Journal of Ovonic Research Vol. 11, No. 2, March - April 2015, p. 79 - 84

STRUCTURAL AND ELECTRICAL PROPERTIES OF PbO - DOPED $SrTiO_3$ CERAMICS

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The structural, micro structural and electric properties have been investigated for lead oxide doped strontium titanate ceramics synthesized via conventional solid state diffusion method which were calcined at 900^0C for 13hr and sintered at 1000^0C for 4hrs respectively. The strong relaxation dynamics in loss factor was observed at higher temperatures. AC- conductivity variations with temperatures were studied and the activation energies (E_a) were calculated of the range 0.24-0.94eV using the lnσ Vs 1/T plots. The crystalline sizes were found to be varying from 77nm-109nm by means of XRD and the FTIR spectrum was recorded over a continuous spectral range of 400-4000cm^{-1} to study the presence of different metal oxides. Dielectric constant plot established the curie transition temperature T_c = 653K revealing the structural transformation from cubic to tetragonal phase.

(Received December 27, 2014; Accepted March 16, 2015)

Keywords: Dielectric properties, glass ceramics, X-ray diffract meter and FTIR

1. Introduction

Strontium titanate is an oxide of cubic perovskite structure with lattice parameter at 3.9076 A^0 at RT. Extensive studies have been made on $SrTiO_3$ because of its electrical properties and applications [1].Therefore $SrTiO_3$ has got recognition as a candidate material for the applications of phase shifters, oscillators, capacitors needed circuitry systems, filters, resonators, DRAMs and sensors [2]. $SrTiO_3$ (ST) exhibited good dielectric, electrical and defect structural properties. At RT undoped ST showed a dielectric constant of 250 [3]. However, when impurities are added up to the pure ST, there may be either enhancement or decrement in the dielectric properties and probably change may be occurred in the diffraction lines.

PbO is a toxic material and when doped to strontium titanate (ST) is found experimentally to be a glass ceramic material. Glass ceramics have been commercially used at wide range and limited work has been done over the borosilicate glass ceramic system, in spite of its wide range of applications. Thakur et al [4] described the crystallization, micro structure and dielectric behavior of ST glass ceramics with various oxide additives. In respect of the structural properties, the present sample showed cubic structure at room temperature like undoped ST. As described in C. R. Gautam et al [5] synthesis of (Pb, Sr) TiO_3has been made by melt and quenche method.Nb_2O_5 doping into PST improves the dielectric constant [5].But nevertheless La_2O_3 doping into PST can make it semiconducting as well as good dielectric material due to space charge polarization [6].Sahu et al [7] evidently described the crystallization of solid solution ferroelectric PST in borosilicate-glassy matrix with the help of DTA and XRD studies. The ferroelectric PST thin films have been termed as the candidate materials for the applications in various tunable microwave devices and in high density dynamic random access memories. On the other hand ferroelectric thin films have got much attention in manufacturing various functional devices for optical applications.

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S.W. Liu et al [8] described linear optical properties, second harmonic generation in reflection geometry and domain micro structure. No report is available in the literature about the dielectric properties and thermoelectric properties of PST ceramics. In this study the author is intended to study the structural, micro structural, electric properties and FTIR spectrum of PST ceramics.

2. Experimental Procedure

In order to prepare PbO doped $SrTiO_3$ powder particles the raw materials were taken as $SrCO_3$ (99.5% purity), TiO_2 (99.54% purity) and PbO (99.9% purity).These starting materials were mixed in their Stoichiometric ratio to form $(PbO)_{0.1}$ doped $(SrTiO_3)_{0.9}$.The resultant compound is initially ball milled for nearly 12hrs using Retsch PM200 ball miller and later calcined at a temperature of 900^0C for 13 hrs in fresh closed aluminium crucibles. Furthermore the samples were pressed into pellets by applying the pressure of 20 Tons and were sintered at 1000^0C for 3hrs in conventional furnaces which can able to go up to 1400^0C temperature. The resultant powder particles and sintered pellets polished with silver paste of thickness 0.14cm and radius 0.61cm were characterized using XRD (BRUKER X-Ray Powder Diffract Meter, CuKα) at room temperature, FTIR and HIOKI 3532-50 LCR HiTESTER (Japan) for structural, functional group analysis and dielectric properties respectively. For the dielectric properties measurements, the sintered pellets sputtered with silver paste on both sides without contacting the edges were kept in platinum electrodes of LCR controller of temperature range from RT to 600^0C operated at the frequencies from 42Hz-5MHz having the heating rate of 0.5^0C/min.

3. Results and Discussions

The crystalline structure of PbO doped ST was evaluated by XRD analysis at RT using BRUKER X-Ray Powder Diffract Meter .The $Cu_{K\alpha}$ radiation with wave length $1.54056A^0$ was used for recording X-ray diffraction pattern. Ni filter was used as the monochromator. The machine was operated with 30 mA beam current and 40kV of power.Fig.1 depicts the XRD pattern of undoped ST and PbO doped ST (referred as PST in fig.1).It can be seen that the two compounds exhibit cubic crystalline structure having single perovskite reflection peaks with the exception of few additional phases corresponding to the presence of $PbTi_3O_7$ (PT) and TiO_2(R) phases [9]. The huge enhancement in the intensity of diffraction lines depends on structure factor (F). At 2-theta angle 32.49^0 the maximum counts 9730 and similar miller indices (h k l) were noticed as (100), (110), (111), (200), (210), (211), (220) and (310) that of undoped ST.

However, the lattice parameters were achieved as a=b=c=3.8930 A^0 and α= β= γ=90^0 and are in good consistent with literature data. Hence it is confirmed that the structure of present compound is cubic. Depends on obtained lattice parameters the practical value of unit cell volume ($59.02x10^{-24}cm^3$) was calculated which is comparable to the unit cell volume of undoped ST as reported in JCPDC file 35-734.Table.1 shows the X-ray profile data of present sample and furthermore the average crystalline size (D_P) of 88.1nm was obtained using Scherer formula [10].

$$D_p = \frac{k\lambda}{\beta \cos\theta}$$

Where k is a constant and is equal to 0.9, θ is diffraction angle, λ=0.154056 nm (CuK_α) and β is full width half maxima.

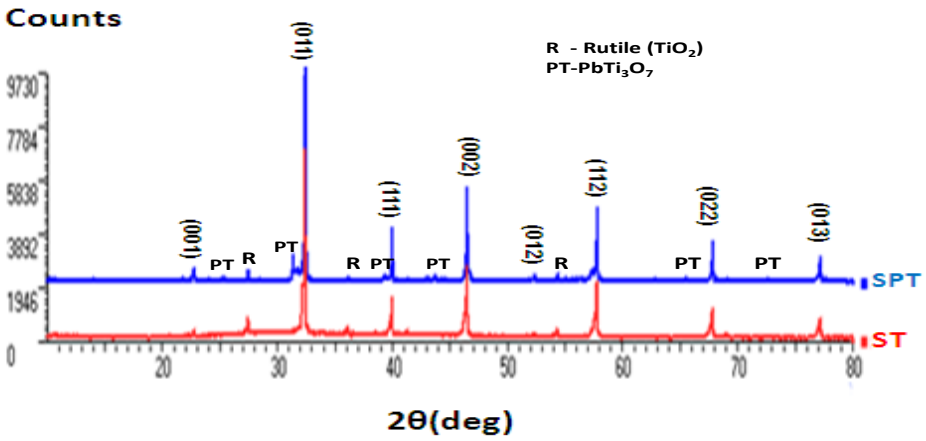

Fig.1 Shows the XRD Spectrum of PbO doped $SrTiO_3$ ceramics

Table.1 Shows the XRD profile of PbO doped $SrTiO_3$

2θ	d-space (A^0)	FWHM	(h k l)	D_p(nm)
22.84	3.893	0.109	(100)	99.8
32.49	2.755	0.037	(110)	109.7
40.04	2.251	0.072	(111)	104.2
46.56	1.949	0.087	(002)	102.9
52.43	1.744	0.235	(012)	77.5
57.86	1.593	0.046	(112)	104.5
67.90	1.379	0.479	(022)	103.2
77.26	1.234	0.076	(013)	105.6

The surface morphology was analyzed by scanning electron microscopy. Fig.2 show the SEM figures of PbO doped ST sintered at 1000^0C which have been made at two different spots having 2,500 X and 10,000X magnifications and in 20µm, 5µm range respectively. In the images almost spherical shape grains containing homogeneous distribution have been observed. The average grain size (G_a) was calculated as 5.8µm, using the following formula.

$$\text{Average grain size } \mathbf{G_a} = \frac{\mathbf{1.5\ L}}{\mathbf{MN}}$$

Where L=the total test line length, M=the magnification,
N=the total number of intercepts which the grain boundary makes with the line.

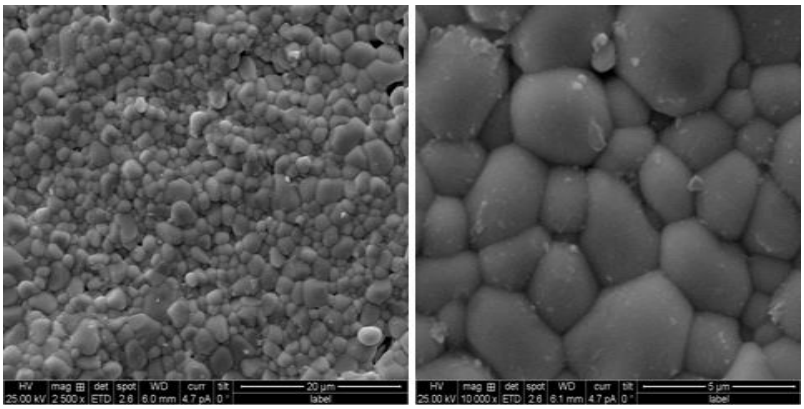

Fig.2 Shows the SEM images of PbO doped $SrTiO_3$ ceramics

In the FTIR spectrum (fig.3) of PbO doped ST, few strong elastic peaks observed were because of the larger number of elastically scattered electrons from specimen. However, these peaks attribute information about the electrons which have undergone distinct energy losses during the scattering from surface of sample. FTIR analysis of present sample was carried out at 400-4000cm^{-1} range and a broad peak (at 1445.40 cm^{-1}) and few small peaks were observed. These peaks may be due to the presence of metal oxygen bonds (M-O) such as Sr-O, Pb-O and Ti-O [11].

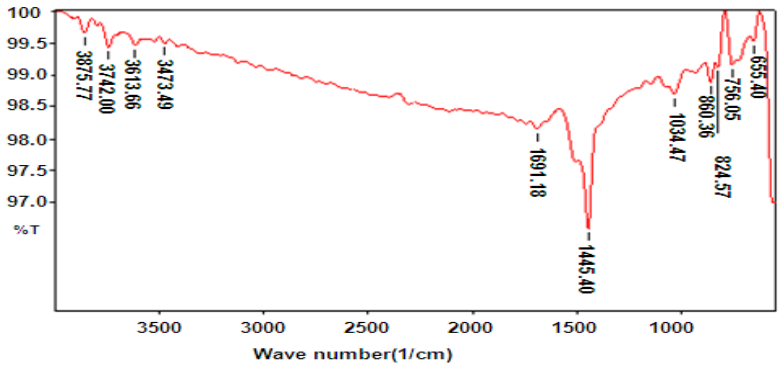

Fig.3 Shows the FTIR Spectrum of PbO doped $SrTiO_3$ ceramics

The dielectric properties have been studied by means of LCR meter (HIOKI 3532-50 HiTESTER). Dielectric constant of PbO doped ST sintered at 1000^{0}C as a function of temperature dependence (from 303K to 693K) at the selected frequencies of 0.1 kHz-5 MHz is plotted in fig.4. Initially the permittivity (ε_r) is increasing gradually with increase of temperature up to T_c and later showing decreasing trend. Obviously, cubic to tetragonal structural transformation at the Curie-temperature of T_c=653K has been observed. This explicitly established a fact that addition of lead oxide diminishes the Curie temperature of pure ST. Moreover, the lead addition cannot induce permittivity of pure ST at room temperature.

The loss factors(tanδ) were noted as 0.00815 and 0.24837 at 0.1 kHz and 5 MHz respectively (at RT).But for the similar frequencies at 693K tanδ values were obtained sequentially as 1.9544 and 0.07543.Hence, it is confirmed that as increasing the temperature, loss is also increasing up to T_c and further decreasing. The temperature dependence of dielectric loss is depicted in fig.5. Mean while, tanδ spectrum of PbO doped ST attributed to the domain wall dynamics around the cubic to tetragonal phase transition.

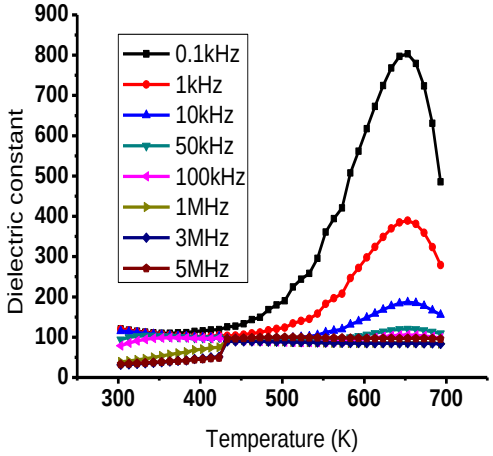

Fig.4 Shows the Dielectric constant Vs Temperature Plots of PbO doped $SrTiO_3$ ceramics

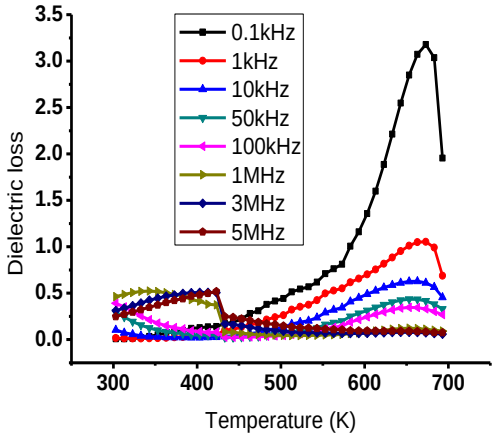

Fig.5 Shows the Loss tangent Vs Temperature Plots of PbO doped $SrTiO_3$ ceramics

Fig.6 shows the ac-conductivity as a function of frequency at various temperatures. As the temperature goes on increasing, the dielectric relaxation becomes thermally activated and hence this can be governed by the Arrhenius equation.

$$\sigma = \sigma_0 \exp\left(\frac{-Ea}{KT}\right)$$

Where K=8.6X10^{-5}eV, σ_0= pre exponential factor, and T= absolute temperature
In general σ_{ac} can be calculated by the following equation

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

Where ε_r =dielectric constant, ε_0=8.9X10^{-12} F/m, ω=2πf and tanδ= loss tangent

Fig. 7 depicts the variation of ac–conductivity (lnσ_{ac}) with reciprocal of temperature (1000/T). The slopes of the curves attribute activation energies and were achieved in the range of 0.23-0.94eV. These were in close agreement with activation energies of undoped ST [12]. The conductivity increases with increase of temperature due to thermal activation process and this must be related to hopping of charge carriers which are bound in the localized states.

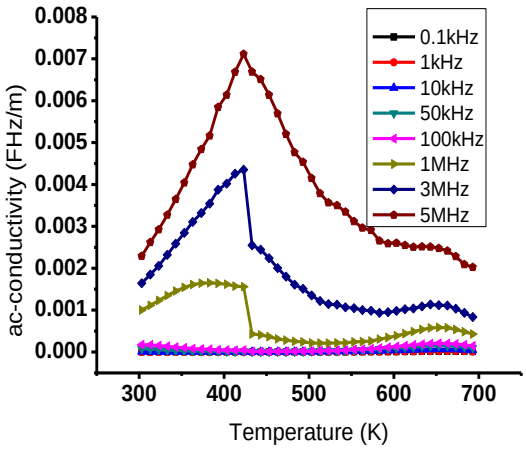

Fig.6shows the ac-conductivity Vs Temperature Plots of PbO doped $SrTiO_3$ ceramics

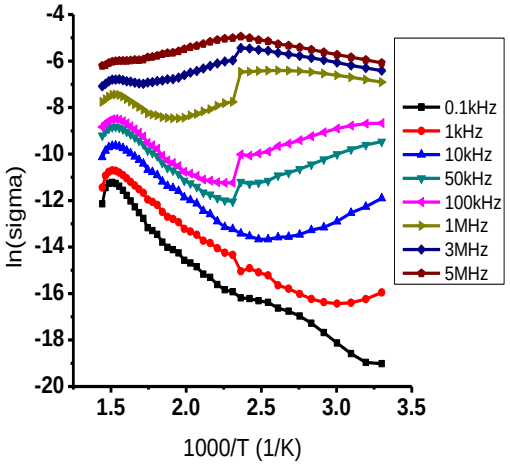

Fig.7shows the lnσ_{ac} Vs 1000/T plots of PbO doped $SrTiO_3$ ceramics

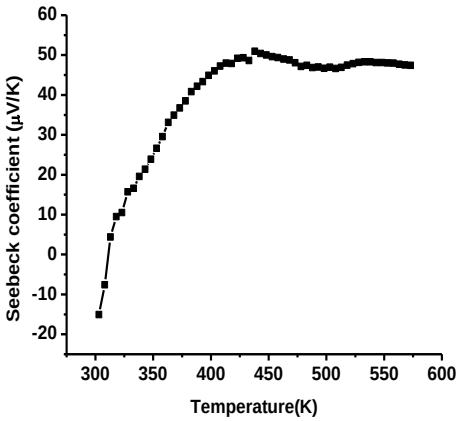

Fig.8: Shows the seebeck coefficient Vs temperature Plot of PbO doped $SrTiO_3$

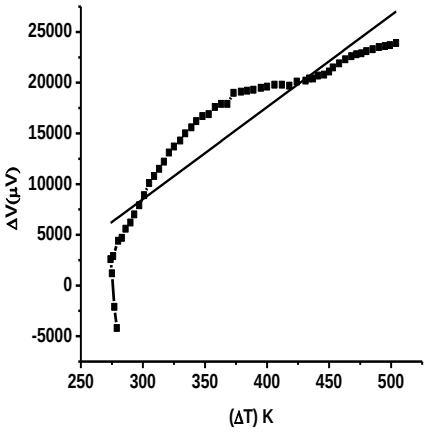

Fig.9: Shows the ΔV Vs ΔT Plot of PbO doped $SrTiO_3$

In order to interpret the conduction mechanism in ceramic composites thermoelectric properties are used. The thermoelectric power of PbO doped $SrTiO_3$ has been studied by measuring the seebeck coefficient. At temperature 303^{0}K the present sample exhibited thermoelectric power of -15.05μV/K and the highest seebeck coefficient 50.94 μV/K observed at 438K temperature. The thermoelectric behavior of lead doped $SrTiO_3$ is shown in the plot. As increasing the value of temperature, the seebeck coefficient (S**)** is increasing due to raise of number of carriers and their mobilities. The sign of the seebeck coefficient gives the type of

conduction in semiconductor whether P-type or N-type. In the present results two kinds of regions were observed and S was found to be –ve during the temperature region 303K-310K confirming that the majority charge carriers were of n-type. On the other hand above 313K S being +ve revealing the p-type behavior of sample. The slope of curve $S=\Delta V/\Delta T$ computed as 90.70μV/K by linear fitting method and more over the carrier concentration of 1.041 $X10^{22}cm^{-3}$ is calculated using the following equation.

$$n= (N/V) X \exp (-Se/K_B)$$

Where $N=10^{22}cm^{-3}$(Density of states), V=0.32 cm^3 (Volume of the sample), K_B/e =86.4 μV/K. The thermo emf Vs temperature plot is drawn in fig.8.

4. Conclusions

In conclusion of this work (i) $(PbO)_{0.1}$ doped $(SrTiO_3)_{0.9}$ prepared via solid-state diffusion method exhibits cubic crystalline structure having single perovskite phases with the exception of few additional phases corresponding to the presence of enriched $PbTi_3O_7$ phases and few TiO_2 phases.(ii) The ac- activation energies were achieved as 0.23eV-0.94eV and (iii) the lead addition decreases the transition temperature of undoped ST.(iv) Lead doping moderates the thermoelectric power of strontium titanate.

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), Tamilanadu, and Prof.K.R.Gunasekhar from IISC-Bangalore for supporting in characterization works such as XRD and SEM of my samples and giving their valuable suggestions.

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