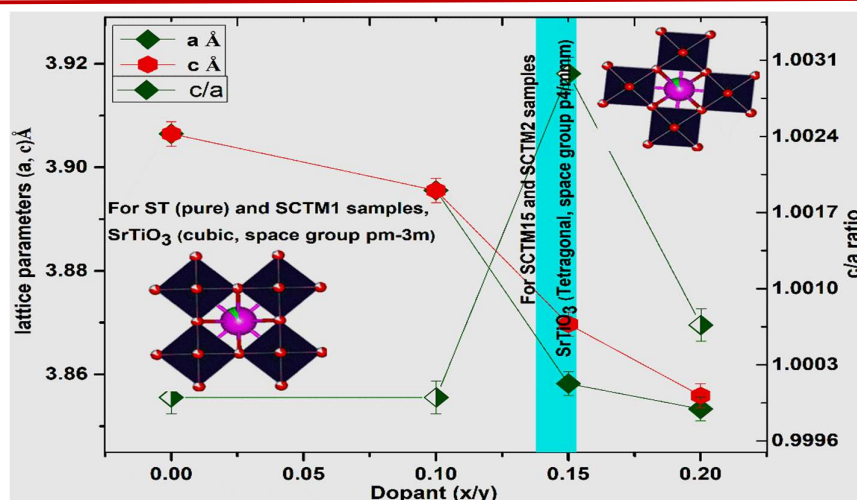


Figure 29 Plot of the lattice parameters (a, c Å) and c/a ratio as a function of dopant (x/y) for STO (take as a reference), SCTM1, SCTM15 and SCTM2 samples respectively.

B. Relaxor Ferroelectricity in (Sr, Ce, Ti, Mg)O₃ Ceramics

Fig. 31 depicts the temperature evolution of dielectric constant and dielectric loss for all samples prepared in N₂/H₂ atmosphere. compared to pure ST, all samples exhibit enhanced dielectric values between room temperature and ~ 200°C. Interestingly, in the sample with the lowest Ce concentration (for SCTM01), the highest dielectric constant at 50°C can be observed to be around 19000. As the Ce concentration increases, the dielectric constant decreases strongly to values of ~ 2000 and ~ 200 for samples SCTM15 and SCTM02, respectively. The formation of the secondary phase may be attributed to a decrease in dielectric permittivity. In contrast to the value of the dielectric permittivity, the temperature stability of the dielectric permittivity is improved with increased Ce concentration. The temperature stability (in the range of 50°C and 200°C) of the dielectric permittivity improves with higher Ce concentration, in contrast to the value of the dielectric permittivity.

C. Microstructure of (Sr, Ce, Ti, Mg)O₃ Ceramics

The surface morphologies and grain size distributions of (Sr, Ce, Ti, Mg)O₃ compounds are shown in Fig 30. All ceramics exhibit a non-uniform grain size distribution, with small similar particles interspersed with larger particles. The average grain size increased from 1.60 μm to 2.30 μm with increasing Ce/Mg concentration, indicating that Ce/Mg doping promotes grain growth.

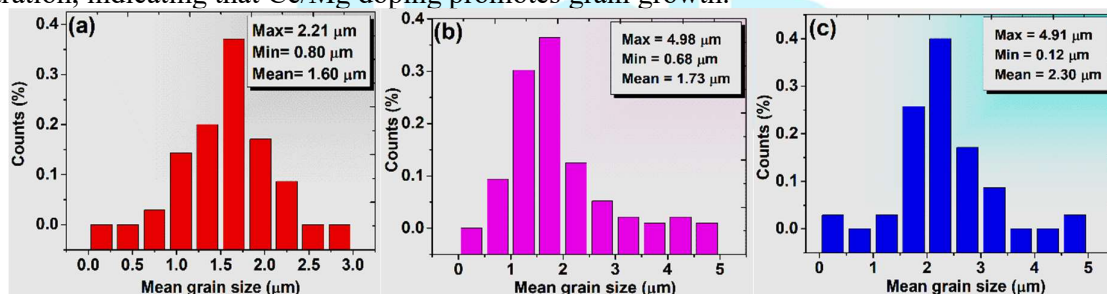


Figure 30 Composition dependent surface morphology and grain size distribution for samples with (a) SCTM1, (b) SCTM15 and (c) SCTM2 respectively.

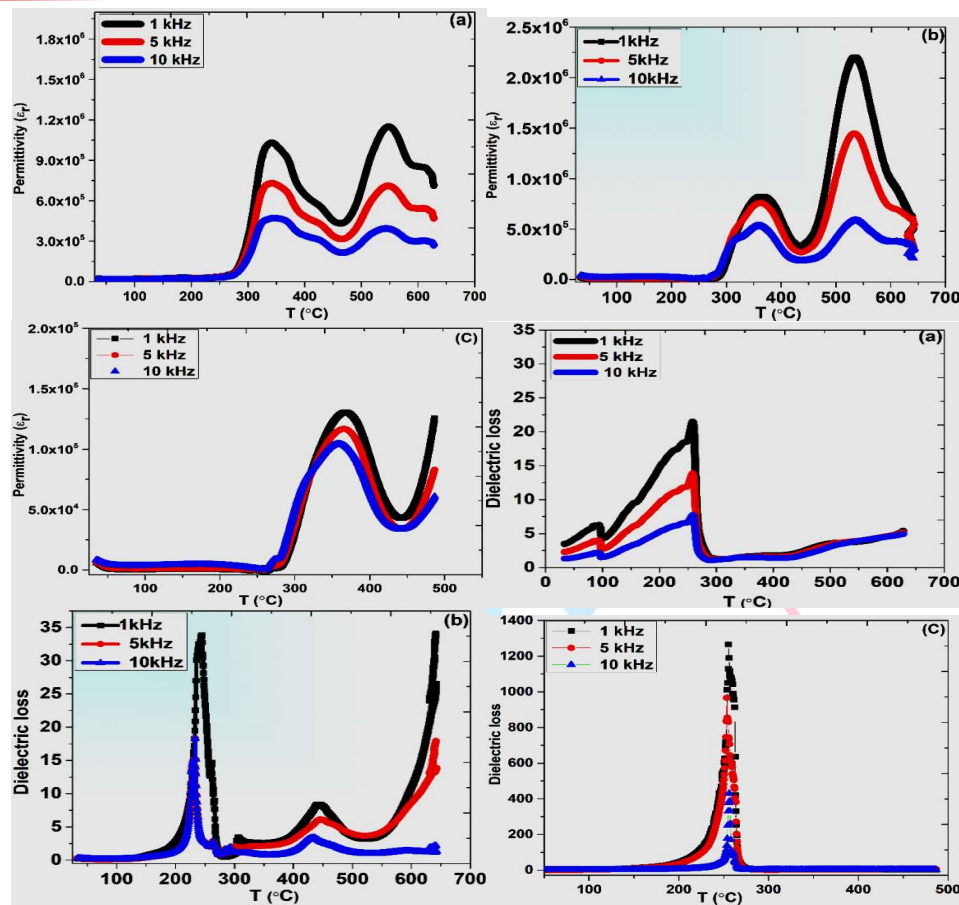


Figure 31. Temperature dependent permittivity and loss ($\tan\delta$) for SCTM1, SCTM15 and SCTM2 compositions respectively.

Fig 32. indicates the hysteresis loop for all samples at different applied frequency. The linear nature of the hysteresis loop further confirm the relaxor nature of the samples with low dielectric loss. To further, confirm remnant polarization test (PUND) was done for all samples. The existence of low remnant polarization is further evidence for the relaxor ferroelectricity nature of the samples as shown in Fig 35.

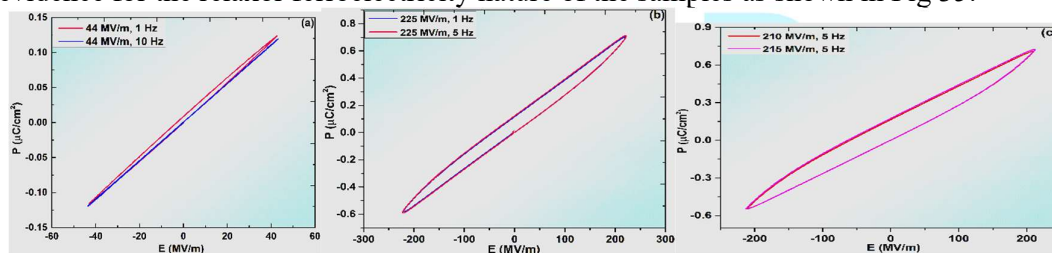


Figure 32 Polarization hysteresis loops (P - E loop) at various applied field measured at different frequency of 1-10 Hz for SCTM1, SCTM15 and SCTM2 samples respectively.

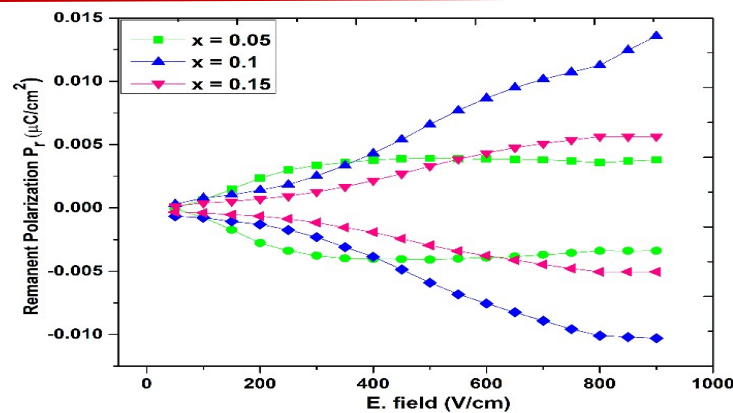


Figure 33. Intrinsic remnant polarization SCTM1, SCTM15 and SCTM2 compositions respectively O_3 .

V. CONCLUSION

The lattice structure, grain structure and temperature dependent dielectric (x , = 0.05, 0.1, 0.15 and y = 0.05) sintered in 5% H_2 and 95% N_2 atmosphere ceramic samples were successfully clarified. The (Sr, Ce, Ti, Mg) O_3 show a structure phase transition at SCTM1 from cubic to tetragonal. The SEM images show that with increasing doping concentration, the grain size increases and shows an almost dense microstructure without any secondary phases, which also supports the XRD results. The samples show relaxor ferroelectric like nature. The ϵ' - T plot, hysteresis loop along with intrinsic ferroelectricity (PUND) clarify the relaxor ferroelectric nature of the ceramics samples. Further, in the temperature span 50°C and 200°C, the ceramic samples showed a good frequency and temperature stability, which show its potential in energy storage devices. These results lead us to conclude that the A/B site donor doping of SrTiO_3 with Ce/Mg is not a viable sintering condition for samples sintered in air. Therefore, we sintered the samples in H_2 and N_2 . As a result, it is obvious that thermodynamics and/or sintering atmosphere may both have a significant impact on the physical characteristics of these materials. The latest advancements in this work may open up new avenues for various characteristics and uses of this extensively functional perovskite material.

VI. FUTURE RECOMMENDATION

Strontium titanate is an excellent dielectric material, it is essential to encourage research in this area for both intrinsic and extrinsic mechanisms. As a consequence, we think that rare-earth (RE-ions) doped SrTiO_3 materials containing Al^{+3} , Zn^{+2} , and Mn^{+2} cations have a promising future and will provide significant advances in energy storage applications.

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