CHARACTERIZATION OF PEROVSKITE-TYPE $XSnO_3$ (WHERE X= Ca, Sr AND Ba) CERAMICS

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Abstract

Perovskite-type CalciumTin Oxide ($CaSnO_3$), Strontium Tin Oxide ($SrSnO_3$) and Barium Tin Oxide($BaSnO_3$) were prepared by solid state reaction method. Analytical reagent (AR) grade $CaCO_3$, $SrCO_3$,$BaCO_3$ and SnO_2 were used as the starting materials with equal molar ratios. The samples were characterized by XRD and SEM.XRD patterns indicated that the samples belong to orthorhombic structure for $CaSnO_3$ and $SrSnO_3$ ceramics and cubic for $BaSnO_3$. The lattice parameters were obtained as a = 5.4982 Å, b = 5.6356 Å and c = 7.8651 Å for $CaSnO_3$, a = 5.7079 Å, b = 5.7072 Å andc = 8.0708 Å for $SrSnO_3$ and a = b = c = 4.1114 Å for $BaSnO_3$ respectively. The crystallite sizes were also obtained as 42.17 nm for $CaSnO_3$,47.34 nm for $SrSnO_3$ and 51.75 nm for $BaSnO_3$ and the obtained crystallite sizes showed that the samples were nanosized ceramic materials. From the SEM micrographs, the grain sizes were obtained as in the range of0.55 μm – 0.58 μm. Electrical conductivities of the samples were investigated in the temperature range of 303 K – 773 K. Electrical conductivity and activation energy of the samples were studied.

Keywords: $CaSnO_3$, $SrSnO_3$, $BaSnO_3$, Perovskite-type, XRD and SEM

Introduction

The double oxides of the general formula ABO_3(where A =Ca, Sr and Ba) formed between the oxides of alkaline – earth metals and those of some of the group IV elements are great industrial and technological importance. These "A" carbonates are the precursors for this research[Abdul-Majeed Azad, (1997)]. This paper is the synthesis and characterization of Alkaline earth stannates from these carbonates and tin oxides (SnO_2). Most of the alkaline-earth stannates have the perovskite structures and they perform the dielectric characteristics because they have one set of electrical conductivity (having both donor and acceptor ions). This work intends to support the

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finding applications in pure form (intrinsic) such as thermally stable capacitors in electronics because of their attractive dielectric characteristics. Moreover, in doped form, these stannates have also been investigated as potential sensor materials for a host of gases, including CO, HC, H_2, Cl_2, NO_2 and humidity etc. In addition they can be used as the transparent solar cells on the window glasses and buildings because of their transparent properties (e.g. having the smaller optical band gap) [Abdul-Majeed Azad, (1999)]. These stannates were also used to investigate the p-type (advance used in electronics devices including flat panel displays, solar cells) and n-type semiconductor (in pure state) [Cerda, (2001); Khuong, P.Ong, (2015)]. In this work, as the alkaline-earth (AE) carbonates $BaCO_3$, $CaCO_3$ and $SrCO_3$ were selected and mixing each with tin oxide (SnO_2) by dry mix. The whole experimental routine are processed and synthesized by the conventionally much-used solid state reaction technique. Characterization method, XRD was used to analyze the phase identification of the samples. Another characterization technique SEM (Scanning electron microscopy) is used to ascertain the reaction pathways leading to the formation of the target compound, particles size and their distribution and, to systematically follow the development of microstructure in the sintered bodies. Thus, in this paper, details of synthesis, processing and micro structural and electrical evolution of the investigated $CaSnO_3$, $SrSnO_3$and $BaSnO_3$samples are presented.

Experimental Details

Preparation of $CaSnO_3$, $SrSnO_3$ and $BaSnO_3$ Ceramics

Firstly, the starting materials of $CaCO_3$, $SrCO_3$, $BaCO_3$and SnO_2 powders were weighed with molar ratios and mixed in crucible. The mixed powder was grounded by an agate mortar and pastel for 2 h to be homogeneous and fine powder. The fine powder was heated at 1200°C for 3 h to obtain the desired materials. The residual samples($SrSnO_3$, $BaSnO_3$) are prepared by this procedure. Figure 1 shows the flow diagram of the preparation of $CaSnO_3$sample.

XRD, SEM and Electrical Conductivity Measurements

X-ray diffraction (XRD) is used to investigate structural properties of crystalline materials. Powder XRD patterns of the $CaSnO_3$, $SrSnO_3$ and $BaSnO_3$samples were observed by RIGAKUMULTIFLEX X-ray Diffractometer.

The microstructural properties of the material have an important role in determining the electrical transport properties. SEM micrographs of $CaSnO_3$, $SrSnO_3$and$BaSnO_3$ were observed by JEOL JSM-5610LV Scanning Electron Microscope (SEM).

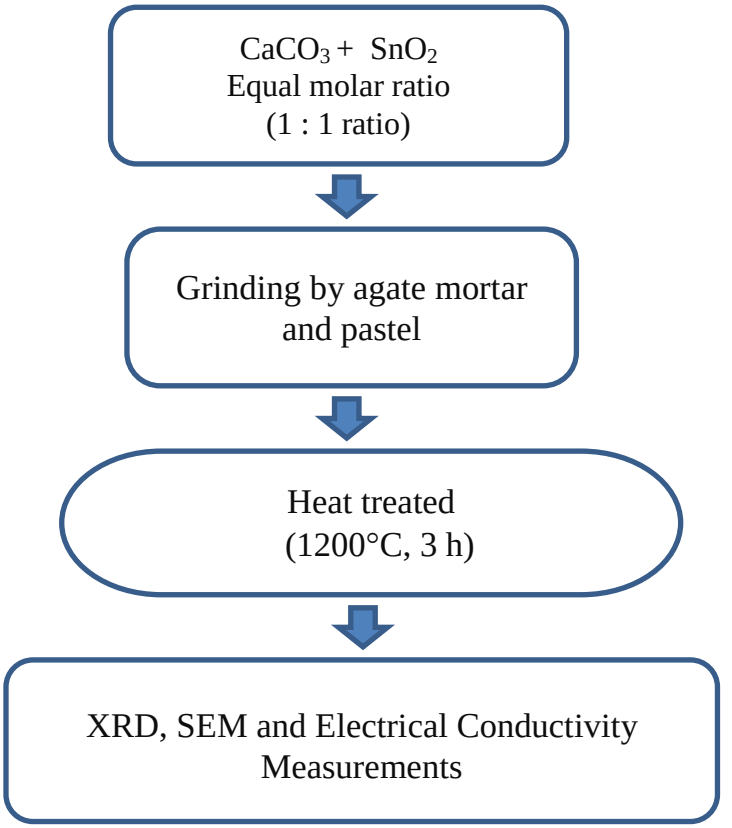

Figure 1: Flow diagram of the preparation of $CaSnO_3$ sample

For the temperature dependent electrical conductivity measurement, the samples were made into pellets by SPECAC hydraulic pellet-maker using

5 ton (~70 MPa). The silver paste was made over the sample to ensure good electrical contacts. The electrical resistances of the samples were observed by FLUKE 45 DUAL DISPLAY MULTIMETER in the temperature range of 303 K – 773 K. CAHO SR-T903 Temperature Controller and K-type thermocouple were used as Temperature Controller and Temperature Sensor. 300 W heater rod was used as the heating element. The electrical conductivity σ was evaluated by using $\sigma = \frac{l}{RA}$ where l is the distance between two electrodes, A is the cross-sectional area of the electrodes and R is the resistance. The dimensions of the sample are 1.14×10^{-4} m^2 in diameter and 3.83×10^{-3} m in thickness. Photograph of the experimental setup of electrical conductivity measurement and schematic diagram are shown in Figure 2 and Figure 3.

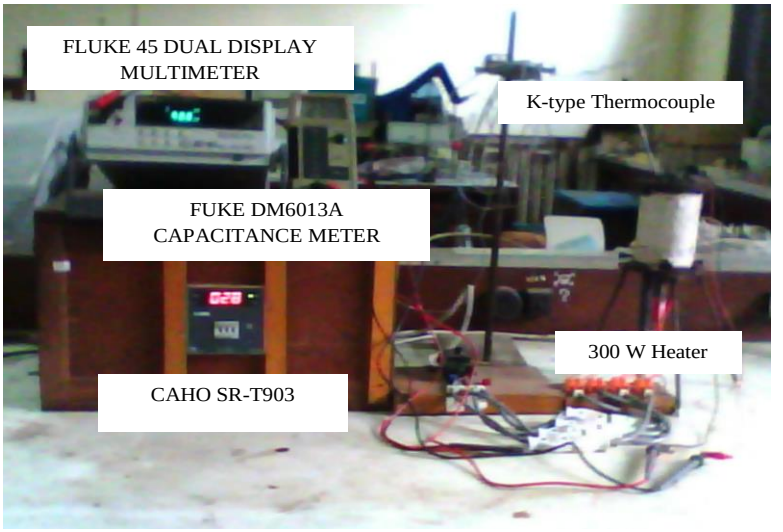

Figure 2: Photograph of the experimental setup for the temperature dependent electrical resistance measurement

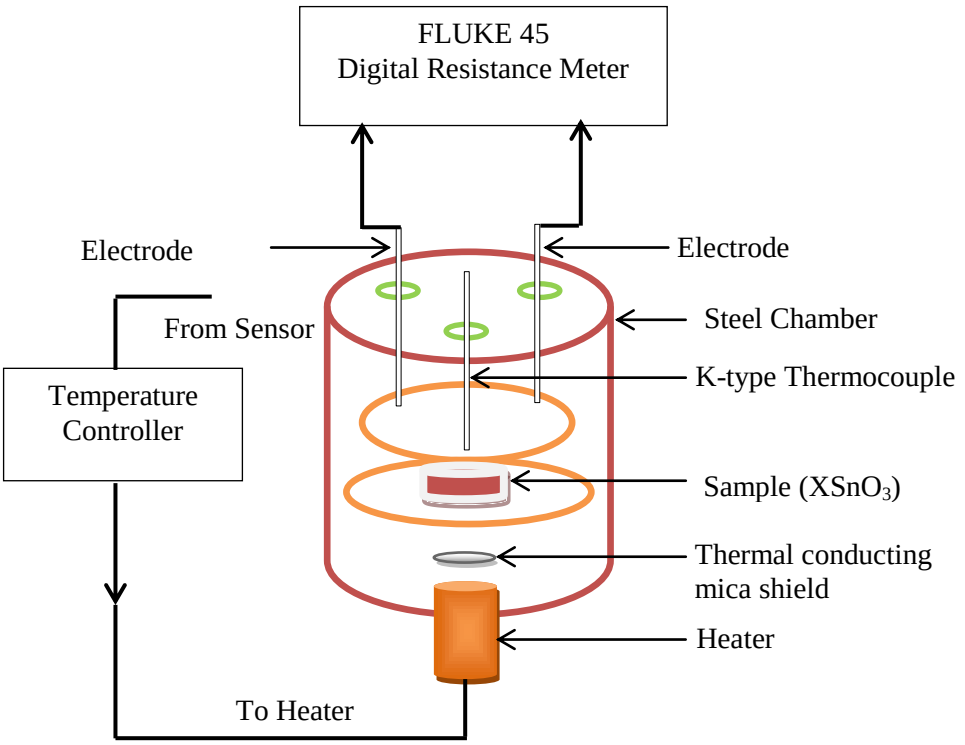

Figure 3: Schematic diagram of the experimental setup for the temperature dependent electrical resistance measurement

Results and Discussion

XRD Study

Figure 4 shows the powder XRD pattern of the $CaSnO_3$. It is found that the many sharp peaks appeared in which the most sharp peaks (dominant) is (112) plane at the diffraction angle 32.15°. The observed peaks could be indexed since they are in complete agreement with standard XRD pattern of $CaSnO_3$ (JCPDS card no.01-074-7233) indicating the formation of crystalline phase pure $CaSnO_3$. Therefore it can be assumed that the crystallinity of $CaSnO_3$ crystallizes be obtained. XRD pattern shows that the $CaSnO_3$ analogous to orthorhombic structure. The calculated lattice parameters are shown in Table 1 and Table 2. Because the lattice parameters 'a' and 'b' have the nearly equal values and 'c' has the higher value but the lattice angle has the 90°. The crystallite size of $CaSnO_3$ is 42.17 nm.

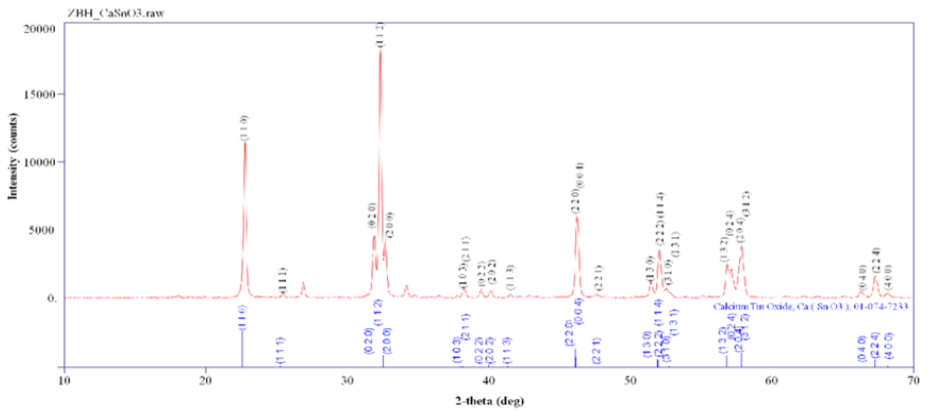

Figure 4: XRD pattern of $CaSnO_3$

XRD pattern of the $SrSnO_3$is shown in Figure 5.This figure shows that the intended target sample $SrSnO_3$ is obtained because the sharp peaks are found as the (002), (020), (004), (114), (312) and (224) planes. All the observed peaks could be indexed since they are in complete agreement with reported XRD pattern of $SrSnO_3$ (JCPDS card no. 01-0704389) indicating the formation of crystalline phase pure $SrSnO_3$. XRD pattern indicates that the single phase orthorhombic structure. The most dominant peak is the (020) plane at the 2θ value of 31.32°. The lattice parameters are presented in Table 1 and Table 2. The crystallite size is obtained as 47.34 nm and hence it is the nanosized polycrystalline mate.

XRD pattern of $BaSnO_3$ is shown in Figure 6. The observed XRD lines were identified by the standard $BaSnO_3$ (JCPDS card no. 00-015-0780). The appearance of very sharp diffraction peaks further indicates the quite small crystallite size in the powder. It can be seen that the most intense peak is (110) plane at the 30.76°.

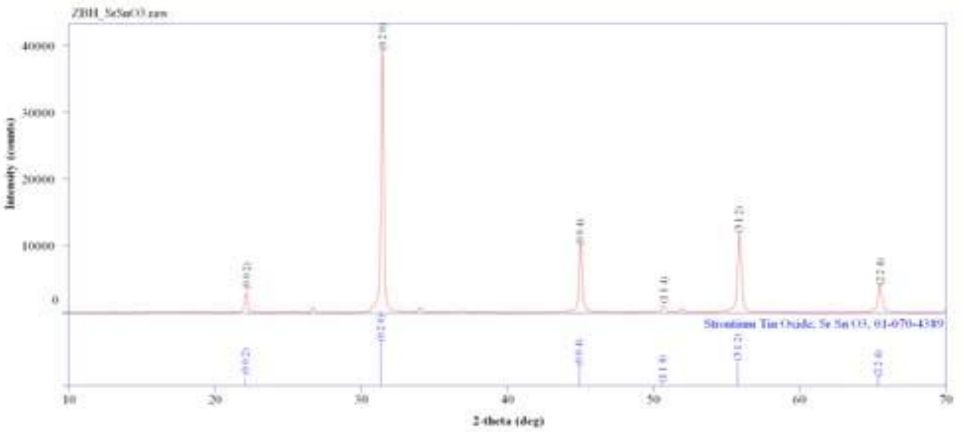

Figure 5: XRD pattern of $SrSnO_3$

The absence of diffraction peaks due either to the starting materials or second phase in the Ba-Sn-O system showed the powder obtained, to be of high quality. According to the XRD pattern, the dominant peaks (especially planes orientation) and the interplaner spacing (d_{hkl}) or lattice spacing, the lattice parameter "a", "b" and "c" can be calculated as shown in Table 1 and it is seen that the all of lattice parameters are in nearly equal to 4.1111 Å. The $BaSnO_3$sample belongs to cubic structure. The lattice parameters are presented in Table 1.

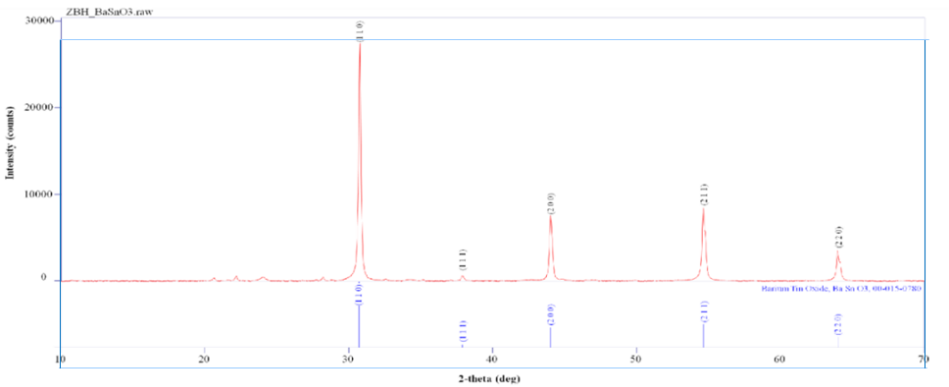

Figure 6: XRD pattern of $BaSnO_3$

Table 1: The lattice parameters and crystallite sizes of perovskite type $CaSnO_3$, $SrSnO_3$and $BaSnO_3$

Name	Maximum peak (hkl)	Lattice constant 'a' (Å)	Unit cell volume 'V' $(nm)^3$	Crystallite size 'D' (nm)
$CaSnO_3$	(112)	5.4982	0.0244	41.7684
$SrSnO_3$	(020)	5.7079	0.0263	46.9505
$BaSnO_3$	(110)	4.1111	0.0695	49.0361

Table 2: The lattice parameters of $CaSnO_3$, $SrSnO_3$and $BaSnO_3$

Name	a (nm)	b (nm)	c (nm)
$CaSnO_3$	0.5498	0.5636	0.7865
$SrSnO_3$	0.5708	0.5707	0.8071
$BaSnO_3$	0.4111		

Microstructural Characteristics of the Samples

From the SEM micrograph of the $CaSnO_3$ powders heated at 1200° C for 3 h is shown in Figure 7, it is observed that the grain sizes are uniform and homogeneous. The grain size is 0.5*6*μm and its average crystallite size is 42.1709 nm. So it can be suggested that the crystallite size is about 10 times smaller than that of the grain size. So the grain size is very small.

SEM micrograph of $SrSnO_3$prepared at 1200°C was shown in Figure 8, where it can be seen clear that the surface morphology is so good because the grain sizes are uniform and homogeneously. The average grain size is 0.60 μm, so it is very small and the interconnectivity between the grains is very closer and it has some porosity in the sample.

SEM micrograph of $BaSnO_3$ is shown in Figure 9. It can be seen that sintering at 1200°C for 3 h, the grain size is ranging from the submicron to as large as $\approx$ *(0.6* μm, i.e., 6×10^{-7} m). It is observed that all the grains are the uniform and homogeneous grain size and it is estimated by using the line intercept method. In addition, it is the narrowing of grain size distribution and good interconnectivity. Thus it has some porosity in the sample. According

the XRD investigation, the cubic perovskite type $BaSnO_3$ crystallizes has the lattice constant of about 4.1111 Å. Therefore it appears that the grains on average are grown to an extent of about 100 times of the unit cell dimension. The obtained average grain sizes are tabulated in Table 3. Presence of some porosity provides the charged ions to move freely so it may cause the ionic current in the sample. Because of some porosity, these samples can adsorb the humidity or other gases so that it can be used as Humidity of gas sensor by measuring its sensitivity.

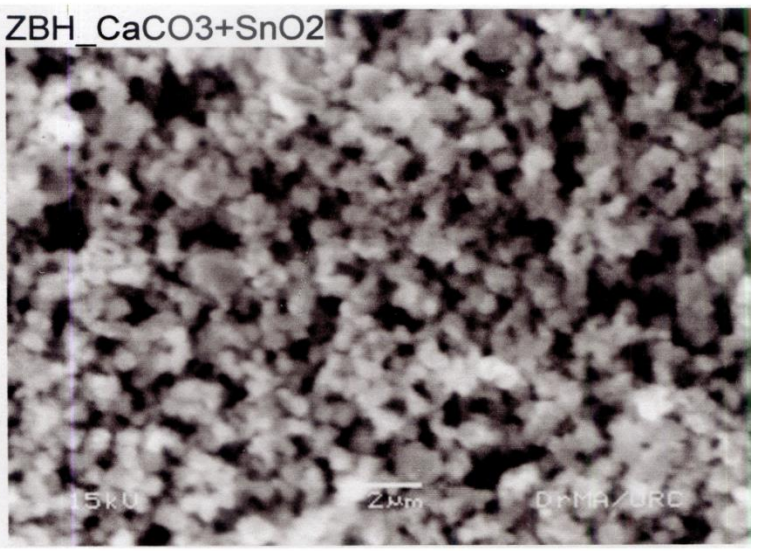

Figure 7: SEM micrograph of the $CaSnO_3$

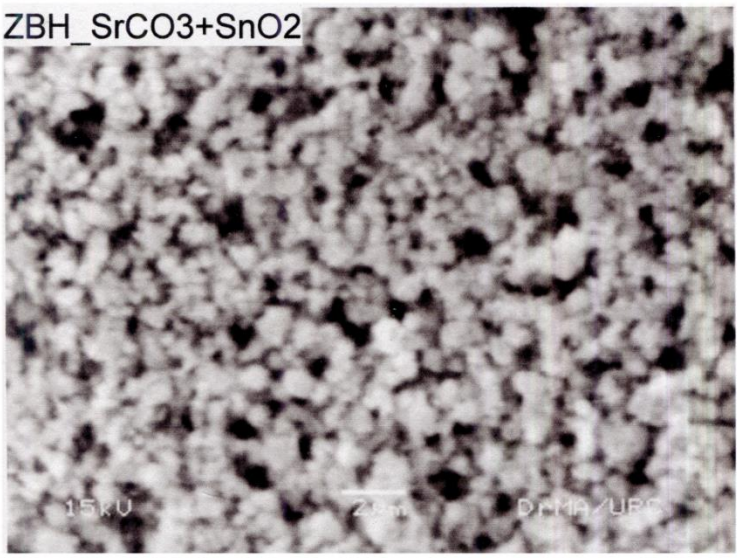

Figure 8: SEM micrograph of the $SrSnO_3$

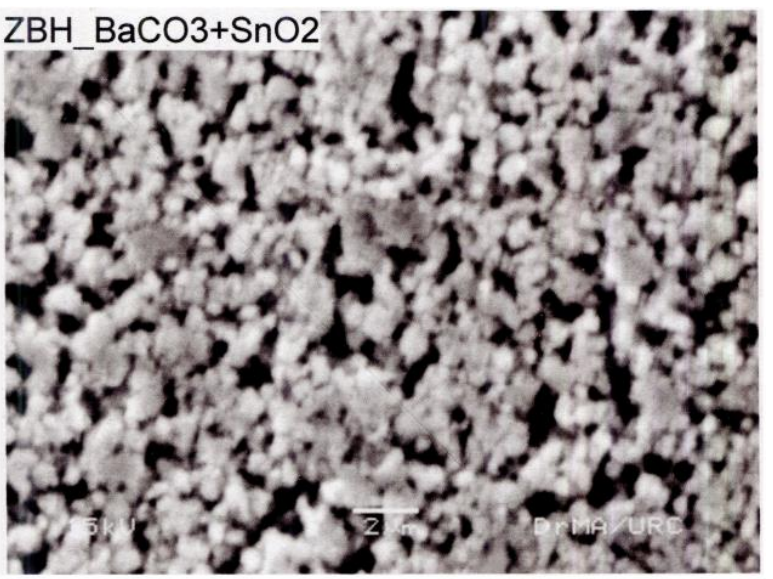

Figure 9: SEM micrograph of the $BaSnO_3$

Table 3: The grain sizes of $CaSnO_3$, $SrSnO_3$and $BaSnO_3$

Sample	Grain size (μ m)
$CaSnO_3$	0.5610
$SrSnO_3$	0.5534
$BaSnO_3$	0.5874

Electrical Conductivity Study

Electrical conductivity of a ceramic with temperature obeys an Arrhenius expression $\sigma = \sigma_0 \exp(-E_a / kT)$, where σ is the conductivity, *σ0is* the pre-exponential factor, E_a is the activation energy for ionic conduction, *k* is the Boltzmann constant and T is the absolute temperature. In the present work, Arrhenius plots of the variation of dc electrical conductivity of the $CaSnO_3$, $SrSnO_3$and $BaSnO_3$samples in the temperature range 303 K - 773 K are shown in Figures10(a – c). According to the theory of ionic conductivity, the slope of the electrical conductivity in each of the figure, e.g., in Figure10(a) for $CaSnO_3$sample, corresponding to the activation energy for creating of defect states due to the ionic motions of the sample. The electrical conductivity σ of the sample can be written in the form:

$$\sigma = \sigma_0 \exp(-E_a / kT)$$

$$\ln(\sigma) = -E_a / kT + \ln \sigma_0$$

$$= (-E_a / k)(1/T) + \ln \sigma_0$$

Comparing the above equation with the experimental linear equation, $y = mx + c$ where the value of slope will give the value of ($-E_a/k$). From Fig 3(a), the activation energy E_a can be obtained by using the slope of the $\ln(\sigma)$ versus 10^3/T graph.

$E_a/k = 5.8981 \times 1000$

$E_a = 5.8981 \times 1000 \times k$

$E_a = 5.8981 \times 1000 \times 1.38\text{E-}23$

$E_a = 8.14 \times 10^{-20}$ J

$E_a = 0.5087$ eV

As shown in Figures10(a –c), temperature dependent electrical conductivities of the sample increased with increased in temperature. The activation energies of the samples were evaluated and listed in Table 4.

From the experimental results, the samples exhibited as super ionicconductors at high temperature because their electrical conductivities are found as $\sigma \geq 10^{-3}$ S m^{-1}. In the $\ln\sigma$ – 1000/T graphs, the starting point (temperature) of superionic phase of the samples indicates with the colored circle. It is obvious that the conductivity of the samples increase with increase in temperature so that the samples behave like as semiconductor behavior.

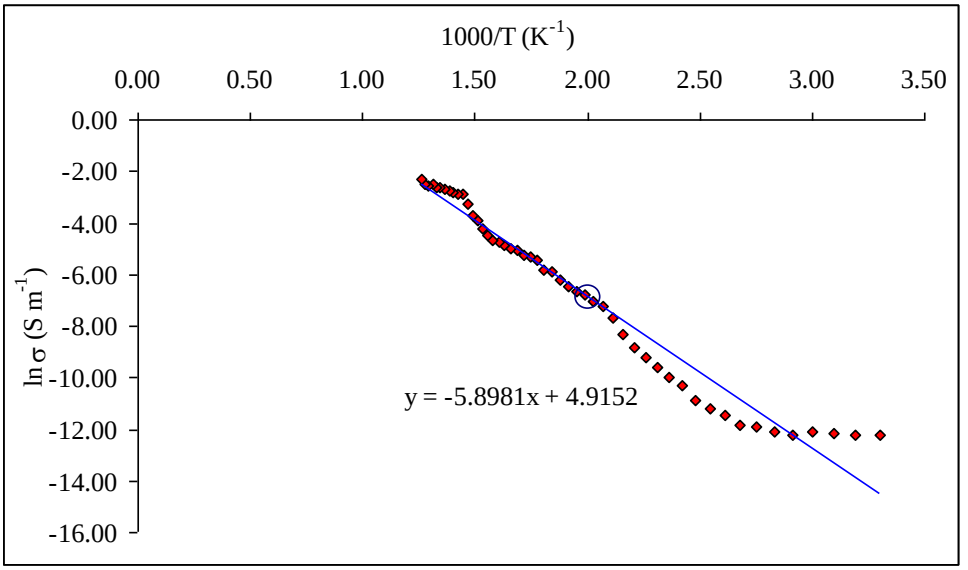

Figure10: (a) Arrhenius plot of the dc electrical conductivity of the $CaSnO_3$

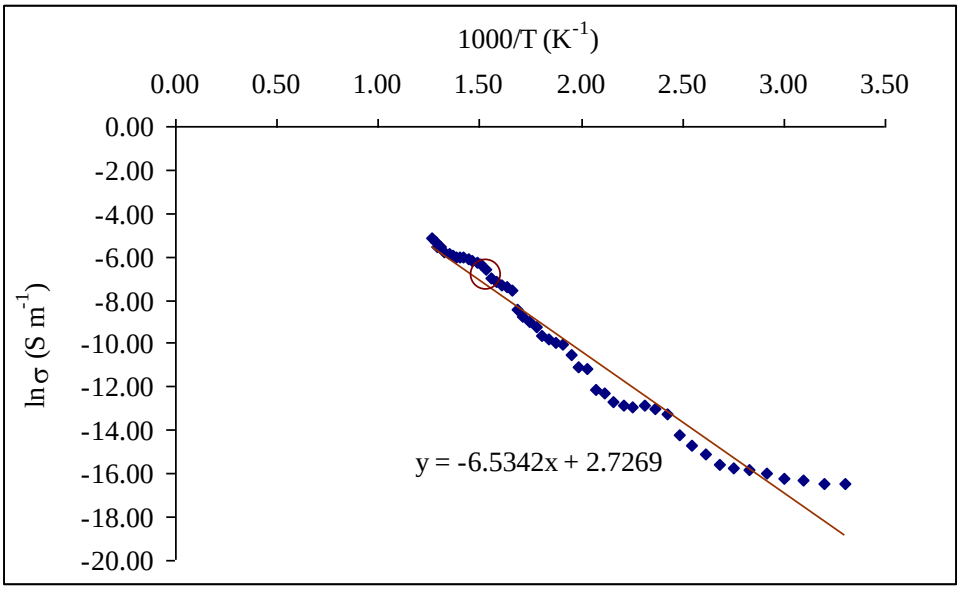

Figure 10: (b) Arrhenius plot of the dc electrical conductivity of the $SrSnO_3$

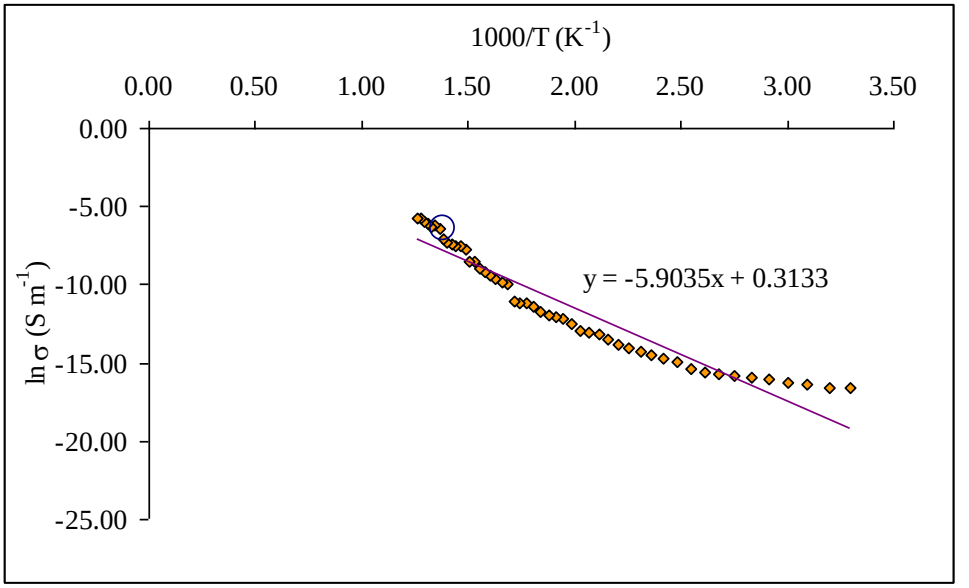

Figure 10: (c) Arrhenius plot of the dc electrical conductivity of the $BaSnO_3$

Table 4: The activation energies of the $CaSnO_3$, $SrSnO_3$and $BaSnO_3$

Sample	Slope	E_a (eV)
$CaSnO_3$	5.8981	0.5087
$SrSnO_3$	6.5342	0.5636
$BaSnO_3$	5.9035	0.5092

Conclusion

Perovskite-type $CaSnO_3$, $SrSnO_3$ and $BaSnO_3$ceramics were successfully prepared by solid state reaction method. Structural phase identification of the samples were examined by XRD. The variation of lattice parameters, unit cell volume and crystallite size were investigated. The crystal structure of $BaSnO_3$ is cubic and that of $CaSnO_3$ and $SrSnO_3$ are orthorhombic structure. The smallest value of crystallite size has been found as $CaSnO_3$ and the smallest grain size has been observed $SrSnO_3$. The grain size of are found to be nearly equal. From the temperature dependent electrical conductivity investigation, the samples exhibited as the superionic conductors. The activation energies are obtained as less than 1 eV. According to literature, the superionic conductors with the activation energies less than 1 eVcan be applied as the solid oxide fuel cell (SOFC) materials.

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