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NOVEL GREEN SYNTHESIS OF STRONTIUM TITANATE ($SrTiO_3$) NANOPARTICLE - A PEROVSKITE MATERIAL

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Abstract

In the modern world, sustainable development is one of the most critical matters that society must address. The hunt for innovative and sustainable solutions has been prompted by the need to lessen our carbon footprint and safeguard resources for future generations. Nano particle prepared via green route is the solution for above mentioned social issue. In order to prepare sized-controlled Strontium titanate nanoparticle, a perovskite material for energy storage devices, we used green combustion with citrus-limon as the fuel. PXRD and SEM tools were used to analyze the structural morphology of the as prepared NP's. Narrow particle size, with blue shift in absorption edge suggest that, method of preparation is a good choice to produce $SrTiO_3$ NP which has enhanced dielectric constant values than other reported method which make use of these particles in Energy storage devices.

Keywords: Citrus Limon; Eco-Friendly; Electrical Property; Optical; Simple Method; Size controlled $SrTiO_3$.

1. INTRODUCTION

We require high energy density materials because technology, from mobile phones to the electricity grid, is re - shaping. Because of their smaller size and higher surface-to-volume ratio, nanomaterials fill all intercalation sites that are available in the particle volume, resulting in high specific capacities and rapid ion diffusion [1]. The perovskite compounds play a significant role in the search for potential energy materials for high efficiency energy devices due to their distinctive adjustable features [2,3]. Pervoskite nanostructure (PNS) characteristics are influenced by their surface energy, and surface to volume ratio in addition to their size [4]. Controlling these fundamental characteristics of nanoparticles is also necessary to lessen the difficulties in utilising them in emerging technologies. Smaller holes in supercapacitors might prevent electrolyte ions from penetrating as much as larger holes in photovoltaics, which offers greater possibilities for charge exchange.A material category with a structural formula ABM_3 are known as pervoskites, where the cation "A" occupies the unit cell's vertices, the cation "B" is in the cell's core, and the anion "M" is on the unit cell faces [5]. Strontium titanate ($SrTiO_3$) one such perovskite nano structured material find its application in many fields due to its unique properties. Designing perovskite energy-related materials requires the utility of novel synthesis techniques for better stabilisation and careful control of structural features.

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$SrTiO_3$nano powders are typically made through a solid-state process that converts $SrCO_3$ to TiO_2 precursors at temperatures of 900 to 1000 ºC. Strontium titanate ($SrTiO_3$) nanocubes were created by Din et al. utilising an alkali hydrothermal technique at low temperatures without additional heating. After 6 hours of hydrothermal sintering, the $SrTiO_3$ powder, which is produced via nanocube aggregation, changes into cubic particles with a particle size of 120-150nm [6].

Solvothermal synthesis was used to form $SrTiO_3$ nanoparticles having cube, sphere, and flake-type morphologies in a water-based solution and polyols. By modifying the initial volume ratio in H_2O/diethylene glycol, it was feasible to change the size of cubic particles enclosed by 1 0 0 faces in the range of 24 to 43 nm [7].

PhiramPanthong et al prepared strontium titanate by sol gel combustion technique. In their work they calcinate the strontium titanate sample at 600-900ºC for 2 hours with the various content ratio citric acid as a propellent. The average particle size around 25 to 30 nm in this work [8].

The strontium titante preparation method involved a number of chemical steps, and only a three- to four-fold annealing and calcination process resulted in the finished material. Also, the by-product emission from the chemical method posed a risk to everyone's health and the environment. In order to avoid environmental damage, massive energy expenditure, and potential health risks, researchers are focusing on green synthesis. This is because green synthesis is better for the environment and human health than conventional chemical synthesis since it is more affordable, reduces pollutants, and improves environmental and health safety. So, we decided to use citrus limon juice a natural product available in low cost ahead of citric acid.

L-ascorbic acid, generally known as vitamin C, is a naturally occurring form of vitamin C that is used in this technique and is widely present in lemon (citrus limon) juice [9]. Lemon juice is used in the chemical reaction as a fuel/firing agent and is completely soluble in water. The main goal of our work is to prepare perovskite structure with narrow particle distribution via simple cost-effective eco-friendly method. In this study, the sol-gel combustion process was used to create strontium titanatenanopowders with citrus limon juice as the fueling. $SrTiO_3$ nanoparticles structure was first studied via X-ray diffraction (XRD) technique, and the synthesized nanoparticle's electric characteristics were examined in a wide frequency and temperature range, optical, morphology and elemental composition were analysed in brief.

2. PREPARATION METHODOLOGY

2.1 Materials

Strontium Nitrate$(SrNO_3)_2$, Titanium tetrabutaoxide($C_{16}H_{36}O_4T_i$), Ammonium hydroxide (NH_4OH) (with 99 percent pure) purchased from Sigma Aldrich without additional cleansing. Citric acid is accompanied by a freshly made citrus limon juice solution that serves as a solvent as well as fuel.

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2.2 Preparation

In order to prepare strontium titanate, we used the ecologically responsible sol-gel combustion method. We used readily available, pure lemon juice as a fuel for this process to occur which has a pH of roughly 2.2 and 5-6% L-ascorbic acid concentration. Naturally grown lemons were crushed and peeled. The pulps were then filtered through fresh muslin fabric to remove the solid particles [10]. Then the prepared limon solution (50 ml) was dissolved in 100 ml distilled water and ammonium hydroxide dropwise added in the citrus limon juice solution till the pH reached 9, next blend it the Strontium nitrate and titanium tetrabutaoxide in the stoichiometric molar ratio of 1:1, and the mixture was stirred for 2h at 80^{0} C to obtain the homogeneous mixture. The obtained transparent solution was cool down to room temperature for about 24 hours. Then the cooled solution was at muffle furnace at 700 ◦C for 2 h. Finally, the obtained fluffy product was given in the figure.1 when the fluffy sample was crushed, we obtained fine $SrTiO_3$nano powder.

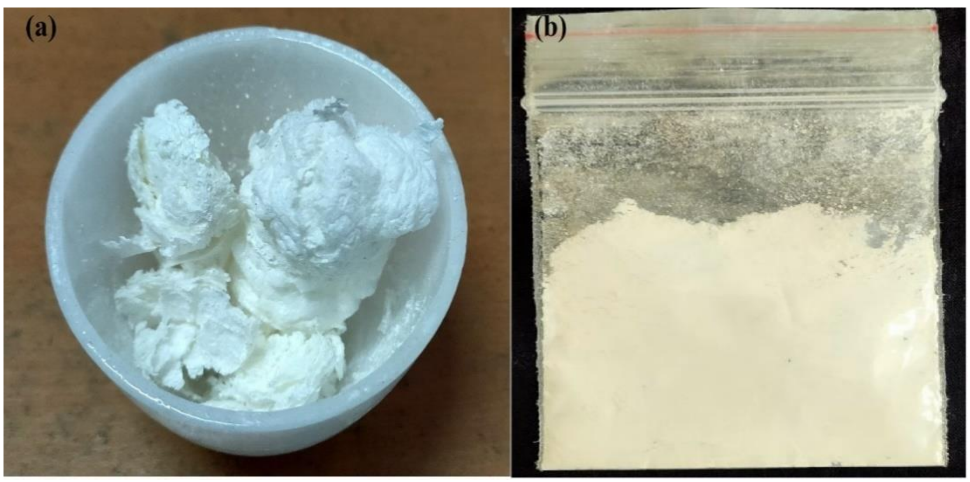

Figure 1: a) Image of final fluffy material obtained b) $SrTiO_3$ NP

3. RESULTS AND DISCUSSION

3.1 XRD analysis

The PXRD patterns of the prepared $SrTiO_3$ NP was depicted in the Figure 2. We found excellent match with JCPDS card no. 89-4934 from the evaluated conspicuous peaks ($SrTiO_3$) well agree with cubic structure with Pm3m space group symmetry. The scarcity of additional peaks indicates the high pure quality of the produced sample. The average crystalline sizes were calculated using Scherrer formula [11]. The average crystallite size obtained via Debye-Scherrer method was 13.6 nm. Sharp peaks in XRD evident the high crystallinity of the prepared sample. Without additional annealing or calcination, smaller size obtained in our current investigation showed that with less cost natural fuel (lemon) combustion method is well suited one to produce $SrTiO_3$ NP than any other process reported earlier [13,14,15,16].

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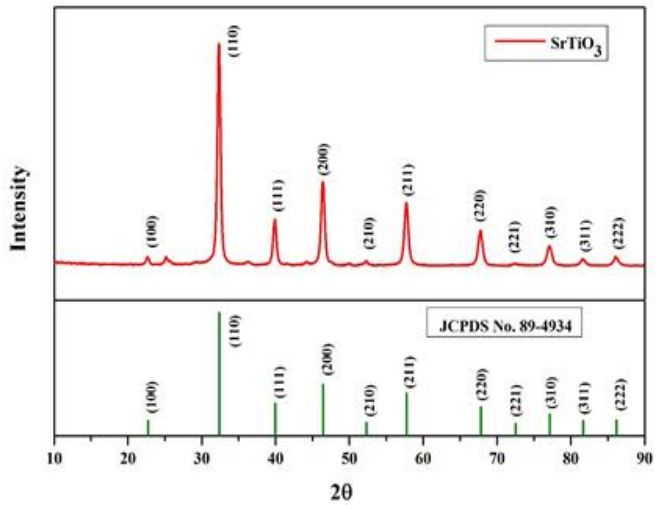

Figure 2: x-ray diffractogram of as prepared strontium titanate NP

Crystallite size and micro strain produced in the $SrTiO_3$ lattice was calculated by plotting W-H plot [17] shown in Figure 3. And calculated lattice parameter along with obtained data from W-H plot are given in Table 1.

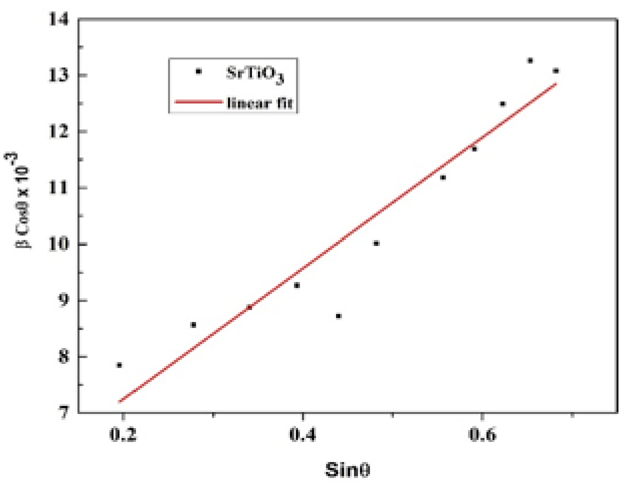

Figure 3: W-H plot for prepared strontium titanate

Table 1: Calculated parameters from pxrd pattern

Prepared Specimen		$SrTiO_3$
Lattice parameter	a=b=c(Å)	3.90
	V(Å)^3	59.63
Average crystalline size (nm)		13.6
Micro Strain		11.6
Dislocation densitym^{-2}		5.87*10^{-15}

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3.2 SEM analysis

Figure 4 shows a SEM micrograph of prepared $SrTiO_3$ NP. The least agglomerating particles were found to be spherical. The presence of pores indicates the prepared sample's wide surface area.

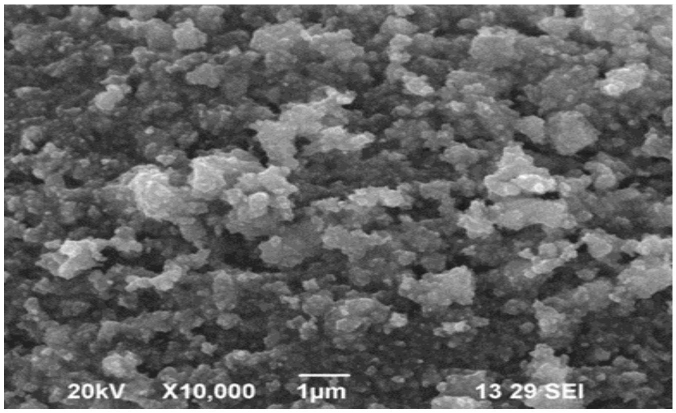

Figure 4: SEM image of prepared SrTiO3

3.3 EDAX

The elemental compositions of the sample were explored through EDX analysis. The element distribution map performed for the $SrTiO_3$ are shown in Figure 5. The peaks located around 1.8, 14.2 and 15.8 eV show the presence of Sr and the peaks around 0.4, 4.5 and 4.9 eV show the presence of Ti and the oxide elements present in 0.5 eV.One can observe only peaks related to Sr, Ti, and O in Figure4, thus expressing the elemental purity of pure $SrTiO_3$ NP. The EDAX study reveals an oxygen deficit in $SrTiO_3$. Through the gift of its extra electrons, zero valent nano ion can intentionally produce an oxygen deficient surface on TiO_3. The oxygen-deficient TiO_3 that has a reduced energy band-gap, smaller pore diameters, and improved photocatalytic characteristics.

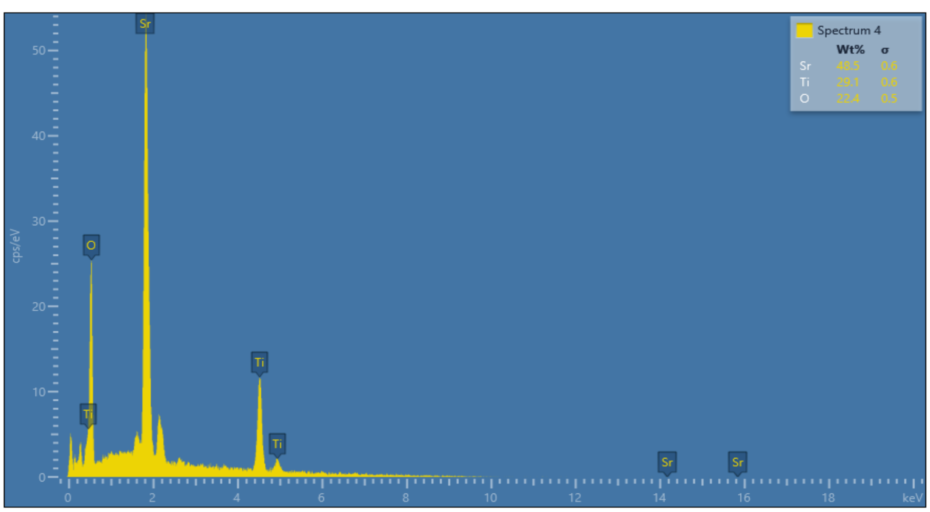

Figure 5: EDAX Spectra of Strontium titanate nanoparticle

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3.4 UV-VIS spectra

Absorbance spectra of pure strontium titanate in the wavelength range 200-1000 nm was illustrated in Figure. 6(a). A strong absorption edge of was observed around 312nm which is lower than that of reported value by other authors [18,19]. Broadening of Absorption edge is happened in our present study this may be due to higher oxygen vacancies than the other methods [20]. The optical energy bandgap (Eg) was estimated by using the following expression [21,22].

$$(\alpha h\nu)^2 = A\,(h\nu - E_g)$$

Where A is a constant and E_g is the optical band gap. The graphical plot for $(\alpha h\nu)^2$ versus hv gives values of energy bandgap (E_g). The E_g values for pure $SrTiO_3$ is 3.2 eV. The obtained bandgap value is less than the previously reported $SrTiO_3$ values, 3.32 eV and 4.15 eV [23,24]. This lower band gap value is used to continue improving Perovskite Solar Cell charge extraction and stability [24,25].

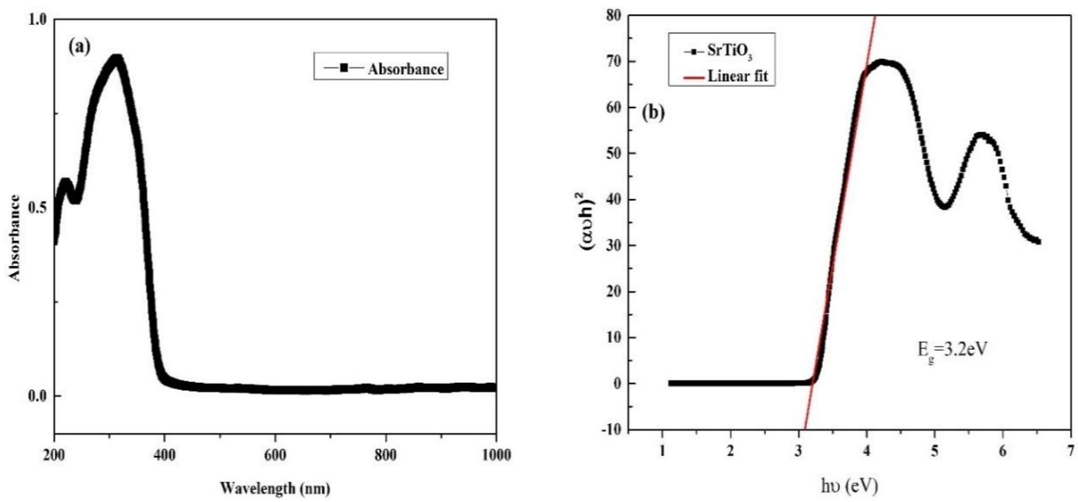

Figure 6: (a) absorbance of the UV–vis spectrum represents with the wavelength of pure $SrTiO_3$ powder, (b) represent the Tauc plot for prepared $SrTiO_3$

3.5 Dielectric analysis

Dielectrics is crucial in the explanation of many optical phenomena in solid state physics and cell biophysics. Dielectric study parameters including dielectric constant, dielectric loss, and AC conductivity can be used to determine a material's electro-optic coefficient [26]. In the current investigation, we used a hydraulic pelletizer with 2 tonnes of pressure to compress the strontium titanate into pellet form. Silver paste was applied to the polished opposite sides of the pellet to assure trustworthiness of electrical connections between the pellet and the electrodes. An Agilent 4284A LCR meter was used to test the dielectric properties of pure $SrTiO_3$ nanoparticles over a wide range of frequencies and temperatures with an accuracy of ± 2% [27,28]. The temperature of the sample was controlled by a temperature regulator. Figure. 6ashows the frequency dependence of dielectric constant of $SrTiO_3$nano particles with varying temperature.

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Dielectric constant of prepared $SrTiO_3$ falls rapidly with increasing frequency and raise with increase in temperature. Dielectric constant distribution is quick at low frequency; this is due to the polarisation of the interfacial layer. Due to the dipoles rotational displacements and resulting orientational polarisation, dielectric constant dispersion at higher frequencies decreases and approaches a well almost frequency-independent response. This indicating the normal dielectric behaviour [29]. The replacement of limon juice does not affect the behaviour of dielectrics, hence it shows normal dielectric behaviour as previously reported papers [10]. Figure. 6b illustrate the dielectric loss of prepared sample with varying frequencies at different temperatures. Dielectric loss increases with temperature, and it is found that raising the frequency reduces the loss factor values [30]. Here the addition of limon juice does not affect the loss factor. The minimized loss factor of prepared strontium titanate offers the enhanced electrical applications in various fields. In fig. 6c clearly explains that the AC conductivity increases with increasing frequency and increase in temperature. Due to grain boundaries this shows frequency independent performance at low frequencies. Normal behaviour of semiconductor materials in terms of their dielectric characteristics appears like this. [31,32]. The conductivity of this substance is usual, and it has the highest dielectric constant and the lowest dielectric loss, which are two essential characteristics for the ideal energy storage system [33]. Beyond 10K, conductivity abruptly increases. Higher dielectric value of these particle suggests the use as filler in organic polymer matrix as EM wave absorber [34].

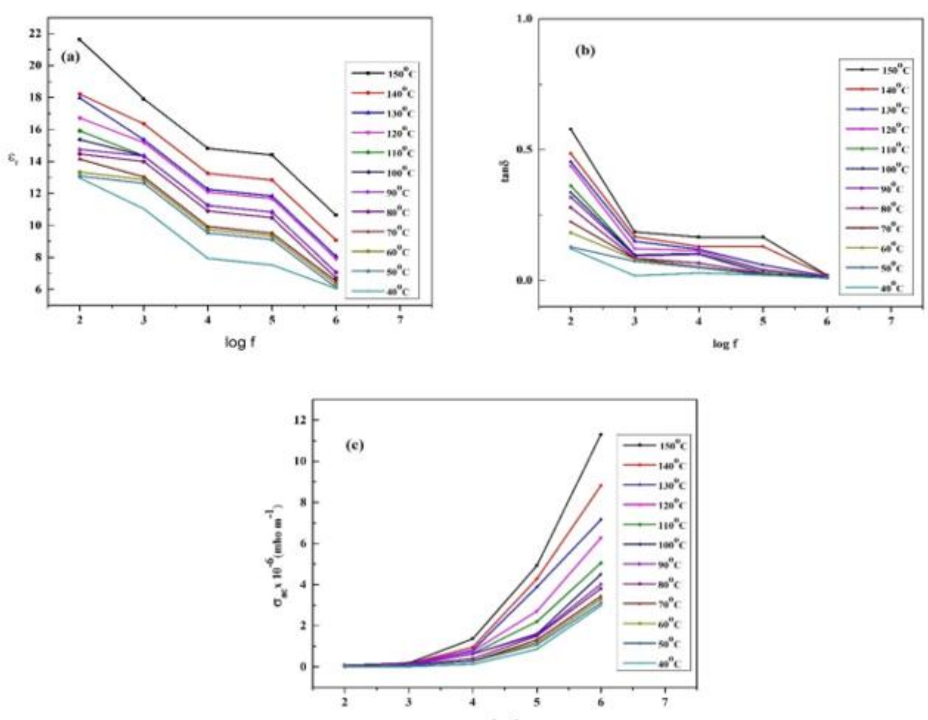

Figure 6: Variation of a) ε_r b) tan δ and c)σ_{ac} with log frequency for various Temperature of $SrTiO_3$ NP

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4. CONCLUSION

An eco-friendly approach for the synthesis of $SrTiO_3$nanopowder by sol-gel combustion method using limon juice as a fuel. From our findings we strongly concluded that this sol-gel combustion using citrus limon as fuel produced the size-controlled nanoparticles when compared to other preparation method without any second step calcination or annealing. Also, Lemon juice enhanced the oxygen vacancies in $SrTiO_3$ lattice than any other preparation method, which inturn tune its optical and electrical behaviour. The average crystallite size was noted as 13.6nm. SEM and EDAX confirmed the purity and uniform size of the prepared sample. High dielectric value than other reported work suggests that, greenly prepared $SrTiO_3$ NP suitable for making energy storage devices.

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