

## SYNTHESIS AND CHARACTERIZATION OF CuO-DOPED SrTiO<sub>3</sub> CERAMICS

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Copper-doped SrTiO<sub>3</sub> (ST) ceramic powders were processed by solid-state route diffusion (SRD) bulk preparation technique. We reported the effect of Cu<sup>+2</sup> ions on the dielectric response of ST and it established the substantial increase in dielectric constant ( $\epsilon_r$ ) than undoped ST from 303K-673K and low loss ( $\tan\delta$ ) for good dielectric applications. In respect of the electrical properties ac, activation energies were computed using  $\ln\sigma$  Vs  $1/T$  plots. The highest thermo electric power of 250 $\mu$ V/K was noticed at temperature 303K for thermoelectric applications. The microstructure was examined with grain sizes 6-9 $\mu$ m of uniform distribution by field emission scanning electron microscope (FESEM). Some additional phases SrCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> and TiO<sub>2</sub> rutiles were detected by X-ray diffraction technique and the FTIR spectrum attributed the presence of metal oxygen (M-O) bonds.

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### 1. Introduction

Copper(II)oxide is a metal oxide of density 6.315g/cm<sup>3</sup> and melting point of 1326<sup>0</sup>C. The crystal structure was determined as monoclinic, mS8 with space group of C<sub>2</sub>/C and point group of 2/m or C<sub>2h</sub>. Copper atom is surrounded by four oxygen atoms in the square planar configuration[1]. Copper(II)oxide is a p-type semiconductor of band gap 1.2eV used to produce dry cell batteries[2]. It can have applications as ceramic resistors, magnetic storage media, gas sensors, semiconductors and solar energy transformation.

ST adopted cubic perovskite structure at room temperature (RT) possessing close packing of Sr<sup>+2</sup> with Ti<sup>+4</sup> occupying the quarter of the octahedral interstices. The crystallographic space group was identified as Pm3m [3] and the lattice constant of 3.905Å<sup>0</sup> [4]. ST is an important material with extensive applications as a dielectric and ferroelectric ceramics. Undoped ST exhibited high dielectric constant of 250 at room temperature (RT)[5] and provides applications in phase shifters, oscillators, microwave resonators, antennas, tunable circuits and storage capacitors. Low loss offers low noise.

When transition metals are added up to the ST magnetic as well as ferroelectric properties can be induced. For instance in recent investigations Mn<sup>+2</sup> ions could induce the electric and magnetic dipoles into the system. Likewise as in ref [6] if Cu<sup>+2</sup> ions occupy the Sr<sup>+2</sup> site, dielectric and magnetic anomalies could be induced as the ionic radius of Sr<sup>+2</sup> (0.144nm) is larger than Cu<sup>+2</sup> (0.121nm). But on the other hand anti ferromagnetic spin ordering is being evolved, if Cu<sup>+2</sup> ions occupy the Ti<sup>+4</sup> sites. In the literature EPR (Electron Paramagnetic Resonance) studies and dielectric measurements at low temperatures have been carried out. Even for the higher frequencies copper doped ST showed high dielectric constant. But in the present investigation the author intended to study the dielectric properties, ac conductivities and thermoelectric properties from 303K-673K.

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## 2. Experimental Procedure

The ceramic samples of  $(\text{CuO})_{0.1}$  doped  $(\text{SrTiO}_3)_{0.9}$  were prepared by solid state diffusion method. At the outset ST powders have been synthesized using the raw materials of  $\text{SrCO}_3$  (99.9% purity) and  $\text{TiO}_2$  (99.9% purity). The mixed powders were calcined at temperature  $1400^\circ\text{C}$  for 13hrs and the shrinkage of compound was apparently identified. Latter  $(\text{ST})_{0.9}$  was mixed with  $(\text{CuO})_{0.1}$  and ball milled for nearly 12 hrs. After wards the samples calcined at  $1050^\circ\text{C}$  for 13hrs and the pellets of thickness 0.14cm and radius of 0.62cm have been prepared. The powders and the pellets sintered at  $1100^\circ\text{C}$  for 4hrs were characterized using XRD (BRUKER X-Ray Powder Diffract Meter,  $\text{CuK}_\alpha$ ) at room temperature, FESEM, EDAX (AMETEK system), FTIR (BRUKER Spectrophotometer) and HIOKI 3532-50 LCR HiTESTER (China) for structural, surface morphological, elemental, 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 over the temperature range from RT to  $600^\circ\text{C}$  operated at the frequencies from 42Hz-5MHz having the heating rate of  $0.5^\circ\text{C}/\text{min}$ . The  $\text{CuK}_\alpha$  radiation with wave length  $1.54056\text{\AA}$  was used for recording X-ray diffraction pattern. Nicol filter was used as the monochromator and the machine was operated with 30 mA beam current and 40kV of power. X-ray diffraction spectrum was analyzed with Xpoder Ver.2010 software over the 2-theta angle range 20-80 degrees which can give full profile of the spectrum and polycrystalline phases.

## 3. Results and Discussions

In fig.1, we reported the comparison XRD spectra of pure ST and doped with 10% CuO content. Diffraction maxima were observed in the diffraction spectra which are corresponding to the cubic perovskite lattice of ST. The effect of copper ions on the lattice parameter of undoped ST was clearly observed in ref [7] at low concentrations i.e. at low concentration of copper addition to pure ST decreases the lattice parameter (a). Similar reports were achieved in the present investigation. The lattice parameter of pure ST was reported in ref [8] and in case of CuO (10%) doped ST (90%) 'a' value was slightly decreased to 0.3893nm. Since the ionic radius of  $\text{Cu}^{+2}$  (0.121nm) is smaller than that of  $\text{Sr}^{+2}$  (0.144nm) [6]. Charge compensation can be obeyed if copper ion occupies the strontium site while it can't be satisfied if  $\text{Cu}^{+2}$  ions are substituted in  $\text{Ti}^{+4}$  sites and oxygen vacancy can be created. However, this diminishes the lattice parameter. Along with single perovskite phases some non-perovskite second phases have been detected that correspond to  $\text{TiO}_2$  rutiles and  $\text{SrCu}_3\text{Ti}_4\text{O}_{12}$  phases specified in fig.1. The appearance of  $\text{TiO}_2$  phases depend on the temperature and the time of calcination. Structure factor (F) is responsible for the enormous enhancement of intensity of the diffraction lines of copper doped ST since 'F' has the directly proportional relation with intensity. The space group was identified as Pm3m [3]. Furthermore the average crystalline size ( $D_p=114.9\text{nm}$ ) using Scherer formula, average dislocation density ( $\rho=8.03 \times 10^{13} \text{m}^{-2}$ ) and average elastic strain ( $E_{\text{strain}}=0.0324$ ) were established according to the following equations. XRD profile data is represented in the table 1.

$$D_p = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

Where k is a constant and is equal to 0.9,  $\theta$  is diffraction angle,  $\lambda=0.154056 \text{ nm}$  ( $\text{CuK}_\alpha$ ) and  $\beta$  is full width half maxima.

$$\rho = D^{-2} \quad (2) \text{ and}$$

$$E_{\text{strain}} = \frac{\beta}{4 \tan\theta} \quad (3)$$

Table.1 Shows the XRD profile data of CuO doped SrTiO<sub>3</sub> ceramics.

2θ	d-space (Å <sup>0</sup> )	FWHM	(hkl)	D <sub>p</sub> (nm)	ρx10 <sup>13</sup> (m <sup>-2</sup> )	E <sub>strain</sub>
22.842	3.8930	0.0818	(100)	110.1	8.25	0.0149
32.492	2.7550	0.0697	(110)	131.8	5.76	0.0435
40.049	2.2506	0.0723	(111)	129.8	5.94	0.0145
46.56	1.9498	0.0781	(002)	123.1	6.59	0.0074
52.439	1.7441	0.1132	(012)	86.9	13.24	0.0273
57.865	1.5928	0.0896	(112)	112.6	7.89	0.0487
67.908	1.3795	0.0939	(022)	113.3	7.79	0.0658
77.26	1.2342	0.1063	(013)	106.3	8.85	0.0377

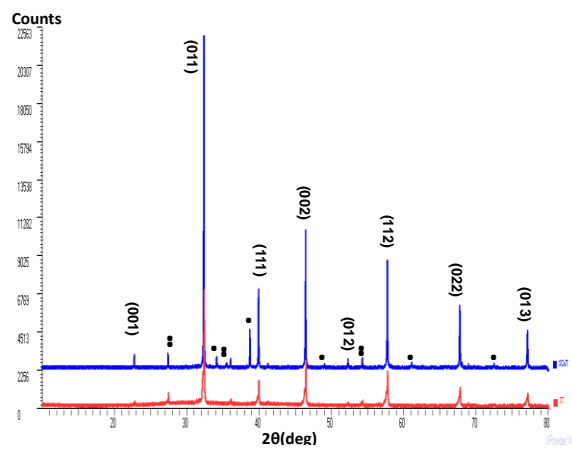


Fig.1 XRD Spectrum of CuO doped SrTiO<sub>3</sub> ceramics (..TiO<sub>2</sub> rutiles and .SrCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>)

The micro structure of polished and heat treated sections of the pellets were examined using Field Emission Scanning Electron Microscopy (FESEM). EDAX was performed both at grains and grain boundaries. X-rays are used to detect the distribution of elements. In fig.2 it can be seen that the surface morphology was studied by FESEM with magnifications 5000x and 10000x over the range 10μm, 4μm and 500 μm. Obviously, uniformity in the distribution of grains and grain boundaries was observed. Almost spherical and square shape grains were identified and the grain sizes were determined of range 6-9μm using the following formula.

$$\text{Average grain size } G_a = \frac{1.5 L}{MN} \quad (4)$$

Where L=the total test line length, M=the magnification, N=the total number of intercepts which the grain boundary makes with the line. In order to determine the concentrations of elements such as Sr, Cu, Ti and O present in ceramic samples EDAX analysis was carried out. Fig.3 illustrates the At%, and Wt% of various elements.

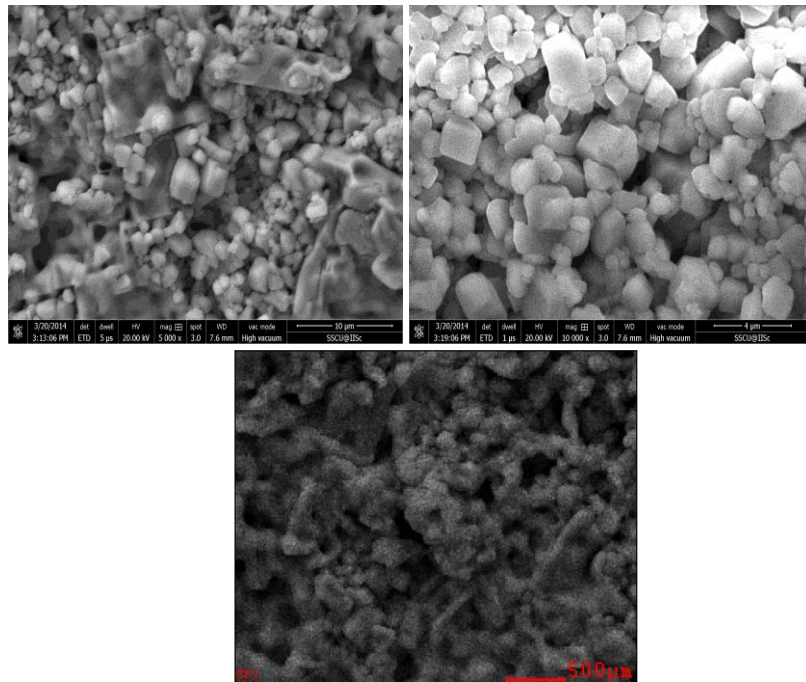


Fig.2 Shows the FESEM image of CuO doped SrTiO<sub>3</sub> ceramics

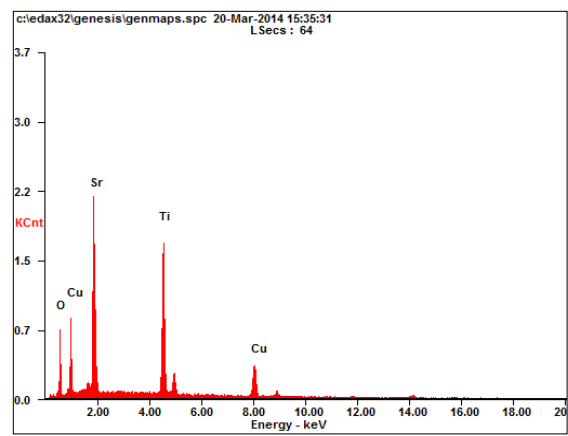


Fig.3 Shows the EDAX Spectrum of CuO doped SrTiO<sub>3</sub> ceramics

Table.2 Shows the EDAX profile data of CuO doped SrTiO<sub>3</sub> ceramics

Element	Wt%	At%
OK	20.14	50.17
SrL	32.49	14.78
TiK	25.98	21.62
CuK	21.39	13.42
Matrix	Correction	ZAF

The temperature dependence of dielectric constant ( $\epsilon_r$ ) and dissipation factor ( $\tan\delta$ ) at frequencies 0.1 kHz-MHz over the temperature range 303K-673K for the ceramic samples  $(\text{CuO})_{0.1}$  doped  $(\text{SrTiO}_3)_{0.9}$  is shown in fig.4&5. It can be seen from the figures that the dielectric constant and loss were gradually increasing with increase of temperature up to 503K and latter sharp increasing trend in both the cases was observed. Subsequently, permittivity and loss were decreasing with increase of frequency. These trends were approximately identical incase of undoped ST. At RT sample showed  $\epsilon_r$  value of 802 which is almost four times the  $\epsilon_r$  value of pure ST. Enormous dielectric response was attributed owing to the incorporation of copper ions into perovskite lattice of ST. Even at elevated temperatures for instance at 673K  $\epsilon_r$  value of 6990 was obtained. In the recent publication [6] at low temperatures of 0-60K dielectric constant of from 250-650 was achieved, but in this investigation permittivity of from 802-6990 in the temperature range 303K-673K. Due to the high dielectric constant and low loss established at RT, copper doped ST has got recognition as a candidate material for the applications in electronic devices such as phase shifters, oscillators, micro wave tunable circuits, resonators and charge stored capacitors. Fig. 6 shows the ac conductivity as a function of frequency at various temperatures. As the temperature goes on increasing, the ac- conductivity becomes increased owing to the hopping of charge carriers and hence this can be governed by the Arrhenius equation.

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{KT}\right) \quad (5)$$

Where  $K=8.6 \times 10^{-5} \text{eV}$ ,  $\sigma_0$ = pre exponential factor, and  $T$ = absolute temperature  
In general  $\sigma_{ac}$  can be calculated by the following equation

$$\sigma_{ac} = \epsilon_0 \epsilon_r \omega \tan\delta \quad (6)$$

Where  $\epsilon_r$ =dielectric constant,  $\epsilon_0=8.9 \times 10^{-12} \text{F/m}$ ,  $\omega=2\pi f$  and  $\tan\delta$ = loss tangent

Fig. 7 depicts the variation of logerithematic term of ac –conductivity with reciprocal of temperature and reveals almost a linear relation between  $\ln\sigma_{ac}$  and  $1000/T$ . The slopes of the curves attribute activation energies and were achieved in the range 0.089-0.319eV over the frequencies 0.1 kHz-5 kHz. These were in close agreement with activation energies of undoped ST [9]. 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.

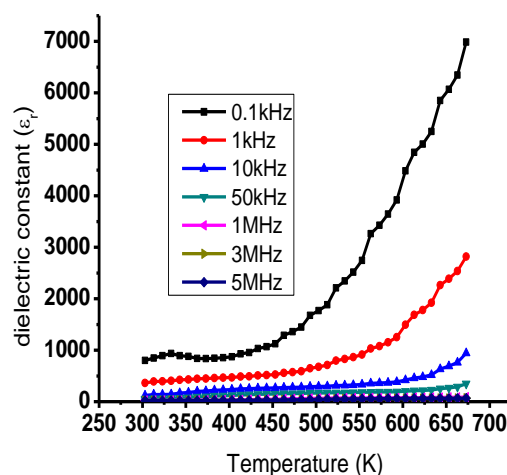


Fig.4 Shows the Dielectric constant Vs Temperature Plots of CuO doped  $\text{SrTiO}_3$  ceramics

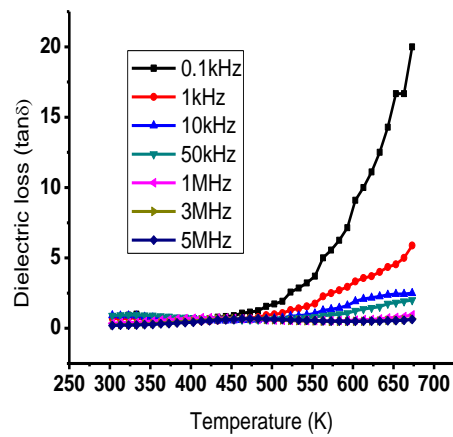


Fig.5 Shows the Loss tangent Vs Temperature Plots of CuO doped SrTiO<sub>3</sub> ceramics

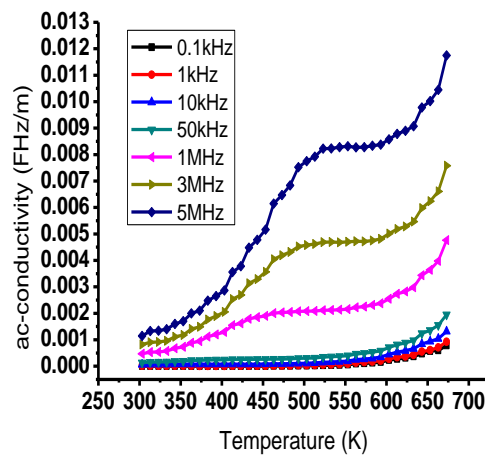


Fig.6 Shows the ac-conductivity Vs Temperature Plots of CuO doped SrTiO<sub>3</sub> ceramics

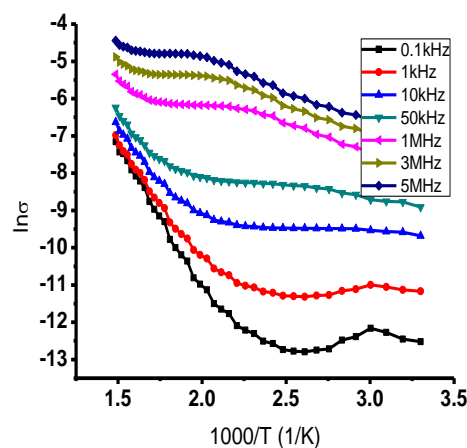


Fig.7 shows the  $\ln\sigma_{ac}$  Vs  $1000/T$  plots of CuO doped SrTiO<sub>3</sub> ceramics

In the FTIR spectrum of CuO doped ST, few 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  $500\text{--}4000\text{cm}^{-1}$  range and broad peaks at  $557.32\text{ cm}^{-1}$ ,  $750.62\text{ cm}^{-1}$  and  $1032.92\text{ cm}^{-1}$  and small peaks were observed. These peaks were due to the presence of metal oxygen bonds (M-O) such as Sr-O, Mg-O and Ti-O [10]

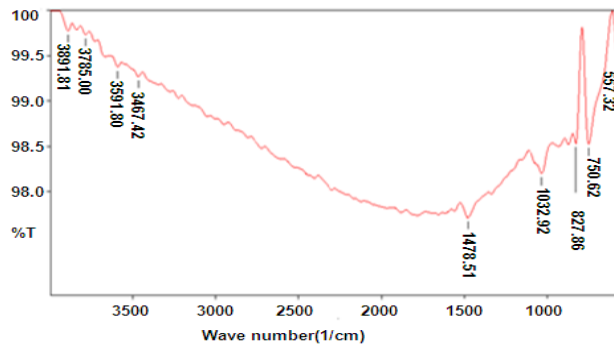


Fig.8 Shows the FTIR Spectrum of CuO doped SrTiO<sub>3</sub> ceramics

Temperature dependence of Seebeck coefficient (thermoelectric power) of CuO doped ST ceramics sintered at 1100<sup>0</sup>C is shown in fig. 9. It can be seen from the figure that the Seebeck coefficient is positive and decreases with increase of temperature up to 370K revealing that holes were introduced by copper addition. Mean while, electron were induced in temperatures 373K-493K as the seebeck coefficient showed negative value and later showing a positive thermoelectric power(S) of constant trend with an overall slope of 479.4μV/K. However, the sample exhibited both insulator and metallic nature during the variation of temperature. Because of addition of CuO there is a moderate decrease in the slope of present sample than undoped ST. The carrier concentration (n) was calculated for the CuO doped ST pellets of thickness 0.14cm and radius 0.62cm as 0.0219X10<sup>22</sup> /cm<sup>3</sup> using the following equation.

$$n = \frac{N}{V} \times \exp\left(\frac{-S_e}{K}\right) \quad (7)$$

Where N=10<sup>22</sup>cm<sup>-3</sup>(Density of states), V=0.169 cm<sup>3</sup> (Volume of the sample),  $\frac{K}{e}$  =86.4 μV/K and S=seebeck coefficient.

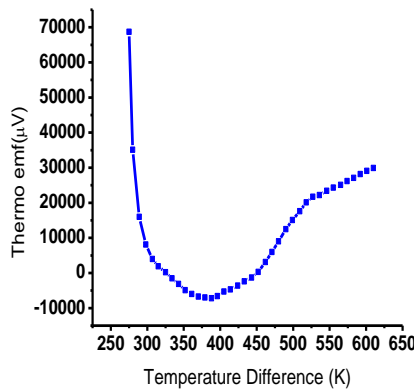


Fig.8 Shows the Thermoemf Vs Temperature Difference Plots of CuO doped SrTiO<sub>3</sub>

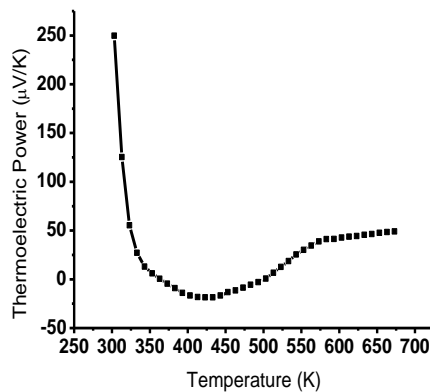


Fig.9 Shows the Seebeck coefficient Vs Temperature Plots of CuO doped SrTiO<sub>3</sub>

#### 4. Conclusions

In conclusion of this work (i)  $(\text{CuO})_{0.1}$  doped  $(\text{SrTiO}_3)_{0.9}$  prepared via solid-state diffusion method (SSR) showed huge enhancement in the dielectric constant rather than the dielectric constant of  $\text{SrTiO}_3$  ceramics when compared with literature.(ii) Thermoelectric properties were investigated from room temperature up to 673K and showed insulating nature with increasing temperature from 303K-370K. Mean while in the temperature range of 373K-493K samples exhibited the metallic nature and (iii) it is observed that the compound exhibits cubic crystalline structure having single perovskite phases with the exception of few additional phases corresponding to the presence of  $\text{TiO}_2$ rutiles and  $\text{SrCu}_3\text{Ti}_4\text{O}_{12}$  phases.

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