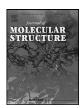
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# Experimental investigation of structural, surface, optical and electrical properties of gallium sesquioxide doped tausonite compounds



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#### ABSTRACT

We report that 1% and 3% wt concentration of gallium sesquioxide  $(Ga_2O_3)$  doped tausonite  $(SrTiO_3)$  compounds have been developed by mechanochemical synthesis followed by calcination process and their microstructural, spectral and opto-electrical characterization are discussed for the first time. The lattice parameter values of the  $Ga_2O_3$  doped  $SrTiO_3$  samples were examined using the X- ray Diffraction (XRD) and Williamson-Hall (W-H) plot. The cubic structure of  $SrTiO_3$  is confirmed by the XRD and Raman studies. The Field Effect-Scanning Electron Microscopy (FE-SEM) images of the  $Ga_2O_3$  doped  $SrTiO_3$  samples were composed of spherical particles with agglomeration throughout the surface. The chemical elements and chemical states of the prepared compound have been tested in the Fourier Transform Infrared (FT-IR), Energy Dispersive X-ray (EDX) and X-ray Photoelectron Spectroscopy (XPS) studies. The optical spectra displayed that the absorption wavelength shifted near the red shift with the increase of the  $Ga_2O_3$  doped  $SrTiO_3$ . The dielectric and electrical conductivity responses of the 1% and 3 wt %  $Ga_2O_3$  doped  $SrTiO_3$  materials were investigated in the dielectric and electrical studies.

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#### 1. Introduction

The incorporation of transition metals or non-metals or mixed transition ions doping in tausonite (SrTiO<sub>3</sub>) material and its consequences can alter the size, shape, optical absorption, and optical band gap of the particles and the photocatalytic, magnetic, thermal and electrical properties. This is due to the dopants creating the distortion of the lattice or surface modification in tausonite. SrTiO<sub>3</sub> has some unique properties, such as the formation of paraelectric or ferroelectric material depending on room temperature or low temperature, good structural and thermal stability, broad optical band gap and optical absorption in the ultraviolet portion and large dielectric constant [1–31]. These unique properties which satisfy the material of SrTiO<sub>3</sub> material and may be suitable for a wide range of applications like optical and electronic devices, photocatalysts, gas sensors, spintronics, and high frequency tunable devices [1–31].

Over the last few years, the doping effects of transition metals (Fe, Cr, Mn, Sn, Co) [1–11], non-metals (N, C) [12,13], rare earth metals (La, Nd, Y, Nb, Gd, Er, Pr, Sm, Ce) [17–27] and mixed

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two elements (La/Fe, La/Co, La/Dy, La/Y, Bi/Cu, Cu/Nb, Bi/Li) [24-31] have been applied to SrTiO<sub>3</sub> materials by different chemical methods, such as solid state reaction, ball milling, sol-gel, combustion, solvothermal, hydrothermal etc. The literatures referred to above investigated the impact of dopants on the crystal structure, particle size and shape, lattice parameters, optical, catalytic and electrical responses of SrTiO3 for optoelectronic devices, photocatalysts etc. Based on the above literatures, the preparation of the doped SrTiO<sub>3</sub> material requires certain conditions like autoclave, high pressure, above 1000 °C temperature, microwave, vacuum, ultrasonicator and inert gas (He or N<sub>2</sub> or H<sub>2</sub>/N<sub>2</sub>) and sometimes a secondary phase etc. In this work, we used Ga<sub>2</sub>O<sub>3</sub> as a doping material for SrTiO<sub>3</sub> material. Ga<sub>2</sub>O<sub>3</sub> material has multifunctional properties like wide optical band gap and good insulator for dielectric coating and optoelectronic device applications. We have prepared Ga<sub>2</sub>O<sub>3</sub> doped SrTiO<sub>3</sub> materials using a solid state synthesis method, sintering at 1000 °C without using any solvent, autoclave, vacuum, inert gas etc. The novelty of this present work is that the effects of Ga<sub>2</sub>O<sub>3</sub> doping on crystal structure and strain, crystallite and particle size and shape, energy gap and electrical activity (relative permittivity, dielectric loss and electrical conductivity) of the tausonite compounds have been studied and reported for the time.

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#### 2. Experimental

#### 2.1. Materials

Strontium (SrCO $_3$ ) (Merck), titanium dioxide (TiO $_2$ ) (Merck) and gallium sesquioxide (Ga $_2$ O $_3$ ) (Merck) were obtained commercially and used as received without further purification.

### 2.2. Preparation of Ga<sub>2</sub>O<sub>3</sub>-doped SrTiO<sub>3</sub> powders

Ga<sub>2</sub>O<sub>3</sub>-doped tausonite materials were produced by mixing carbonate salt of strontium (SrCO<sub>3</sub>), titanium dioxide (TiO<sub>2</sub>) and gallium sesquioxide (Ga2O3) as a dopant via the mechanochemical synthesis followed by a calcination process. 3.20 g of SrCO<sub>3.</sub> 1.68 g of  $TiO_2$  0.04 and 0.12 g of  $Ga_2O_3$  (1 and 3 wt%) selected compounds were measured and the following chemicals were admixed together to be in a hot plate pre heated at 200 °C for 1hr. Further, the obtained mixed chemicals' powder was well ground for 1 hr in an agate mortar, followed by calcination at 400 °C for 6 hrs in a muffle oven. The reason for the choosing the above calcined temperature was to completely eliminate the carbonate from the mixed powder. Furthermore, the above burnt powder was transferred to the mortar and well ground for 3600 seconds. After that, the fine ground powder was kept in an alumina crucible and preserved in the furnace sintered at 1000 °C for 6 hrs. After ample cooling, the Ga<sub>2</sub>O<sub>3</sub> doped tausonite (SrTiO<sub>3</sub>) powders were taken out from the electronic furnace.

The probable formation mechanism of the  $Ga_2O_3$  doped  $SrTiO_3$  compounds are expressed below: [24].

$$Sr_{(1-x)}CO_3 + TiO_2 + x(Ga_2O_3) \rightarrow Sr_{(1-x)}TiO_3 : x(Ga) + CO_{2\uparrow}$$
 (1)

Where x = 1% and 3% gallium sesquioxide dopant concentration.

# 2.3. Characterization

The crystal phase of the prepared ceramic compounds was characterized with the assistance of the X'pert PRO XRD instrument (Cuk $\alpha$ =1.54056Å). The chemical bond between the elements was examined by the Nicolet spectrometer- model 6700 FTIR spectra. The crystal phase was identified by the Renishaw in the VIA model Raman spectrometer instrument using the laser light as an excitation source with an optical wavelength of 785 nm. The surface morphology and chemical elemental analysis were examined by the HITACHI S-3400N. The optical behavior was tested on the Shimadzu- UV-VIS-NIR spectrometer instrument. Chemical states were detected through the PHI 5000 versa probe III-XPS instrument. The calcined ceramic compounds were pelletized; polished and a single electrical conductor made of copper was fixed using silver paste coated on two faces of the pellet, which reacts as a conductive (electrode) material. Then, the dielectric properties were studied on the HIOKI 3532-50 LCR Hi TESTER instrument for different temperatures (305 K to 573 K) and recorded at different frequencies ranging between 10<sup>2</sup> and 10<sup>6</sup> Hertz.

#### 3. Results and discussions

# 3.1. Powder X-ray diffraction (XRD) analysis

We have already reported the preparation of pure  $SrTiO_3$  material via the solid state reaction method and its powder XRD pattern [23]. In this present work, we have prepared 1% and 3 wt% concentrations of gallium sesquioxide doped  $SrTiO_3$  and their XRD pattern is displayed in Fig. 1 (a&b). The powder XRD patterns of the doped samples were recorded at the diffraction angle  $(2\theta)$  in the range of 20 ° to 80 ° on the x-axis and the intensity on the y-axis for the determination of their crystalline phase.

The XRD patterns of the Ga<sub>2</sub>O<sub>3</sub>-doped SrTiO<sub>3</sub> samples indicated the reflected diffraction peaks of (100), (110), (111), (200), (210), (211), (220) and (310) planes, respectively. The detected sharp reflected diffraction planes and peak positions were compared to the reported reflected peak positions of the SrTiO<sub>3</sub> compound in the XRD pattern. After examining the obtained reflected peak position in the XRD pattern with the reported reflected peak position, the prepared 1% and 3% Ga<sub>2</sub>O<sub>3</sub> doped SrTiO<sub>3</sub> samples confirmed the formation of cubic perovskite crystal structure of the SrTiO3 compound (JCPDS.No.01-084-0443) [23]. However, there was no modification in the crystalline phase of the XRD pattern of the synthesized samples by the addition of the Ga<sub>2</sub>O<sub>3</sub> doping to the host lattice. This was due to the difference between the ionic radii of the dopant (Ga = 00.62 nm) and the parent ions (Sr = 0.132 nm) [35] which confirmed the incorporation of Ga<sub>2</sub>O<sub>3</sub> into the strontium titanate lattice. Further, no additional impurity compounds, such as Ga<sub>2</sub>O<sub>3</sub> or SrCO<sub>3</sub> were found in the XRD pattern of the synthesized gallium doped SrTiO<sub>3</sub> samples, suggesting the confirmed formation of a mono phase with high phase purity. The purpose of adding a lower concentration of Ga<sub>2</sub>O<sub>3</sub> doping was to retain the high purity single phase of the prepared SrTiO<sub>3</sub> material. Suppose, we increase the dopant concentration in the host material, it can create a secondary phase in the XRD pattern. In addition, the sharp diffraction peaks showed that the prepared Ga<sub>2</sub>O<sub>3</sub>-doped SrTiO<sub>3</sub> samples were of a very crystalline nature. The XRD pattern of the 3% Ga<sub>2</sub>O<sub>3</sub>-doped SrTiO<sub>3</sub> sample indicated that the high intensity reflection plane (110) was shifted to a higher angle with a slightly narrow broadening peak compared to that of the 1% Ga<sub>2</sub>O<sub>3</sub>-doped sample, as shown in Fig. 1b, which may increase the crystallite size due to the lattice deformation (strain). In addition, we observed increasing cystallinity with the increasing of the Ga<sub>2</sub>O<sub>3</sub> dopant concentration in the SrTiO<sub>3</sub> material. The mean size of crystallites (D) was calculated from the XRD pattern through Scherer's equation [24]:

$$D = k\lambda/\beta \cos\theta \tag{2}$$

Where,  $\lambda$  is the wavelength of the  $Cuk_{\alpha}$  radiation (0.15405 nm),  $\theta$  is the diffraction angle and k is a geometric factor (k = 0.89 for spherical particles). Full Width Half Maximum (FWHM) values are detected from the high intensity peak of (110) in the XRD pattern of the  $Ga_2O_3$  doped samples.

The FWHM values are detected to be 0.2521 and 0.2389 from the sharp intensity peaks (110) at diffraction angles located at 32.44° and 32.64°, respectively for the 1% and 3%  $Ga_2O_3$  doped  $SrTiO_3$  samples. After that the above FWHM and reflected angle position values are substituted in Scherer's equation and it was determined that the crystallite sizes were 36.5 and 38.5 nm respectively, for 1% and 3%  $Ga_2O_3$ -doped  $SrTiO_3$  samples. Based on the above findings, the crystalline size of the  $SrTiO_3$  compound increased with an increase in the concentration of  $Ga_2O_3$  dopant in the XRD pattern. Some lattice parameter values of the  $Ga_2O_3$  doped samples have been computed from XRD data and are given in Table 1.

From Table 1, we could notice decreasing d-spacing, lattice constant and volume of the unit cell with increasing the  $Ga_2O_3$  doped concentration in the  $SrTiO_3$  sample. The calculated lattice parameter values of the  $Ga_2O_3$  doped  $SrTiO_3$  samples, are comparable with the previously reported lattice parameter values of the doped  $SrTiO_3$  material [1,3,5,31].

# 3.2. Williamson-Hall (W-H) plot analysis

The average crystallite size (D) and crystalline strain ( $\varepsilon$ ) values of 1% and 3%  $Ga_2O_3$  doped STO was determined through the Williamson-Hall (W-H) plot by using this formula: [24]

$$\beta \cos \theta = k\lambda / D + \varepsilon (4 \sin \theta) \tag{3}$$

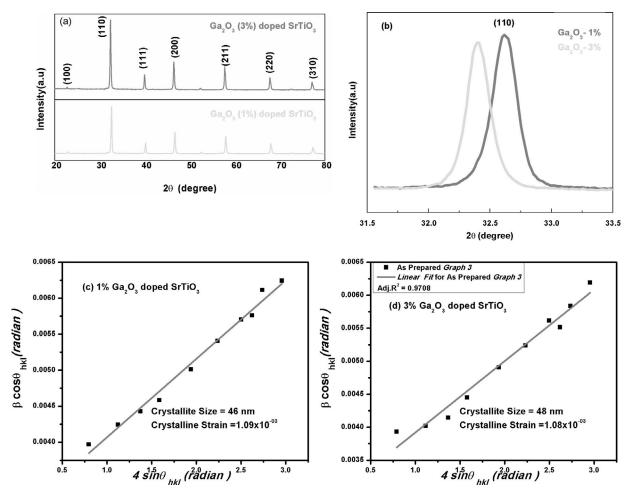


Fig. 1. (a) XRD pattern of  $Ga_2O_3$  (1% & 3%) doped  $SrTiO_3$  samples. (b) High Intensity diffraction peak (110) of  $Ga_2O_3$  (1% & 3%) doped  $SrTiO_3$  samples. W-H plot of (c) 1% and (d) 3%  $Ga_2O_3$ -doped  $SrTiO_3$  samples.

 $\begin{tabular}{ll} \textbf{Table 1} \\ \textbf{Some lattice parameter values of the $G_{a_2}O_3$ doped samples were computed from the XRD data.} \\ \end{tabular}$ 

Ga <sub>2</sub> O <sub>3</sub> doped SrTiO <sub>3</sub> samples	d-spacing values are calculated by using formula $d = n\lambda/2\sin\theta$ (Å)	Lattice constant (a) values are calculated by using formula $a=d/\sqrt{(h^2+k^2+l^2)}$ (Å)	Volume of the unit cell $(a)^3$ $(\mathring{A})^3$
1% Ga <sub>2</sub> O <sub>3</sub> doped SrTiO <sub>3</sub>	2.73	3.86	57.51
3% Ga <sub>2</sub> O <sub>3</sub> doped SrTiO <sub>3</sub>	2.70	3.82	55.74

Table 2 Crystallite size and strain, slope, intercept, Adj  $R^2$  of the  $Ga_2O_3$  doped  $SrTiO_3$  samples using W-H plot with the assistance of linear fit curves.

Ga <sub>2</sub> O <sub>3</sub> doped SrTiO <sub>3</sub> samples	Crystallite size estimated by using W-H plot	Crystalline strain	Intercept	Slope	AdjR <sup>2</sup> using linear fit
1% Ga <sub>2</sub> O <sub>3</sub>	46 nm	$\begin{array}{c} 1.09 \times 10^{-3} \\ 1.08 \times 10^{-3} \end{array}$	0.0029	0.0010	0.9866
3% Ga <sub>2</sub> O <sub>3</sub>	48 nm		0.00284	0.00108	0.9708

The average crystallite size and crystalline strain values of the 1% and 3%  $Ga_2O_3$  doped  $SrTiO_3$  were determined through the Williamson-Hall (W-H) plot using the XRD data and their determined values are mentioned in plots (Fig. 1.c). The crystallite size and strain, slope, intercept, and Adj  $R^2$  of the  $Ga_2O_3$ -doped  $SrTiO_3$  samples using the W-H plots with the assistance of linear fit curves are given in Table 2. From Table 2 we could observe the increasing crystallite size and intercept, and decreasing slope

and  $\mbox{Adj} R^2$  values on increasing the  $\mbox{Ga}_2\mbox{O}_3$  concentration in the  $\mbox{SrTiO}_3.$ 

We noticed the increasing average crystallite size and decreasing crystalline strain with the increase in the dopant concentration in the SrTiO<sub>3</sub> (Table 2). The estimated average crystallite size values are comparable with the calculated crystallite size using Scherer's formula. The crystalline strain is directly related to the crystal imperfections like dislocation or oxygen vacancy [32]. In ad-

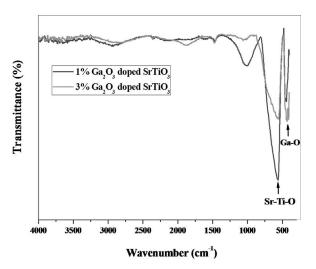


Fig. 2. FT-IR spectra of Ga<sub>2</sub>O<sub>3</sub> (1% & 3%) doped SrTiO<sub>3</sub> samples.

dition, the dislocation density is inversely proportional to the volume of the unit cell. Thus, from Table 1, we found that the dislocation density is slightly higher for the 3%  $Ga_2O_3$  doped  $SrTiO_3$  compared to that of the 1%  $Ga_2O_3$  doped sample using the volume of the unit cell, which indicates that a slightly higher value of strain for the 3%  $Ga_2O_3$  doped sample is indirectly correlated with the obtained strain values of the  $Ga_2O_3$  doped samples, as seen from the W-H plot. Dislocation plays a vital role in the resistance switching phenomenon [32].

# 3.3. Fourier transform infrared (FT-IR) spectra analysis

We plotted the wavenumber on the x-axis vs transmittance on the y-axis to identify the interaction between the chemical elements of the synthesized Ga<sub>2</sub>O<sub>3</sub>-doped strontium titanate, as represented in Fig. 2. We recorded a wavenumber range of 4000-400 cm<sup>-1</sup> for the detecting chemical bonds. The intense absorption bands appeared in the wavenumber range of  $400-700 \text{ cm}^{-1}$ , and are assigned to the normal characteristic stretching modes of the metal oxides (M-O) of stronium-oxygen (Sr-O), titanium-oxygen (Ti-O), gallium-oxygen (Ga-O) and titanium-oxygen-titanium (Ti-O-Ti) [33]. These types of normal characteristic modes were reported in the electromagnetic radiation of infrared (IR) bands wavenumbers less than 1000 cm<sup>-1</sup>. This was due to the deformation modes of titanium-oxygen (Ti-O) bonds in the TiO<sub>6</sub> octahedran stretching mode distortion or the distortion of Ti-O-Ti bridges. There was no additional band perceived in the FT-IR spectra, which indicated that the prepared samples corroborate the formation of strontium titanate material.

# 3.4. Raman spectra analysis

The vibrational-rotational spectra are generally plotted between the wavenumber on the x-axis and intensity on the y-axis to detect the chemical bond elements. This plot is commonly called the Raman spectroscopic study. The Raman spectra of the Ga<sub>2</sub>O<sub>3</sub> doped SrTiO<sub>3</sub> samples are laid out in Fig. 3. In both the Ga<sub>2</sub>O<sub>3</sub> doped SrTiO<sub>3</sub> samples, two broad scattering peaks appear around as (230-410) and (610-760) cm<sup>-1</sup> in the Raman spectra, which represent the second order Raman scattering modes respectively. In general, SrTiO<sub>3</sub> exhibits a cubic structure, so that Raman scattering was allowed only for second order. This was due to the presence of a broad active lattice vibration (phonon) mode [34].

The first order Raman scattering was not allowed because the lattice vibration mode becomes null at the middle of the allowed

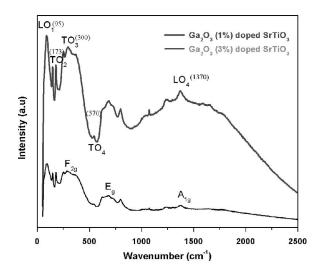


Fig. 3. Raman spectra of Ga<sub>2</sub>O<sub>3</sub> (1% & 3%) doped SrTiO<sub>3</sub> samples.

energy region (Brillouin zone). The Raman spectra of the active intense peak was noticed around 110 and 610 cm $^{-1}$  and ascribed to the longitudinal optical phonon and transverse modes [35], respectively. The transverse optical modes  $TO_2$  and  $TO_4$  were assigned to the bending mode vibrations of oxygen. In addition, the transverse optical mode  $TO_3$  represents the rotation of oxygen ions [36]. The longitudinal phonon ( $LO_4$ ) mode peak at 1370 cm $^{-1}$  reveals the wider, due to the induced deformation arising from an irregular distribution of  $Ga_2O_3$  in the  $SrTiO_3$  surface lattice [37]. The peak intensity keeps on the Raman LO mode increasing for 3%  $Ga_2O_3$  doped  $SrTiO_3$  a small active phonon mode seems around as 1076 cm $^{-1}$ . This was due to the degrees of lattice vibration was disturbed by the incorporation of  $Ga_2O_3$  dopant in cubic structured  $SrTiO_3$  material.

# 3.5. Field effect-scanning electron microscopy (FE-SEM) analysis

We have given the undoped SrTiO $_3$  sample micrographs for comparison with the  $Ga_2O_3$  doped  $SrTiO_3$  samples micrographs (FE-SEM) for finding the variation of the microstructural behavior (Fig. 4 (a-c)). This was due to the surface modification that occurred (ie. particulate systems likely to change their total surface tension) when increased  $Ga_2O_3$  dopant concentration was incorporated into the host lattice of  $SrTiO_3$ . In addition, we could notice the distinct morphology like cubical particles, spherical particles with non-uniform size and irregular sheets/spherical particles (as inset with a blue arrow in Fig. 4) for the undoped, 1% and 3%  $Ga_2O_3$  doped  $SrTiO_3$  samples. In addition, particles are clearly visible, suggesting that the prepared  $Ga_2O_3$  doped  $SrTiO_3$  samples are quite crystalline in nature.

#### 3.6. UV-visible absorption spectra analysis

The UV-Visible absorption spectra and Tauc plot of the  $Ga_2O_3$  doped  $SrTiO_3$  samples are depicted in Fig. 5 (a&b). In general, if a sharp optical absorption edge is found in the optical absorption spectra, the optical band gap energy could be calculated directly using the energy gap formula  $E_g=1240/\lambda_{abs}$ . This energy gap is called the direct band gap.

However, the absorption peak of Ga<sub>2</sub>O<sub>3</sub> doped SrTiO<sub>3</sub> samples is not detect sharp band edge; so it exhibits an indirect band gap nature of SrTiO<sub>3</sub> compound. We will find out the optical energy gap energy values from the indirect energy band gap na-

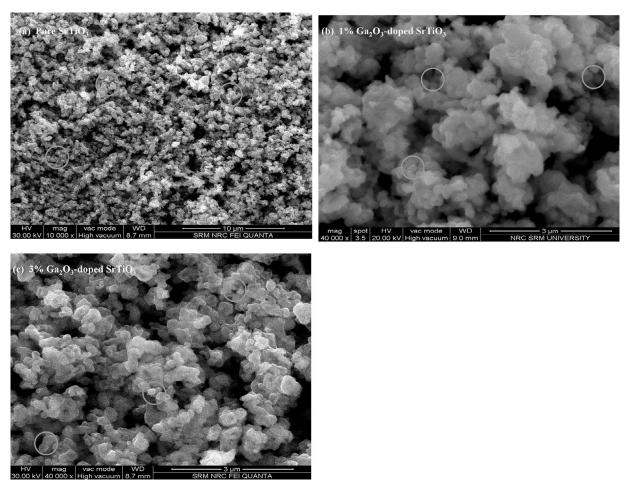


Fig. 4. FE-SEM images of (a) undoped SrTiO<sub>3</sub>, (b) 1% and (c) 3% Ga<sub>2</sub>O<sub>3</sub>-doped SrTiO<sub>3</sub> samples.

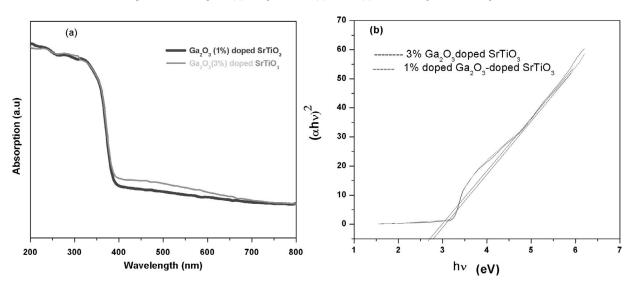


Fig. 5. (a) UV-absorption spectra and (b) Tauc plot of 1% and 3%  $Ga_2O_3$ -doped  $SrTiO_3$  samples.

ture of SrTiO $_3$  via the Tauc plots. The energy gap values were determined around 3.11 eV and 3.07 eV for 1% and 3%  $Ga_2O_3$  doped STO samples from the Tauc plot using optical absorption data. The energy gap decreasing of SrTiO $_3$  material with the increasing of Mn impurity concentration was reported by Wu et al. [7], which are correlate the phenomena with obtained energy gap values of  $Ga_2O_3$  doped SrTiO $_3$  samples. This was due to the red

shift was happened in the optical absorption spectra. In addition, optical band gap values are decreased with the addition of  $Ga_2O_3$  doped into the host lattice  $SrTiO_3$ . This decreasing optical band gap could have occurred, when the light source interacts with the  $Ga_2O_3$  dopant incorporated into the host lattice to create a multi-inner energy state in the valence band and conduction band.

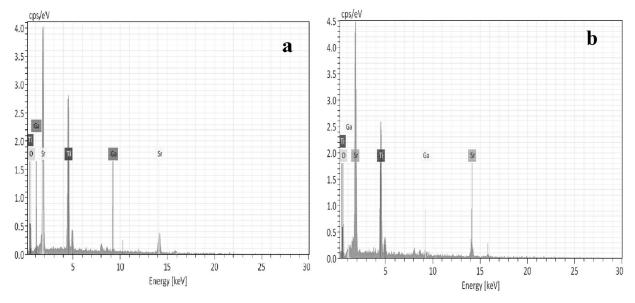


Fig. 6. EDX spectra of (a) 1% and (b) Ga<sub>2</sub>O<sub>3</sub> (3%) doped SrTiO<sub>3</sub> samples.

# 3.7. Energy dispersive X-ray (EDX) spectra analysis

We traced only strontium (Sr), titanium (Ti) and oxygen (O) with gallium (Ga) elements in the EDX images of the Ga<sub>2</sub>O<sub>3</sub> doped SrTiO<sub>3</sub> prepared samples as displayed in Fig. 6. These results indicate the evidence of the incorporation of Ga in strontium material. For the 1% Ga doped sample, the Sr element peak was located at energy level of 1.98 and 14 keV. In addition, the Ti element's position peak is at energy (0.5 and 4.5 KeV). Moreover, the O element is located at energy 0.51 KeV. The Ga element is position peak at 0.48 and 6.2 KeV, respectively. For the 3% Ga doped sample, we noticed the Sr peak position at energy (1.98 and 14.1KeV), Ti peak at energy (0.2 and 4.5 KeV), O element peaks at energy (0.5 KeV) and Ga element at 1.1 and 9.2KeV), respectively. Based on the EDX results, the peak position energy level is slightly changed due to the galium oxide dopant concentration in the host lattice.

# 3.8. X-ray photoelectron spectroscopy (XPS) analysis

The chemical oxidation state of metals and non-metal elements and their corresponding binding energy of the 3% Ga<sub>2</sub>O<sub>3</sub> doped SrTiO<sub>3</sub> sample are presented in XPS, as represented in Fig. 7. In the Ga<sub>2</sub>O<sub>3</sub> doped SrTiO<sub>3</sub> sample (Fig. 7a), metals like Sr, Ti, Ga and the non-metal (O) element were traced in the XPS. The deconvolution spectra of the Sr 3d ion are illustrated in Fig. 7b. A strong spinorbit interaction between the Sr  $(3d_{3/2})$  and Sr  $(3d_{1/2})$  has been found. The binding energies of Sr  $(3d_{3/2})$  and Sr  $(3d_{1/2})$  positions are 133 and 134.6 eV [1]. When the Ga impurity is introduced into the SrTiO<sub>3</sub> material, the drift in the binding energy of Sr 3d state is forwarded to the lower edge in the XPS studies. In addition, it showed that Ti<sup>3+</sup> signals were detected (Fig. 7c), giving Ti<sup>3+</sup>/Ti<sup>4+</sup> proportion of the 7.0 eV for Ga doped SrTiO<sub>3</sub> sample. The binding energies of Ti  $(2P_{3/2})$  and Ti  $(2P_{1/2})$  states are located at 458.1 and 463.8 eV [1]. In addition, the strong spin -orbit effect is displayed for the Ti (2p) state and is evident of the symmetric interaction between the Ti  $(2p_{3/2})$  and Ti  $(2p_{1/2})$  states and also between the Sr  $(3d_{3/2})$  and Sr  $(3d_{1/2})$  states. The position of the chemical oxidation state of the non-metal (oxygen) in the 3% Ga doped SrTiO<sub>3</sub> sample is shown in Fig. 7d. Fig. 7d, records the binding energy around 528.2 and 530.2 eV. In the Ga3d5 spectrum the peak was observed in 19.2 eV and it has been attributed to the trivalent Ga ion. Finally, based on the above XPS studies, it is confirmed that the Ga dopant has been incorporated into the  $SrTiO_3$  lattice. Furthermore, the XPS spectra have shown that the oxygen vacancy is present in the gallium oxide doped  $SrTiO_3$  material.

# 3.9. Dielectric analysis

Fig. 8 (a&b) displays the frequency dependent dielectric constant of the  $Ga_2O_3$  doped  $SrTiO_3$  samples at different temperatures (305, 323, 373, 423, 437, 523 and 573 K). In general, the polarization will be highly responsive in the lower frequency portion and inactive in the higher frequency region in nanomaterials samples [38]. In Fig. 8, we could notice that the high dielectric constants were observed in the lower frequency portion; this was because of the presence of interfacial polarization [39].

The electrons present in the samples were not able to remain within the field, when the frequency of the applied electric field increased and as a result, their directional delays beyond the field applied were altered. This was due to the interfacial polarization disappeared in the high frequency portion, which reduced the relative permittivity (dielectric constant). We could see that the 3%  $Ga_2O_3$  doped  $SrTiO_3$  observed high relative permittivity (40000) at lower frequency portion compared to that of the 1%  $Ga_2O_3$  doped sample (dielectric constant value ~ 10000) at 573K. In addition, the dielectric constant values of both the  $Ga_2O_3$  doped  $SrTiO_3$  samples increased with increasing temperatures [31]. This was due to the increasing contribution of space charge polarization [31].

Fig. 9 (a&b) displayed the frequency dependent dielectric loss of the Ga<sub>2</sub>O<sub>3</sub> doped SrTiO<sub>3</sub> samples at various temperatures. When there is an increase in the applied frequency, the dielectric loss gently decreases as exhibited in Fig. 9. We could detect that in the 3% Ga<sub>2</sub>O<sub>3</sub> doped SrTiO<sub>3</sub> sample, the dielectric loss value is slightly lesser compared to that of the 1% Ga<sub>2</sub>O<sub>3</sub> doped sample. The lower dielectric constant values obtained for the 3% doped SrTiO<sub>3</sub> sample suggested its excellent dielectric properties.

In addition, the variation of the dielectric constant values of  $Ga_2O_3$  doped samples depends on the temperatures. From the Fig. 9, we could notice that the dielectric loss increases with increasing of temperatures for the 1% and 3%  $Ga_2O_3$  doped  $SrTiO_3$  samples. This was due to the thermally activated behavior of the dielectric relaxation of the system [40].

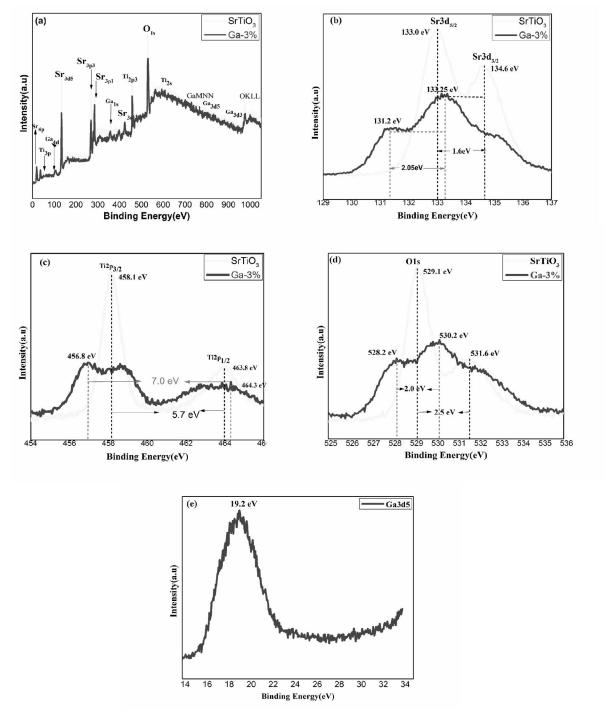
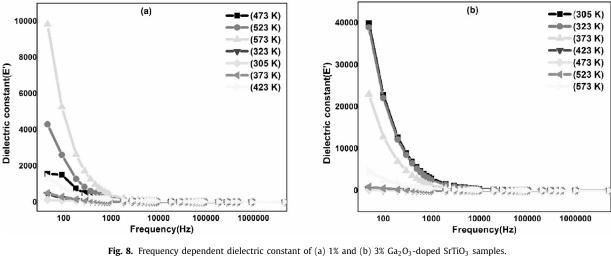


Fig. 7. XPS of 3%  $Ga_2O_3$  doped  $SrTiO_3$  sample.

# 3.10. Electrical conductivity analysis

Fig. 10 (a&b) demonstrates the frequency dependent electrical conductivity of the 1% and 3%  $Ga_2O_3$  doped  $SrTiO_3$  samples at various temperatures. From Fig. 10, the 3%  $Ga_2O_3$  doped  $SrTiO_3$  sample was observed to have slightly higher electrical conductivity compared to the 1% of  $Ga_2O_3$  doped sample. Generally, electrical conductivity increases as the optical band of nanomaterials is reduced. Based on the above concept, a slightly higher electrical conductivity was observed for the 3%  $Ga_2O_3$  doped  $SrTiO_3$ , which is in

good agreement with the obtained optical band gap  $(E_g)$  value of the  $3\%~Ga_2O_3$  doped (3.07~eV) compared to that of the  $1\%~Ga_2O_3$  doped SrTiO $_3$  material  $((E_g=3.11~eV).$  In addition, From the Fig. 10, we could observed that the electrical conductivity increases with an increasing the temperatures. This was due to the movement of hopping of charge carriers between the ions present in the material  $[40,\!41\,].$  The behavior of conductivity exhibits two distinct portions in the studied frequency range. In the low frequency region, the charge carriers have ample time to assemble at the interfaces of the electrode, and hence result in the electrode polarization ef-



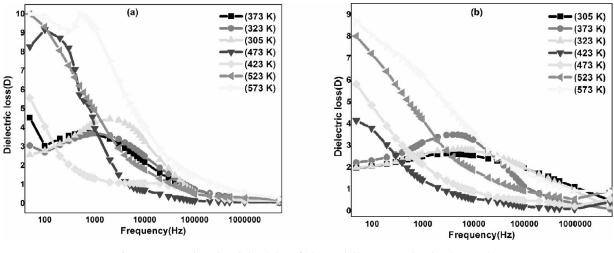


Fig. 9. Frequency dependent dielectric loss of (a) 1% and (b) 3% Ga<sub>2</sub>O<sub>3</sub>- doped SrTiO<sub>3</sub> samples.

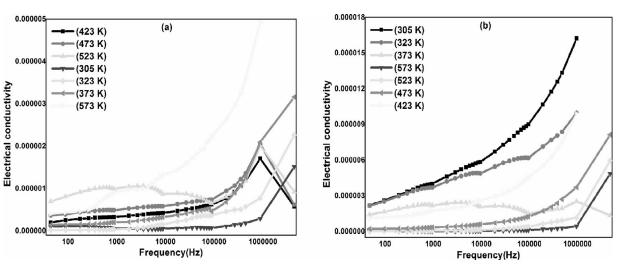


Fig. 10. Electrical conductivity of (a) 1% and (b) 3% Ga<sub>2</sub>O<sub>3</sub> doped SrTiO<sub>3</sub> samples.

fect [42]. The conductivity is less at the low frequency scale due to the presence of the grain boundary effect, which corresponds to the absence of the mobility charge carriers [43]. Moreover, the change in the electrical conductivity values of the Ga2O3 doped samples in the higher frequency region depends on the temperatures.

### 4. Conclusions

In summary, we synthesized 1% and 3 wt% of Ga<sub>2</sub>O<sub>3</sub> doped SrTiO<sub>3</sub> material via the mechanochemical synthesis followed by the calcination process. The XRD pattern of the synthesized Ga<sub>2</sub>O<sub>3</sub> doped SrTiO<sub>3</sub> materials confirmed the presence of a single phase

and cubic perovskite crystal structure. The Sr-O and Ti-O bond and feasible incorporation of gallium oxide ions into the parent lattice were detected by the FT-IR analysis. The Raman modes showed that the cubic phase of SrTiO<sub>3</sub> was confirmed which was supported by the cubic structure obtained from the XRD data. Non-uniform spherical and irregular sheets/spherical particles were identified from the morphology studies. The 3% Ga<sub>2</sub>O<sub>3</sub> doped SrTiO<sub>3</sub> material has a slightly reduced energy gap relative to the 1% Ga<sub>2</sub>O<sub>3</sub> doped sample, and this was confirmed by optical spectra studies. The possible oxidation states of elements, the main drift in the binding energy of the elements, and surface defects (oxygen vacancy) in the synthesized Ga<sub>2</sub>O<sub>3</sub>-doped SrTiO<sub>3</sub> material have been discussed in the XPS studies. The frequency dependent range's relative permittivity and dielectric losses have been examined while the space charge polarization occurs. Hence the Ga<sub>2</sub>O<sub>3</sub>-doped SrTiO<sub>3</sub> ceramic compounds can find potential applications in the fabrication of optoelectronic devices.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interest or personel relationship that could have appeared to influence the work reported in this paper.

#### **CRediT authorship contribution statement**

**G. Saravanan:** Methodology, Writing - original draft. **K. Ramachandran:** Investigation, Writing - original draft, Writing - review & editing. **J. Gajendiran:** Investigation, Writing - original draft, Writing - review & editing. **S. Gnanam:** Writing - review & editing.

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# References

- [1] A. Karaphun, S. Hunpratub, E. Swatsitang, Effect of annealing on magnetic properties of Fe-doped SrTiO<sub>3</sub> nanopowders prepared by hydrothermal method, Microelectron. Eng. 126 (2014) 42–48.
- [2] R. Li, F. Liu, C. Zhang, J. Liu, J. Zhou, L. Xu, Electrical properties of Fedoped SrTiO<sub>3</sub> with B-site-deficient for SOFC anodes, Ceram. Int. 45 (2019) 21684–21687.
- [3] X. Wang, Z. Wang, Q. Hu, C. Zhang, D. Wang, L. Li, Room temperature multiferroic properties of Fe-doped nonstoichiometric SrTiO<sub>3</sub> ceramics at both A and B sites, Solid State Commun. 289 (2019) 22–26.
- [4] H. Fujishita, Y. Arai, H. Okamoto, T. Yamaguchi, Low temperature dielectric and magnetic properties of Fe-ion-doped SrTiO<sub>3</sub>, Phys. B 521 (2017) 1–5.
- [5] A. Lacz, L. Lancucki, R. Lach, B. Kamecki, E. Drozdz, Structural and electrical properties of Cr-doped SrTiO<sub>3</sub> porous materials, Int. J. Hydrogen Energy 43 (2018) 8999–9005.
- [6] D. Yang, X. Zhao, X. Zou, Z. Zhou, Z. Jiang, Removing Cr (VI) in water via visible-light photocatalytic reduction over Cr-doped SrTiO<sub>3</sub> nanoplates, Chemosphere 215 (2019) 586–595.
- [7] G. Wu, P. Li, D. Xu, B. Luo, Y. Hong, W. Shi, C. Liu, Hydrothermal synthesis and visible-light-driven photocatalytic degradation for tetracycline of Mndoped SrTiO<sub>3</sub> nanocubes, Appl. Surf. Sci. 333 (2015) 39–47.
- [8] V. Trepakov, M. Makarova, O. Stupakov, E.A. Tereshina, J. Drahokoupil, M. Cernanský, et al., Synthesis, structure and properties of heavily Mn-doped perovskite-type SrTiO<sub>3</sub> nanoparticles, Mater. Chem. Phys. 143 (2014) 570–577.
- [9] Y. Qiao, W. Li, Y. Zhang, L. Jing, C. Gao, W. Cao, et al., Hole-pinned defect-dipoles induced colossal permittivity in Bi doped SrTiO<sub>3</sub> ceramics with Sr deficiency, J. Mater. Sci. Technol. 44 (2020) 54–61.

- [10] M.H. Fisoldin, M.S. Idris, R.A.M. Osman, K.N.D.K. Muhsen, Z.A.Z. Jamall, Electrical properties of Sn doped SrTiO<sub>3</sub>, AIP Conf. Proceed. 2203 (2020) 020044.
- [11] I.A. Sluchinskaya, A.I. Lebedev, electronic and magnetic properties of structural defects in SrTiO<sub>3</sub> (Co), J. Alloys Comp. 820 (2020) 153243.
- [12] J. Xu, Y. Wei, Y. Huang, J. Wang, X. Zheng, Z. Sun, et al., Solvothermal synthesis nitrogen doped SrTiO<sub>3</sub> with high visible light photocatalytic activity, Ceram. Int. 40 (2014) 10583–11059.
- [13] I. Tamiolakis, D. Liu, F.X. Xiao, J. Xie, I.T. Papadasd, T. Salim, et al., Meso-porous implantable Pt/SrTiO<sub>3</sub>:C,N nanocuboids delivering enhanced photocatalytic H<sub>2</sub>-production activity via plasmon-induced interfacial electron transfer, Appl. Catal. B: Environ. 236 (2018) 338–347.
- [14] M. Qin, F. Gao, J. Cizek, S. Yang, X. Fan, L. Zhao, et al., Point defect structure of La-doped SrTiO3 ceramics with colossal Permittivity, Acta Mater. 164 (2019) 76–89.
- [15] J. Liu, C.L. Wang, Y. Li, W.B. Su, Y.H. Zhu, J.C. Li, L.M. Me, Influence of rare earth doping on thermoelectric properties of SrTiO<sub>3</sub> ceramics, J. Appl. Phys. 114 (2013) 223714.
- [16] P. Blennow, A. Hagen, K.K. Hansen, L. Reine Wallenberg, M. Mogensen, Defect and electrical transport properties of Nb-doped SrTiO<sub>3</sub>, Solid State Ion. 179 (2008) 2047–2058.
- [17] I. Velasco-Davalos, F. Ambriz-Vargas, R. Thomas, Ruediger, surface preparation of (110) oriented pure and Nb doped SrTiO<sub>3</sub> single crystal substrates by microwave assisted hydrothermal method, Surf. Coat. Technol. 283 (2015) 108–114.
- [18] J.Q. Zheng, Y.J. Zhu, J.S. Xu, B.Q. Lu, C. Qi, F. Chen, J. Wu, Microwave assisted rapid synthesis and photocatalytic activity of mesoporous Nd-doped SrTiO<sub>3</sub> nanospheres and nanoplates, Mater. Lett. 100 (2013) 62–65.
- [19] A.M. Dehkordi, S. Bhattacharya, J. He, H.N. Alshareef, T.M. Tritt, Significant enhancement in thermoelectric properties of polycrystalline Pr-doped SrTiO<sub>3</sub> -δ ceramics originating from nonuniform distribution of Pr dopants, Appl. Phys. Lett. 104 (2014) 193902.
- [20] X. Wang, Q. Hu, L. Li, X. Lu, Effect of Pr substitution on structural and dielectric properties of SrTiO<sub>3</sub>, J. Appl. Phys. 112 (2012) 044106.
- [21] A.M. Dehkordi, S. Bhattacharya, T. Darroudi, J.W. Graff, U. Schwingenschlögl, H.N. Alshareef, et al., Large thermoelectric power factor in Pr-doped SrTiO<sub>3</sub>-δ ceramics via grain-boundary-induced mobility enhancement, Chem. Mater. 26 (2014) 2478–2485.
- [22] D.K. Singh, J. Manam, D.K. Singh, J. Manam, Optical spectroscopic and thermal quenching behaviour of perovskite SrTiO<sub>3</sub>:Sm<sup>3+</sup> orange emitting phosphors for lighting applications, J. Mater. Sci.: Mater. Electron. 29 (2018) 5579–5588.
- [23] G. Saravanan, K. Ramachandran, J. Gajendiran, E. Padmini, Effect of ceria concentration of Strontium titanate on the structural, optical, dielectric and electrical properties, Chem. Phys. Lett. (2020) 137314.
- [24] M. Abdi, V. Mahdikhah, S. Sheibani, Visible light photocatalytic performance of La-Fe co- doped SrTiO<sub>3</sub> perovskite powder, Opt. Mater. 102 (2020) 109803.
- [25] D. Luo, W. Xiao, F. Lin, C. Luo, X. Li, Effects of a-site deficiency on the electrical conductivity and stability of (La, Co) co-doped SrTiO<sub>3</sub> anode materials for intermediate temperature solid oxide fuel cells, Adv. Powder Technol. 27 (2016) 481–485.
- [26] J. Han, Q. Sun, Y. Song, J. Han, Q. Sun, Y. Song, Enhanced thermoelectric properties of La and Dy co-doped, Sr-deficient SrTiO<sub>3</sub> ceramics, J. Alloys Comp. 705 (2017) 22–27.
- [27] C.Y. Guo, X. Qi, RF magnetron sputter deposition and electrical properties of La and Y doped SrTiO<sub>3</sub> epitaxial films, Mater. Des. 179 (2019) 107888.
- [28] T.S. Jamil, H.A. Abbas, A.M. Youssief, E.S. Mansor, F.F. Hammad, The synthesis of nano-sized undoped, Bi doped and Bi, Cu co-doped SrTiO<sub>3</sub> using two sol-gel methods to enhance the photocatalytic performance for the degradation of dibutyl phthalate under visible light, C, R. Chimie. 20 (2017) 97–106
- [29] J. Liu, Q. Liu, Z. Nie, S. Nie, D. Lu, P. Zhu, Dielectric relaxations in fine-grained SrTiO<sub>3</sub> ceramics with Cu and Nb co doping, Ceram. Int. 45 (2019) 10334– 10341
- [30] J.H. Lin, C.S. Hwang, F.R. Sie, Preparation and thermoelectric properties of Nd and Dy co-doped SrTiO<sub>3</sub> bulk materials, Mater. Res. Bull. 122 (2020) 110650.
- [31] M.S. Alkathy I, K.C. James Raju I, Effect of Bi and Li co-substituted SrTiO<sub>3</sub> ceramics on structural and dielectric properties, J. Mater. Sci.: Mater. Electron. 27 (2016) 8957–8965.
- [32] J. Chen, T. Sekiguchi, J. Li, S. Ito, W. Yi, A. Ogura, Investigation of dislocations in Nb-doped SrTiO<sub>3</sub> by electron-beam-induced current and transmission electron microscopy, Appl. Phys. Lett. 106 (2015) 102109.
- [33] B.V. Prasad, C. Narsinga Rao, J.W. Chen, D. Suresh Babu, Abnormal high dielectric constant in SmFeO<sub>3</sub> semiconductor ceramics, Mater. Res. Bull. 46 (2011) 1670–1673.
- [34] V. Eswaramoorthi, S. Sebastian, R. Victor Williams, Influence of Ga doping on the structural optical and electrical properties of Ba<sub>0.6</sub>Sr<sub>0.4</sub>TiO<sub>3</sub> Thin films, Int. J. Sci. Technol. 4 (2015) 86–91.
- [35] S.D. Shenoy, P.A. Joy, M.R. Anantharaman, Effect of mechanical milling on the structural, magnetic and dielectric properties of Co precipitated ultrafine zinc ferrite, J. Magn. Magn. Mater. 269 (2004) 217–226.
- [36] X. Wei, G. Xu, Z.H. Ren, Y.G. Wang, G. Shen, G.R. Han, Composition and shape control of single-crystalline Ba<sub>1-x</sub>Sr<sub>x</sub>TiO<sub>3</sub> (x = 0-1) nano crystals via a solvothermal route, J. Cryst. Growth 310 (2008) 4132–4137.
- [37] F.A. Rabuffetti, H.S. Kim, J.A. Enterkin, Y.M. Wang, C.H. Lanier, L.D. Marks, et al., Synthesis-dependent first-order raman scattering in SrTiO<sub>3</sub> nanocubes at room temperature, Chem. Mater. 20 (2008) 5628–5635.

- [38] T. Xian, H. Yang, L. Di, J. Ma, H. Zhang, J. Dai, Photocatalytic reduction synthesis of SrTiO<sub>3</sub>-graphene nanocomposites and their enhanced photocatalytic activity, Nanoscale Res. Lett. 9 (2014) 327.
- [39] M.C.F. Alves, S.C. Souza, H.H.S. Lima, M.R. Nascimento, M.R.S. Silva, J.W.M. Espinosa, et al., Influence of the modifier on the short and long range disorder of stannate perovskites, J. Alloys Comp. 476 (2009) 507–512.
   [40] S. Sagadevan, S. Vennila, J. Anita Lett, A.R. Marlinda, N.A.B. Hamizi, M.R. Johan,
- [40] S. Sagadevan, S. Vennila, J. Anita Lett, A.R. Marlinda, N.A.B. Hamizi, M.R. Johan, Tailoring the structural, morphological, optical, thermal and dielectric characteristics of ZnO nanoparticles using starch as a capping agent, Results Phys. 15 (2019) 102543.
- [41] U. Adem, N. Mufti, A.A. Nugroho, G. Catalan, B. Noheda, T.T.M. Palstra, Dielectric relaxation in YMnO<sub>3</sub> single crystals, J. Alloys Comp. 638 (2015) 228– 232.
- [42] Y. Xu, T. Liu, Y. He, X. Yuan, Dielectric properties of Ba0.6Sr0.4TiO3-Sr(Ga0.5Ta0.5)O3 solid solutions, IEEE Trans. Ultrason. Ferroelectr. Freq. Cont. 55 (2008) 2369-2376.
- [43] R. Schmidt, A. Basu, A.W. Brinkman, Z. Klusek, P.K. Datta, Electron-hopping modes in  $NiMn_{(2)}O_{(4+\delta)}$  materials, Appl. Phys. Lett. 86 (2005) 501–503.