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Synthesis and Characterization of Mn doped $SrTiO_3$ ceramics

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Abstract

$Sr_{1-X}Mn_XTiO_3$(x=0.5) precursor powders have been synthesized via conventional solid state reaction method. The powder particles were calcined at 1050^0C temperature. Subsequently these were pressed into pellets and undergone sintering at 1250^0C temperature. The samples prepared were characterized by XRD, SEM, FTIR and EDAX for structural, surface morphological and elemental composition analysis. Besides this dielectric constant (ε_r), dielectric loss (tanδ), ac conductivity (σ_{ac}), dc conductivity (σ_{dc}) and see beck-coefficient(S) were calculated by making use of HIOKI 3532-50 LCR HiTESTER and TEP measurement kit. The obtained results revealed that the dielectric constant is increasing with increase of temperature and decreasing with increase of frequency ranging from 100Hz-5MHz.The maximum dielectric constant obtained at RT is 75.5 and at 310^0C is 2122.0 at the frequency 100Hz.The dielectric loss is increasing with increase of temperature and decreasing with increase of frequency ranging from 100Hz-5MHz.The maximum loss measured as 1.754386 at 400^0C (at 5KHz) and the minimum loss measured as 0.052826 at 90^0C(at 10KHz).

Keywords: *Solid state reaction method; XRD; SEM; Dielectric constant; Dielectric loss.*

1. Introduction

In microwave communication and data processing system larger numbers of microwave devices are needed [1]. In this concern filters, tunable microwave phase shifters and resonators are used. This needs a dielectric material acquiring high tunability, high dielectric constant and low loss at microwave frequencies. The high tunability offers varying the frequencies in wide range and low dielectric loss provides low noise. Therefore ST and Mn doped $SrTiO_3$ like materials have got recognition as selective materials for these applications. The resultant compound differs only in some peculiar properties such as dielectric, thermoelectric properties as well as XRD, SEM like characterization properties. However the high dielectric constant provided by this compound has applications in microwave communications, resonators and filters [2]. Moreover this investigation deals with the variations of dielectric constant (K), dielectric loss (tanδ), thermoelectric power (S), ac conductivity (σ_{ac}), X-ray diffraction microscopy and scanning electron microscopy etc of Mn incorporation into the Sr-site of perovskite lattice ST. Manganese is an element possessing multiple oxidation states like Mn^{+2} and Mn^{+4}.STstructure allows Mn cations on both Sr and Ti sites of the lattice. Indeed the previous authors reported that Mn ceramics with ST prepared according to the chemical formula $Sr_{1-X}Mn_XTiO_3$ (SMnT) showed differed dielectric and structural properties with respect to $SrMn_{1-y}Ti_yO3$ (STMn) [3]. But in this study the author specific intension is to study the thermoelectric properties, ac conductivity (σ_{ac}), dc conductivity (σ_{dc}) and FTIR spectrum which have not been studied mostly in the literature in addition to the XRD, SEM and dielectric properties. It is well known that in the presence of a temperature gradient (ΔT), the distribution of carrier velocities varies across a material and thus there will be an electric field generated which ultimately gives rise to a thermo electromotive force (ΔV).Metal oxides due to their high stability at high temperature in air, easy manufacture, and low cost, has attracted much attention recently as new high-temperature thermoelectric materials. Studies on them have been accelerated by the global need to utilize exhausted waste heat. Co-based oxides with a layered structure such as $NaCo_2O_4$ (Co-124),$Ca_2Co_2O_5$ or $Ca_3Co_4O_9$ (Co-349),$SrCuTiO_3$ and $Bi_2Sr_2Co_2O_y$ (BC-222) have been reported as strong candidate materials [4].

2. PREPARAION OF THE SAMPLE:

$Sr_{1X}Mn_XTiO_3$(x=0.5) precursor powders have been prepared via conventional solid state reaction method. In order to prepare the Mn doped $SrTiO_3$ particles initially $SrCO_3$, $MnCO_3$ and TiO_2 were taken as the raw materials of 99.9% purity. Subsequently $SrCO_3$, $MnCO_3$ and TiO_2 were incorporated into a fresh crucible and kept in furnace which can enable to go up to the temperatures 1300^0C. These three materials were mixed in their stoichiometric ratio and as a result $Sr_{1-X}Mn_XTiO_3$(x=0.5) powders were prepared. The obtained Mn doped $SrTiO_3$ particles were grinded by

making use of agate motor into a fine powder. Later they are ball milled for nearly 10hrs and calcined at a temperature 1050^0C in air for nearly 8hrs.Afterwards the calcined sample is cooled to room temperature. The formed compound is again grinded and pressed into pellets by adding a binder PVA using pellet machine with an application of pressure ranging from 10 to 20 tons. Furthermore the pellets prepared were undergone sintering at a temperature 1250^0C for 2hrs.The pellets were coated with silver paste on both sides. Subsequently the samples were characterized by X-ray diffract meter (XRD), Scanning electron microscope(SEM),and Energy dispersive X-ray spectrometer(EDAX) for structural and micro structural, elemental composition analysis respectively.

3 .RESULTS AND DISCUSSION

3.1 Dielectric Properties: Dielectric constant (K), dielectric loss (tanδ), and ac conductivity (σ_{ac}) come under the dielectric properties. The results were obtained using HIOKI 3532-50 LCR HiTESTER and the obtained results revealed that the dielectric constant is increasing with increase of temperature and decreasing with increase of frequency ranging from 100Hz-5MHz.The maximum dielectric constant obtained at RT is 75.5 and at 310^0C is 2122.0 at the frequency 100Hz.The dielectric loss is increasing with increase of temperature and decreasing with increase of frequency ranging from 100Hz-5MHz.The maximum loss measured as 1.754386 at 400^0C (at 5KHz) and the minimum loss measured as 0.052826 at 90^0C(at 10KHz).The plots were also drawn for temperature Vs dielectric constant, frequency Vs dielectric constant, temperature Vs dielectric loss, frequency Vs dielectric loss. The high dielectric constant at RT provides applications in microwave communication system, resonators and filters etc. The low loss measured (tanδ=0.05285) provides low noise.

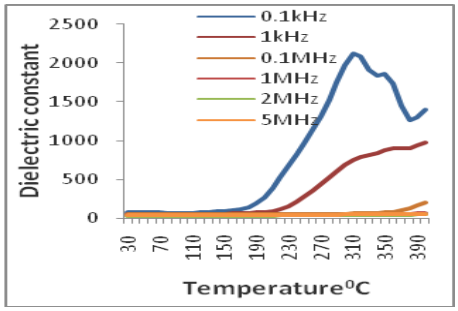


Fig: 1 shows the dielectric constant Vs temperature Plot of Mn doped $SrTiO_3$

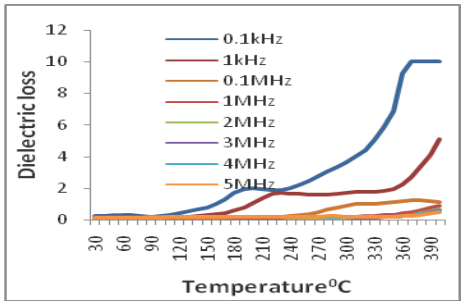


Fig.2: Shows the dielectric loss Vs temperature plot of Mn doped $SrTiO_3$

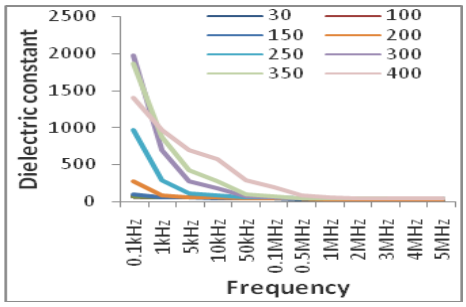


Fig: 3 shows the dielectric constant Vs frequency Plot of Mn doped $SrTiO_3$

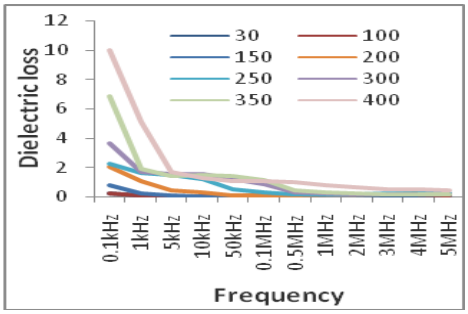


Fig.4: Shows the dielectric loss Vs frequency plot of Mn doped $SrTiO_3$

3.2. AC-Conductivity: Ac conductivity ($\sigma_{ac}=\varepsilon_0\varepsilon_r\omega$ tanδ) is increasing as increasing the temperature. At higher temperatures and frequencies there is a sharp increase from 1MHz-5MHz (310^0C-400^0C) in ac conductivity due to the strong hopping mechanism. The following plots elucidate the variation of ac-conductivity with respect to the variation of temperature and frequencies. At the temperature of 400^0C (5MHz) the maximum value of σ_{ac} exhibited is 0.00725694.

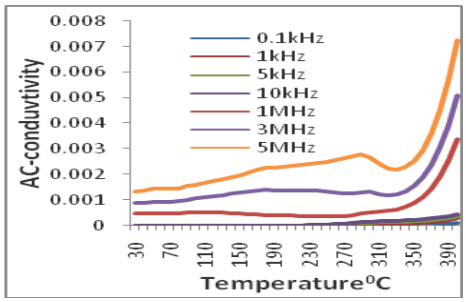


Fig.5: Shows the temperature Vs ac-conductivity Plot of Mn doped $SrTiO_3$

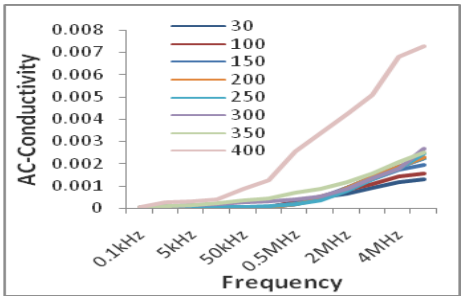


fig.6: shows the frequency Vs ac-conductivity plot of Mn doped $SrTiO_3$

3.3 Thermoelectric Properties: Thermoelectric power is a powerful experiment to identify the types of electronic carriers. The thermoelectric power (seebeck coefficient) is given by **S**= (ΔV/ ΔT). In case of $Sr_{1-x}Mn_xTiO_3$(x=0.5) the thermoelectric power is decreasing with increase of temperature. It was observed that all compounds don't show the same thermoelectric behavior with the temperature variation. The maximum seebeck coefficient obtained is 13167 μv/^{0}C at 308K.

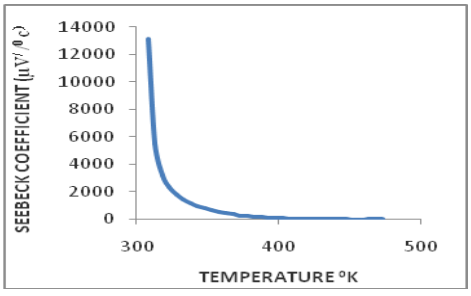


Fig.7 shows the seebeck coefficient Vs temperature Plot of $Sr_{1-x}Mn_xTiO_3$(x=0.5)

3.4. DC-Conductivity: DC-conductivity (σ_{dc}=L/RA) of $Sr_{1-x}Mn_xTiO_3$(x=0.5) was performed and it exhibited the increasing nature with respect to the temperature from RT to 320^{0}c. Up to 310^{0}c dc-conductivity is increasing gradually and after 310^{0}c there is an abrupt increase in the graph (fig.8).Apart from this lnσ Vs 1000/T plot has been also performed in fig.9.From the plots drawn natural logarithm of dc-conductivity (lnσ) against the reciprocal of temperature (1000/T) activation energy (E_a) of Mn doped $SrTiO_3$ ceramic material was found as 0.07694eV [2] using the following formula. In the graphs shown the activation energy and conductivity are increasing with increase of temperature and it is observed that the activation energy is very low at RT and is decreasing w.r.t the temperature up to 94^{0}c . After 94^{0}c E_a goes on increasing. It may be due to generation of charge carriers and mobility due to raising temperature

$E_a=2K_b$ lnσ / (1000/T) Where $K_b=8.86X10^{-5}$eV (Boltzmann constant)

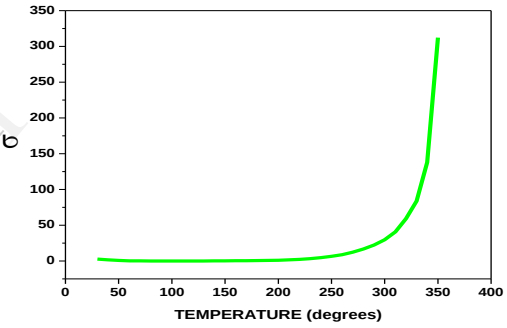


Fig.8 Shows Temperature Vs dc-conductivity Plot of $Sr_{1-x}Mn_xTiO_3$(x=0.5)

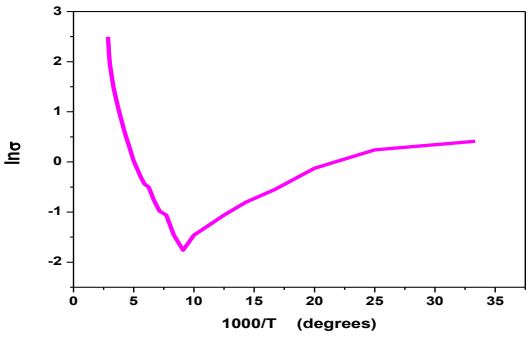


Fig.9 Shows lnσ Vs 1000/T plot of $Sr_{1-x}Mn_xTiO_3$(x=0.5)

3.5. XRD analysis: XRD is powerful tool to the structural prediction of the Specimen. The following shows the XRD spectrum of Mn doped $SrTiO_3$ and

the 2-theta Vs intensity plot. From the profile of XRD of the present sample inter-planar spacing (d) and (hkl) values are calculated. Using the following Scherer formula the average particle size of the sample is calculated as 40.8nm.

$D_p = K\,\lambda/\beta Cos\theta$ Where K is a dimension less parameter and is numerically equal to 0.9

Besides these average dislocation density (ρ) and average elastic strain (E_{strain}), were also calculated as $601x10^{12}m^{-2}$ and 0.264695 respectively using the following formulae.

$$\rho = 1/D^2 \text{ and } E_{strain} = \beta/4\tan\theta$$

The results from the lattice parameters (a, b, c and α, β, γ) and volume of unit cell (a^3) it is confirmed that the structure of unit cell is cubic [5]. In the following table distinct lattice parameters 3.903 and 3.896 were obtained [6]. Miller indices observed at the specified peaks in X-ray diffraction spectrum ofthesampleare(001),(011),(111),(002),(012),(112),(022),(003),(013) while the other are peaks corresponding to the presence of $MnTiO_3$.

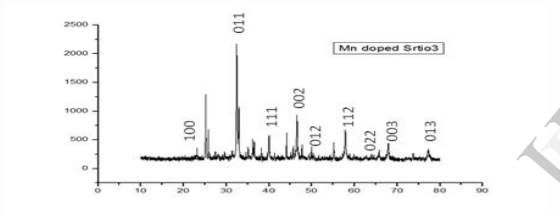


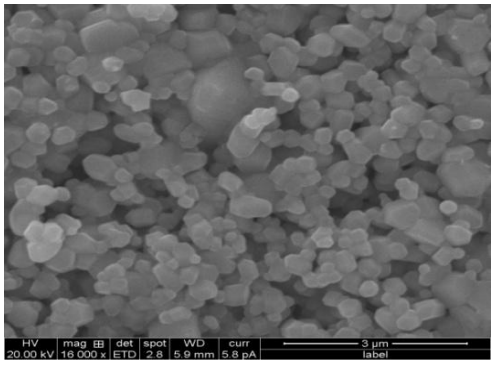
Fig.10.Shows XRD of Mn doped $SrTiO_3$

Table.1. represents the XRD data:

2θ	d-space	(hkl)	FWHM	a=b=c	α= β= γ	V= a^3
23.14	3.8406	001	0.543	3.903	90	59.46
39.98	2.2528	111	0.323	3.896	90	59.14

3.6. SEM and EDAX analysis: Scanning electron microscopy is used effectively in microanalysis and failure analysis of solid materials. The two dimensional image reveals information about selected point locations over a selected area by displaying spatial variations in properties including chemical characterization, texture and orientation of materials. This approach is useful in qualitatively or semi-quantitatively determining chemical compositions, crystalline structure and crystal orientations. The average grain size (G_a) of $Sr_{1-X}Mn_XTiO_3$(x=0.5) calculated as 1.15µm 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.



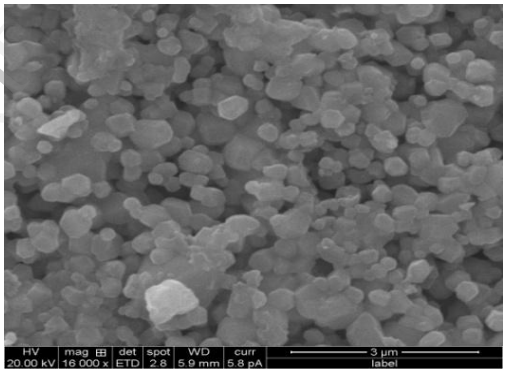


Fig.11.SEM images of $Sr_{1-X}Mn_XTiO_3$(x=0.5) ceramics

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

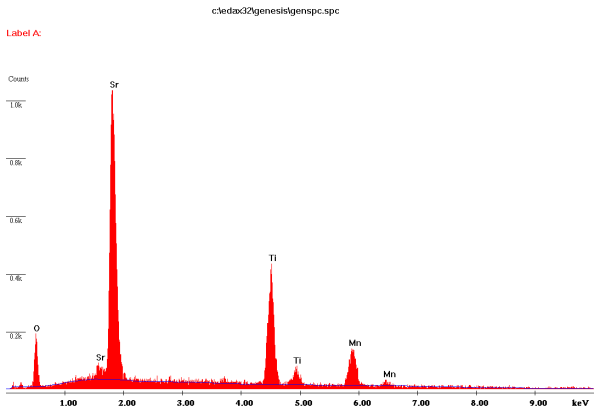


Fig12.EDAX image of $Sr_{1-X}Mn_XTiO_3$(x=0.5)

Elem	Wt %	At %
O K	10.85	33.28
SrL	48.49	27.15
TiK	24.78	25.39
MnK	15.88	14.18
Total	100.00	100.00

3.7. FTIR analysis: FTIR analysis helps clients understand materials and products. FTIR testing identifies chemical compounds in polymers, coatings, pharmaceuticals, foods and other products. This also offers both qualitative and quantitative analysis for organic and inorganic samples. In the following FTIR transmittance (%T) spectra of Mn doped SrTiO3 the broad bands observed at wave number 563.7512 cm^{-1}, 1480.9524 cm^{-1}, 3618.2463 cm^{-1} and 3770.3541 cm^{-1}.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.[7]and the rest two peaks were probably the Mn-O stretching vibrations. Since the material is of ceramic type no functional group was present.

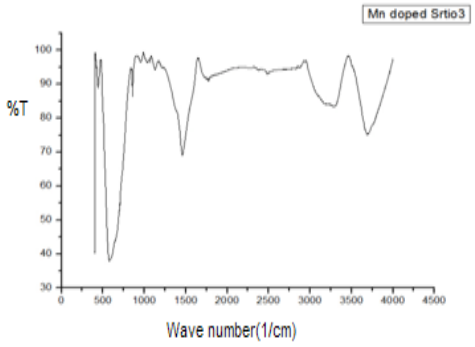


Fig.13.Shows FTIR spectrum of Mn doped $SrTiO_3$

4. CONCLUSIONS: Strontium titanate with manganese showed good thermoelectric, dielectric properties. The micro structure of the sample is observed at high sintering condition i.e. at 1250^0C.In the EDAX spectrum the maximum peak obtained for Sr. AC -conductivity (σ_{ac}) shows sharp increase from temperature 310^0C due to linear hopping mechanism, dc conductivity (σ_{dc}) is decreasing with respect to the temperature up to 94^0c and further it goes on increasing. FTIR and EDAX described the presence of groups Ti-O, Mn-O and the elements Oxygen, Strontium, Titanium, and Manganese. In SEM figure larger number of grains and few grain boundaries are observed.

5. ACKNOWLEDGEMENTS: This work was financially supported by a project of University Grants Commission (UGC)-NEW DELHI, INDIA. Also thanks to Vellore Institute of Technology (VIT) and IISC-Bangalore for supporting in characterization works such as XRD and SEM of my samples and giving their valuable suggestions.

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