Characterization and Electrical Properties of Doped SrTiO₃ Ceramics

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ABSTRACT: Pure, manganese and zinc doped SrTiO₃ ceramic powder particles were synthesized via conventional solid state route diffusion method. After ball milling, these samples were calcined at 1250⁰C, 1050⁰C and 1050⁰C for 9hr, 8hr and 8hrs respectively. Further these pellets were sintered at 1300⁰C, 1250⁰C and 1250⁰C for4hr, 2hr and 2hrs respectively. Subsequently the samples were characterized using XRD, SEM, EDAX and FTIR for the elucidation of structural, surface morphological, elemental and optical properties respectively. The average crystalline sizes were accomplished as 28.14nm, 40.85nm and 98.73nm respectively and lattice parameters were calculated as 3.9541A⁰, 3.903 A⁰ and 4.8702 A⁰ respectively using X-Ray diffraction spectra. Apart from these AC, DC-activation energies were computed using lnσ Vs 1/T plots and optical energies were found with the help of FTIR spectra. The average grain sizes were calculated as 1.41μm, 1.15μm and 1.65 μm respectively from Scanning Electron Microscopy images.

Keywords: X-ray Diffract meter, Scanning Electron Microscopy, FTIR, Solid state route method, AC-conductivity

INTRODUCTION

SrTiO₃ is an ABO₃ perovskite structured material and exhibits excellent optical transparent properties in visible region and therefore it is being used as a candidate material in optoelectronic devices[1].At room temperature strontium titanate exhibits cubic structure and at approximately 110K the structure was changed from cubic to tetragonal[2].Manganese doped SrTiO₃ revealed a single cubic perovskite phase similar to SrTiO₃ and second phase peaks begin to appear in the XRD structure which are suitable to the peaks of MnTiO₃ with increase of Mn content in the lattice site of SrTiO₃[3].The average grain size of Mn doped SrTiO₃ doesn't depend upon the concentration Mn content but depends on the sintering conditions.AC-Conductivity studies of Mn doped SrTiO₃ revealed that ac-conductivity is increasing with increase of temperature due to the hopping mechanism and the activation energies E_a = 0.068eV,0.087eV and 0.079eV when τ_0 =2.1x10^{-14} s, 0.8x10^{-14} s and 0.7x10^{-14} s were carried out using Cole-Cole equation and Arrhenius law $\tau = \tau_0 \exp(-E_a/KT)$[4].The increase in the activation energy is due to increase of the concentration of polar dipoles and because of intensification of dipole interaction through the phonons of SrTiO₃ lattice[4]. ZnO is an excellent material for having outstanding optical and electronic properties like wide band gap round about 3.37 eV [5-6]. Zn doped SrTiO₃ and pure SrTiO₃ expressed the band gap of 3.2eV in its UV-Visible absorption spectra and it exhibits photo catalytic activity[7-8]. In this investigation the author is intended to study the FTIR spectra, AC and DC-Conductivity properties which have not been studied almost in the literature to the best of the author's knowledge along with XRD, SEM and EDAX analysis.

Preparation Of The Samples

In order to synthesize the pure, Mn and Zn doped SrTiO₃ ceramic powder particles SrCO₃ (99.5% purity), TiO₂ (99.5% purity), MnO₂ (99.5% purity) and ZnO (99.5% purity) were taken as the raw materials. In these materials initially to prepare pure SrTiO₃, Mn and Zn doped SrTiO₃ ceramic powders, (SrCO₃, TiO₂), (SrCO₃, MnO₂,

TiO_2) and ($SrCO_3$, ZnO, TiO_2) were weighed and mixed in their Stoichiometric ratio. Furthermore these were ball milled for nearly 20hr, 16hr and 12hr respectively. After wards samples were calcined at 1250^0C, 1050^0C and 1050^0C for 9hr, 8hr and 8hrs respectively. Further the pellets were sintered at 1300^0C, 1250^0C and 1250^0C for4hr, 2hr and 2hrs respectively. Pellets were cooled to room temperature at the rate of 5^0C /min. and these were coated with silver paste on either side of the pellets without contacting the corners. Later samples were characterized using XRD, SEM, EDAX, FTIR and HIOKI 3532-50 LCR HiTESTER for the elucidation of structural, surface morphological, elemental, optical and ac-conductivity properties respectively.

RESULTS AND DISCUSSIONS

XRD analysis

XRD technique is used to determine the structure of compound and in the present investigation Pure, manganese and zinc doped $SrTiO_3$ structures have been revealed as cubic. Lattice parameters were found as $3.9541A^0$, $3.903 A^0$ and $4.8702 A^0$ (a=b=c) for $SrTiO_3$, $Sr_{0.5} Mn_{0.5}TiO_3$ and $Sr_{0.5} Zn_{0.5}TiO_3$ respectively and are in consistent with standard values in literature[9, 3, 10]. From XRD profile (h k l) value were calculated as (100),(110),(111),(200),(210),(211),(220) and (310).Furthermore the average crystalline sizes(28.145nm,40.85nm and 98.73nm) using Scherer equation (D_p)[11],average dislocation densities (138×10^{13}m^{-3}, 601×10^{12} m^{-3} and 842×10^{12} m^{-3}) and average elastic strains (0.1725,0.2646 and 0.2693) were established for ST, Mn and Zn doped ST respectively using the following formula .As the crystalline size is nano this depresses the calcination and sintering temperatures of the specimen[12].

Average crystalline sizes (D_p) = K λ/β Cosθ

Where K is a constant and is equal to 0.9 & λ=0.15418 nm (CuK$_\alpha$).

Average dislocation density (ρ) =1/D^2 and

Average elastic strain (E_{strain}) = β/4tanθ

Where β is full width half maxima.

As just described in Andrei L.Kholkin et al[3] XRD profile of $Sr_{1-x}Mn_xTiO_3$ at x=0 the phases are consistent with undoped strontium titanate and up to x<0.10 there is no second phase appearance except single phase but mean while i.e. x≥0.10 SMnT showed some second phases starting to appear which are consistent with $MnTiO_3$ phases. On the other hand the XRD profile of $SrTi_{1-y}Mn_yO_3$ showed a cubic structure without having any second phases for various concentrations of manganese at x≤0.15.In this investigation at x=0.5 the XRD profile was carried out and exhibited some second phases along with single phase structure. It is confirmed that the specified(star symbol) phases in following XRD are due to presence of $MnTiO_3$ and this explicitly establishes a fact that formation of second phases depend upon the occupation of manganese into the site of ST. In $Sr_{0.5}Zn_{0.5}TiO_3$ ceramics also some second phase structures have been appeared and were consistent with $ZnTiO_3$ phases. More over due to presence of two impurities (Mn and Zn) the resultant structure was not changed from cubic to any other structure. Due to the presence of second phases in XRD the compound loses its good properties such as optical, dielectric, photo catalytic, thermoelectric and conductivity properties etc.

SEM and EDAX analysis

Scanning electron microscopy is used effectively in micro analysis and failure analysis of solid materials. This approach is useful in qualitatively or semi-quantitatively determining chemical compositions, crystalline structure and crystal orientations. The following SEM figures are made at the different spots having different magnifications and in 5µm, 3 µm range. In the SEM images few dislocations and grains along with grain boundaries have been observed. The average grain sizes (G_a) of $SrTiO_3$, $Sr_{0.5}Mn_{0.5}TiO_3$ and $Sr_{0.5}Zn_{0.5}TiO_3$ calculated as1.41µm, 1.15µm and 1.65 µm respectively using the following formulae.

Average grain size $G_a = 1.5$ L/MN.

Where L=the total test line length, M=the magnification,

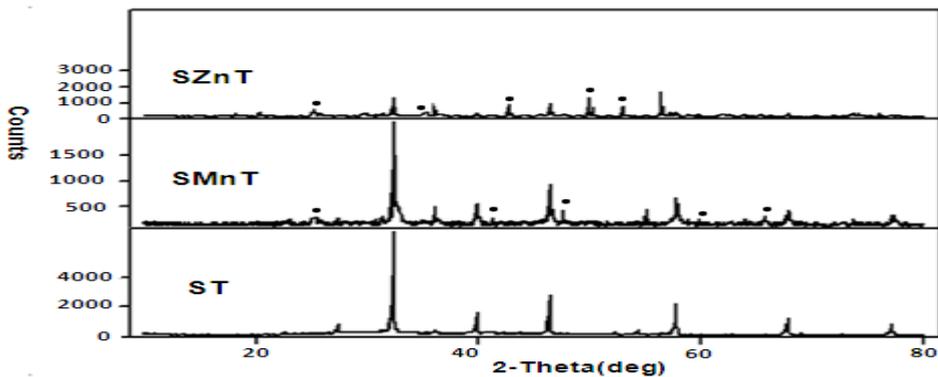N=the total number of intercepts which the grain boundary makes with the line.

Figure. 1 XRD results of pure $SrTiO_3$ (ST), $Sr_{0.5}Mn_{0.5}TiO_3$ (SMnT) and $Sr_{0.5}Zn_{0.5}TiO_3$ (SZnT) ceramics
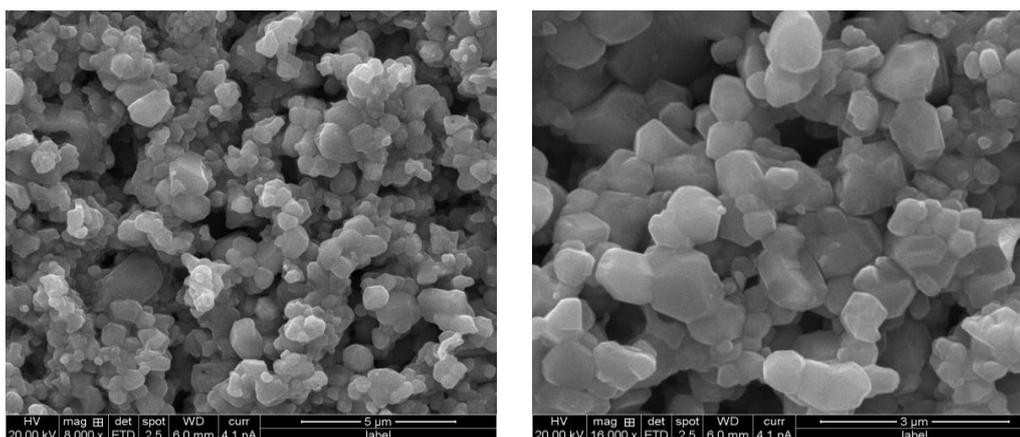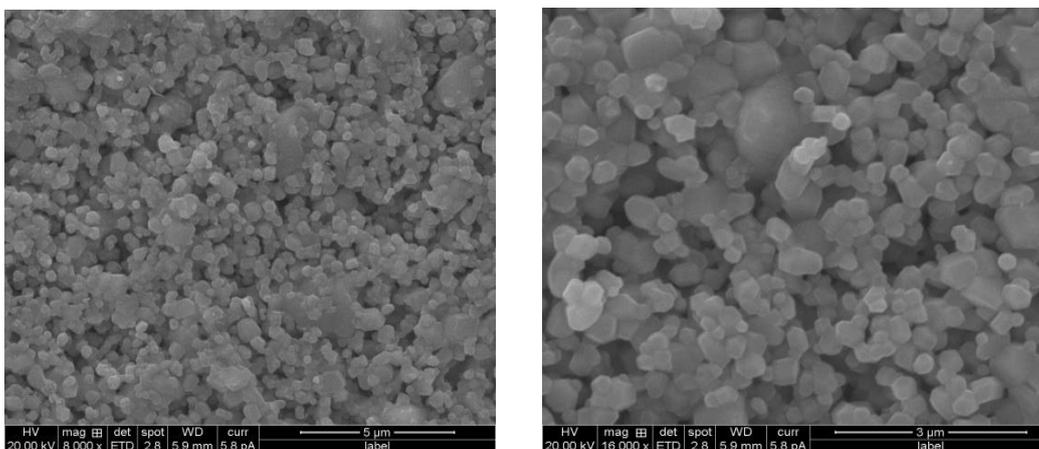

Figure 2.SEM images of undoped $SrTiO_3$ Ceramics

Figure3.SEM images of $Sr_{0.5}Mn_{0.5}TiO_3$ ceramics.
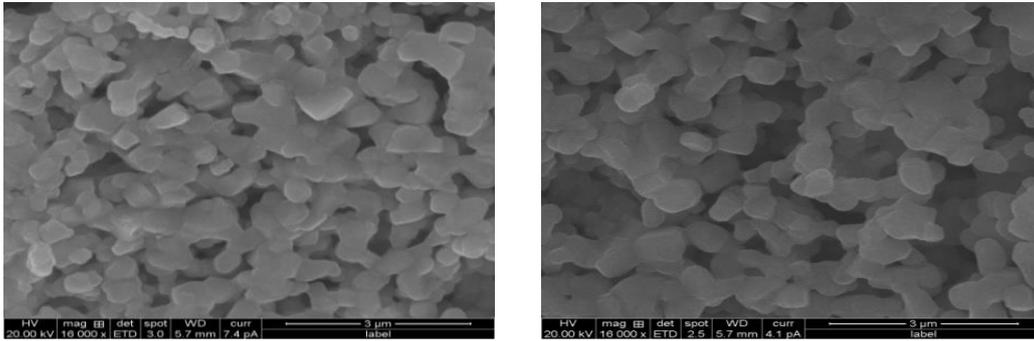
Figure 4.SEM images of $Sr_{0.5}Zn_{0.5}TiO_3$ ceramics.

It is obvious from the SEM images of $SrTiO_3$, $Sr_{0.5}Mn_{0.5}TiO_3$ and $Sr_{0.5}Zn_{0.5}TiO_3$ that the grain growth is high for ST while lower grain growth is observed for SMnT and SZnT ceramics. This due to the fact of sintering temperature of pellets[13].

An EDAX detector is used to separate the characteristic X-rays of different elements into an energy spectrum and EDAX system software is used to analyze the energy spectrum in order to determine the abundance of specific elements. Energy peaks corresponds to the various elements in the sample. Energy Dispersive X-ray Spectroscopy can be used to find the chemical composition of material down to a spot size of a few microns and to create element composition maps over a much broader raster area. Together, these capabilities provide fundamental compositional information for a variety of materials, including polymers and metals. The following image shows the elements present in sample and their concentrations. In the following EDAX images the elements present in the compounds with their concentrations were shown.
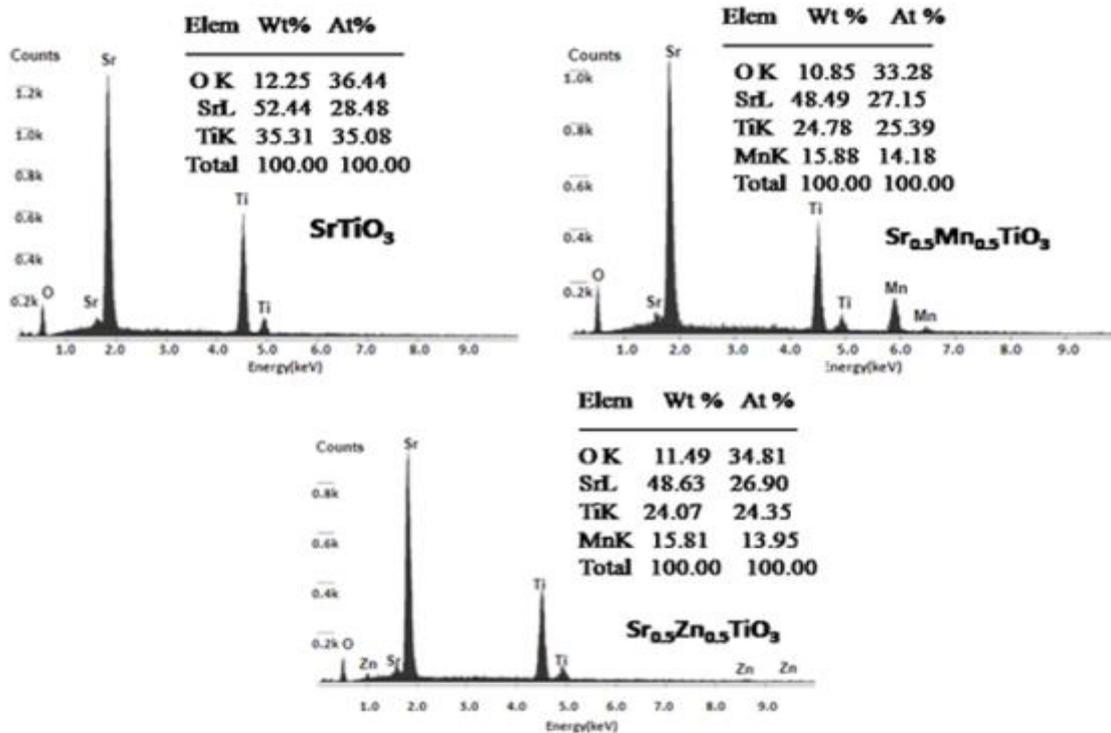

Figure 5 EDAX images of pure $SrTiO_3$, $Sr_{0.5}Mn_{0.5}TiO_3$ and $Sr_{0.5}Zn_{0.5}TiO_3$ ceramics

FTIR analysis

In the following FTIR transmittance spectra of undoped $SrTiO_3$ the peak transmittance 19.47% observed at wave number 1181.4749cm^{-1} which corresponds to Ti-O stretching mode and at this wave number optical energy was measured as 0.147x10^{-2}eV. FTIR transmittance (%T) spectra of Mn doped $SrTiO_3$ the broad bands observed at wave number 563.7512 cm^{-1}, 1480.9524 cm^{-1}, 3618.2463 cm^{-1} and 3770.3541 cm^{-1} and optical energies at these bands   measured were 0.7041x10^{-3}eV ,0.18497x10^{-2}eV,0.45191x10^{-2}eV and 0.47099x10^{-2}eV respectively. The peaks at 563.7512 cm^{-1} and 1480.9524 cm^{-1} were probably due to Ti-O stretching vibrations, just as Yamaguchi et al[14] and the rest two peaks were probably the Mn-O stretching vibrations. The transmittance spectrum of present sample called the $Sr_{0.5}Zn_{0.5}TiO_3$ acquired broad bands at the wave numbers 625.62247 cm^{-1} and 817.757920 cm^{-1} due to the presence of Ti-O stretching vibrations[14] and the other band at wave number 1508.377512 cm^{-1} may probably due to presence of Zn-O stretching vibrations. The optical energies of these broad bands were calculated as 0.7807x10^{-3}eV, 0.10205x10^{-2}eV and 0.18839x10^{-2}eV respectively.
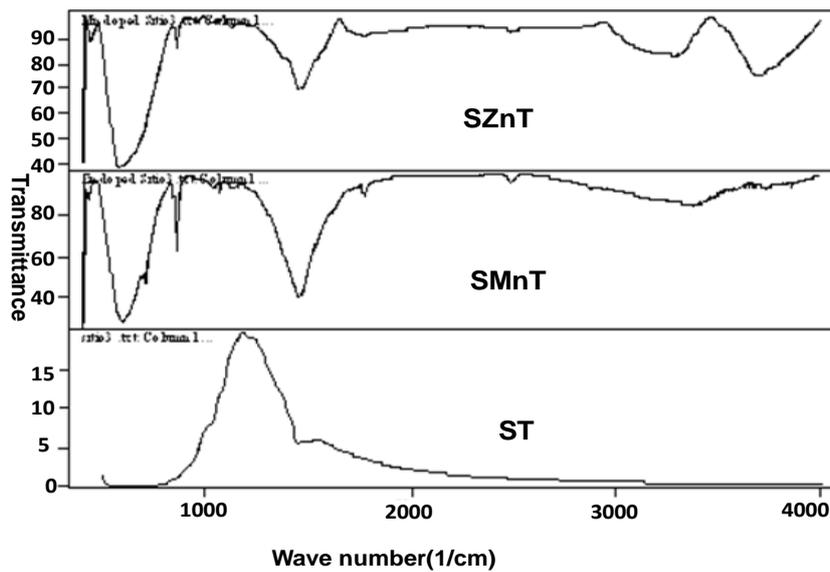

Figure 6.FTIR spectra of $SrTiO_3$ (ST), $Sr_{0.5}Mn_{0.5}TiO_3$ (SMnT) and $Sr_{0.5}Zn_{0.5}TiO_3$ (SZnT) ceramics

AC-Conductivity

The following plots illustrate the variation of ac-conductivity (σ_{ac}) with increase of frequency ranging from 100Hz-5MHz for different temperatures of undoped $SrTiO_3$,$Sr_{0.5}Mn_{0.5}TiO_3$, and $Sr_{0.5}Zn_{0.5}TiO_3$ ceramics using HIOKI 3532-50 LCR HiTESTER. The results expressed that the ac-conductivity is increasing as increasing frequency and temperature of the sample. At higher frequencies and temperatures the increase in ac-conductivity is very high. This may be due to the strong hopping mechanism. The increase in the graph is linear and therefore this is linear hopping mechanism. In the present investigation the samples $SrTiO_3$, $Sr_{0.5}Mn_{0.5}TiO_3$ and $Sr_{0.5}Zn_{0.5}TiO_3$ showed the maximum σ_{ac}-value of 0.259826 FHz /m at 1MHz frequency (300^0C), 0.00725694 FHz /m at the temperature of 400^0C (5MHz) and 7.80193E-06 FHz /m value at 400^0C (at 1MHz) when   computed using the following equation.

$\sigma_{ac}= \varepsilon_0\ \varepsilon_r\omega\ tan\delta$

Where ε_0=8.852x10^{-12} F/m (permittivity of free space), ε_r = dielectric constant,
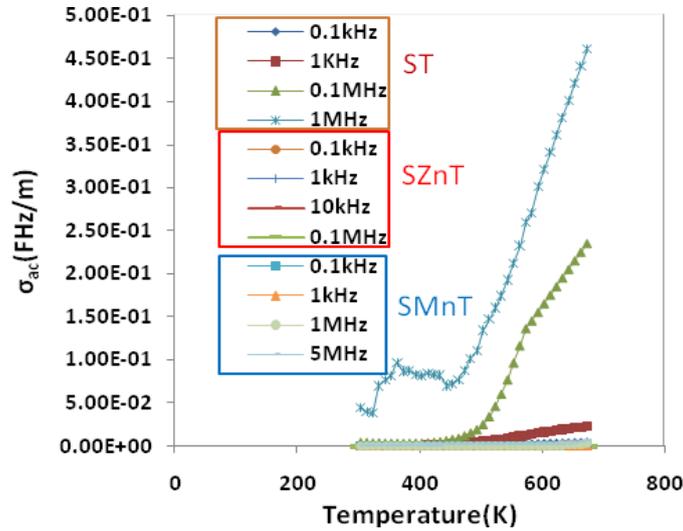
ω=2πf and tanδ=dielectric loss

Figure 7. σ_{ac} Vs Temperature plots of pure SrTiO$_3$ (ST), Sr$_{0.5}$Mn$_{0.5}$TiO$_3$ (SMnT) and Sr$_{0.5}$Zn$_{0.5}$TiO$_3$ (SZnT) ceramics

The ac-activation energies were calculated as 0.017eV (at 0.1kHz), 0.0033 eV (at 1kHz) for ST, 0.047eV (at 0.1kHz),0.057eV(1kHz) for Mn doped ST and 0.071eV(0.1kHz),0.11eV(1kHz) for Zn doped ST using Arrhenius law as

$\sigma_{ac} = \sigma_0 \exp (-E_a/K_bT)$

Where E$_a$ =ac-activation energy K$_b$=8.6x10^{-5}eV

From the results it is confirmed that as increasing the frequency, ac-activation energies go on increasing.

DC-Conductivity

DC-conductivity of SrTiO$_3$, Sr$_{0.5}$Mn$_{0.5}$TiO$_{3,}$ and Sr$_{0.5}$Zn$_{0.5}$TiO$_3$ ceramics were performed using HIOKI 3532-50 LCR HiTESTER at a fixed frequency of 100Hz. DC-conductivity of SrTiO$_3$, is increasing with increase of temperature up to 350K due to electro static interaction between a conduction electron or hole which results in displacement of nearby ions and later decreases up to 425K due to decrease of electro static interaction which causes to decrease of hopping mechanism. For further temperatures due to linear hopping mechanism dc-conductivity goes on increasing. This kind of activated hopping mechanism i.e. for the process of jumping of carriers, the mobilities are found to be proportional to –E/K$_b$T and from Heikes and Johnson expression for conductivity[15] the activation energies were computed as 0.9484eV, 0.9624 eV and 0.9579 eV for SrTiO$_3$, Sr$_{0.5}$Mn$_{0.5}$TiO$_{3,}$ and Sr$_{0.5}$Zn$_{0.5}$TiO$_3$ ceramics. This establishes a fact that there is no considerable variation of activation energies of the three samples. The increasing and decreasing behavior of dc-conductivity and lnσ_{dc} with reference to the temperature and 1000/T were clearly described in the following plots. DC-conductivities and activation energies were calculated using the following equations.

$\sigma_{dc}=L/RA$

$\sigma_{dc} = \sigma_0 \exp (-E_a/KT)$

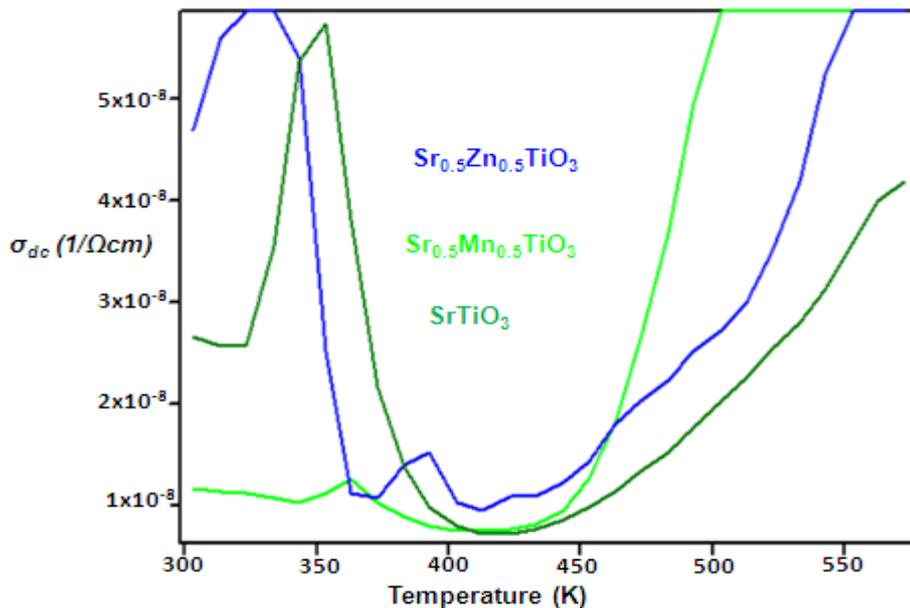Where E$_a$= dc-activation energy, K$_b$=8.6x10^{-5}eV (Boltzmann constant) and T=absolute temperature

Figure 8. σ_{dc} Vs Temperature plot of $SrTiO_3$, $Sr_{0.5}Mn_{0.5}TiO_3$, and $Sr_{0.5}Zn_{0.5}TiO_3$ ceramics
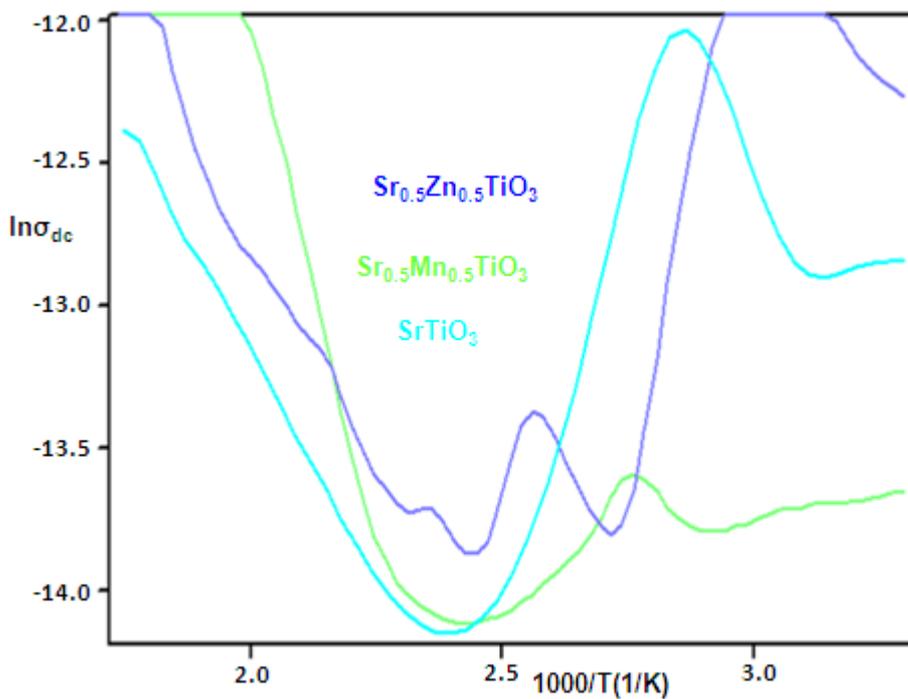
Figure 9. $ln\sigma_{dc}$ Vs 1000/T plots of $SrTiO_3$, $Sr_{0.5}Mn_{0.5}TiO_3$, and $Sr_{0.5}Zn_{0.5}TiO_3$ ceramics

CONCLUSIONS

In conclusion this work revealed that (i) in XRD spectra the formation of single phase structures of Mn and Zn doped strontium titanate depend upon the dopant site occupancy. There is no obvious difference among the pure, Mn and Zn doped Strontium titanate in the crystalline surface morphology characteristics except variation of

7

grain growth which is a temperature dependent parameter and XRD peak positions with an exception of few specified second phases due to increase of concentrations of dopants. (ii) since the present compounds are not organic type, no organic functional groups were present i.e. the broad bands in FTIR spectra of SrTiO$_3$, Sr$_{0.5}$Mn$_{0.5}$TiO$_3$, and Sr$_{0.5}$Zn$_{0.5}$TiO$_3$ ceramics are due to Ti-O, Mn-O and Zn-O stretchings. (iii) When making a comparison with ac and dc- conductivity activation energies of present compounds ac-activation energies are lower than that of dc-activation energies. The variations of both conductivities are different for different samples.

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