Synthesis & Characterization of $Sm_{2/3}Cu_3Ti_4O_{12}$ Ceramics by Microwave Processing Route

by

Shilpa Rani Sahu

Roll no-411ph2117

Department of Physics

National Institute of Technology, Rourkela

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Under the Supervision of

Dr. Pawan Kumar

National Institute of Technology,Rourkela

CERTIFICATE

It is certified that the work contained in this report entitled "Synthesis & Characterization of $Sm_{2/3}Cu_3Ti_4O_{12}$ Ceramics by Microwave Processing Route" by Shilpa Rani Sahu has been carried out under my supervision and this work has not been submitted elsewhere for any other educational purpose.

Dr. Pawan Kumar

Department of Physics

National Institute of Technology

Rourkela-769008

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Starting from day one, Ph.D. scholar Sridevi di and Subrat sir has been helped me with my project till the completion of this report.

At last, but not the least, I am grateful to my parents, my lovely brother who have always motivated me for anything that I have wished in my life. They encouraged me to pursue research as a career.

Shilpa Rani Sahu

Dedicated to my parents

CONTENT

ABSTRACT

$Sm_{2/3}Cu_3Ti_4O_{12}$ (SmCTO) was prepared using microwave synthesis route. Calcinations were done at 1000^oC for 15 and 30 min, respectively. Sintering was done by microwave method at 1050 ^oC for 20, 40, and 60 min respectively. XRD analysis, density measurement, micrographical analysis through scanning electron microscopy, dielectric constant and dielectric loss measurement with temperature at different frequencies were done. Highest density was achieved in the sample sintered at 1050 ^oC for 20 min. From the XRD studies, single perovskite phase with cubic structure was confirmed. Among all the SmCTO ceramics, the sample sintered for 60 min showed better dielectric constant values and hence useful for capacitor applications.

Chapter 1

1.1 Introduction

The dielectric materials which make use of very high dielectric constants and low dielectric losses are generally used in applications such as capacitor [1]. These solid capacitors are compact in size and rugged and are utilized widely in the devices such as computers, cell phones etc. Dielectric ceramics are usually the basis of ceramic capacitors. Dielectric constant is usually determined from the polarizability of the material. The word “dielectric” is being derived from a Greek word, which means “across” or “through”. Hence, the dielectric can be referred to a material which permits the passage or flow of the electric field or flux. These materials have some interesting properties because here the electric field has the ability to polarise the material to create an electric dipole. The dipole is an object where the equal number of positive and negative charges is separated by a small distance and the electric dipole moment is given by

$$\mu = q \, . \, dl \text{ ----------(1)}$$

Where, q can be either of the two point charges of opposite signs i.e. positive or negative, which are separated by distance dl [2]. The electric dipole is a vector quantity. From the Faraday’s law, it was concluded that the capacitance of any condenser can be increased if the space between the conductors is filled with a dielectric material. If the capacitance of the condenser with the region between the conductors evacuated be C_0 and C be its capacitance when the region is filled with any dielectric, then the ratio

$$C / C_0 = \varepsilon_r \text{ ---------- (2)}$$

which is independent of the shape or dimension of the conductor. Here, ε_r is the relative permittivity or the dielectric constant of the medium. The dielectric constant of the material is a macroscopic quantity which measures how effective the electric field is in polarising the material [3].

1.2 Literature Survey

1.2.1 Why $Sm_{2/3}Cu_3Ti_4O_{12}$

Previously it has been reported that the perovskite material $Sm_{2/3}Cu_3Ti_4O_{12}$ (SmCTO) were synthesized by conventional solid state reaction and sintered at 1000-1100°C. The single-phase composition was confirmed from the analysis of X-ray diffraction of the ceramics. Samples dielectric properties were investigated in the temperature range from -55 to 300°C at frequencies 10 Hz – 2 MHz [4]. Considerable attention is given to $Sm_{2/3}Cu_3Ti_4O_{12}$ due to its abnormal high dielectric constant ($\varepsilon' \sim 10^3$–10^5) over the temperature range from 100 to 600 K. By considering the dielectric and nonlinear electrical properties of these perovskite-type materials, it is believed that these ceramics are promising materials for many applications. Normally, the degree of electronic device miniaturization utilizing capacitive components is decided by the ε' value [5]. As there were not many investigations about this material, so we are doing this project with SmCTO to know more about its properties. As SmCTO is a very high dielectric material and causes low tangent loss of the material which causes to research further more in our project.

1.2.2 Objectives

1. To study the dielectric properties of $Sm_{2/3}Cu_3Ti_4O_{12}$ synthesized by microwave route.
2. Synthesized $Sm_{2/3}Cu_3Ti_4O_{12}$ were characterized and reported their properties.
3. To study the calcined temperature of $Sm_{2/3}Cu_3Ti_4O_{12}$ TGA-DSC was done.

4. To compare the densifications, $Sm_{2/3}Cu_3Ti_4O_{12}$ was sintered at different sintering temperature.

Microwave Sintering

- ✖ Microwaves are photons. Microwaves frequencies ranging from 300 MHz to 300 GHz and wavelengths few cm to a few mm.
- ✖ Microwave heating is a process in which the materials couples with microwaves , absorbs the electromagnetic energy volumetrically and converted to heat.
- ✖ In Microwave heating the heat is generated within the material first and then heats the entire volume.
- ✖ Advantage of this heating mechanism are due to the following facts:-

  1-Enahanced diffusion process

  2- Very rapid heating rates and considerably reduce processing times.

  3- Improved mechanical and physical properties etc.
- ✖ In addition to shorter processing times, microwave sintering also enhances the microstructure and mechanical properties of ceramics.
- ✖ Microwave sintering has achieved worldwide acceptance due to its significant advantages against conventional sintering methods.
- ✖ Generally higher density and better grain distribution can be achieved through microwave sintering.
- ✖ Better physical and mechanical properties can be obtained using microwave sintering [6].

Chapter-2

2.1 Synthesis Procedure

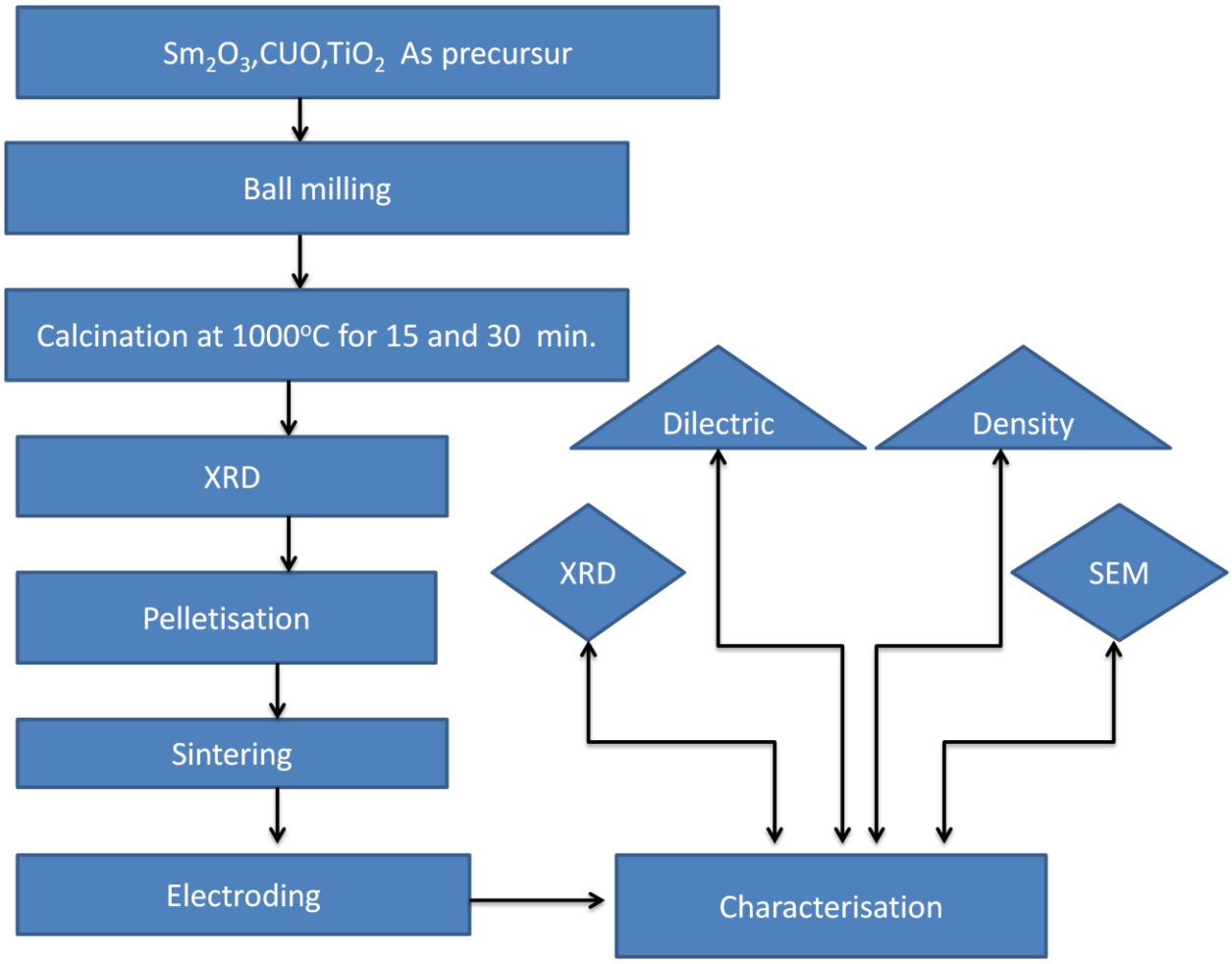

Fig 1 Flow chart of synthesis procedure of SmCTO ceramics

2.1.1 Mixing and Milling

In this project $Sm_{2/3}Cu_3Ti_4O_{12}$ was prepared by the microwave method. Sm_2O_3 (99.99% purity), CuO (99.9% purity) and TiO_2 (99.9% purity) were employed as starting raw materials. The raw

materials were mixed homogenously by balls milling in ethanol for 12 h. . In the milling process the particle experience mechanical stresses at their contact points due to compression with other particles.

2.1.2 Calcination

The sample was calcined at 1000 ℃ for 15 minutes and 30 minutes. The calcined powders were ground and pressed into pellets by a uniaxial compression at 7Pa. During the calcination process ferroelectric phase is obtained as a result of solid phase reaction between the constituents. The calcination temperature is very much important because it affects the electrical and mechanical properties of the ceramics . The homogeneity and the density of the resultant ceramic will also be high If the calcination temperature is high . Calcination temperature also affects the density and electromechanical properties of the ceramic product. So, one has to be very careful while deciding the calcination temperature [8].

2.1.3 Pelletization

For sintering the powdered sample was pressed in the form of cylindrical pellets of 0.5 grams each. The Pelletization involves the uniaxial pressing using rigid dies with a pressure of 6 atmospheres. This method is also called as cold isostatic pressing.

2.1.4 Sintering

Finally, these pellets were sintered in air at 1050 ℃ for 20 ,40 and 60 minutes . Microwave heating is volumetric and is fast and gives uniform and dense grain morphology. Microwave heating is a process in which the materials couples with microwaves absorb the electromagnetic energy volumetrically, and transform into heat. Microwave heating generates heat within the

material first and then heats the entire volume. This heating mechanism has very rapid heating rates and considerably reduced energy consumption. [6]

2.1.5 Electroding

The sintered pellets were coated with silver paste and heated for 5-10 minutes to dry the coating and for good adhesion. The silver coating should strongly adhere to the ceramic and should be thin uniform. It should also have zero resistance, physical durability and good chemical.

X-ray diffraction and scanning electron microscopy (SEM) were used to characterize the phase formation and microstructure of the $Sm_xCu_3Ti_4O_{12}$ ceramics. The dielectric properties of the samples were measured using a LCR Meter over the frequency ranging from 1HZ to 1MHz. The measurements were performed over the temperature ranging from 42 to 400 °C. Each measured temperature was kept constant with an accuracy of ±1 °C.

Chapter-3

3.1 Characterization Techniques

3.1.1 XRD (X-Ray Diffraction)

X-ray scattering techniques are a family of non-destructive analytical techniques which reveal information about the, crystal structure, physical properties and chemical composition of materials and thin films. In X-ray diffraction we observed the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle and wavelength or energy. It consist of three basic elements, a sample holder, an X-ray tube and an detector which can detect X-ray [6]. To produce electrons we heated the filament and apply the voltage for accelerating the electrons toward a target, and electrons are bombarded with the target material to generate the X-rays in a cathode ray tube. [9]

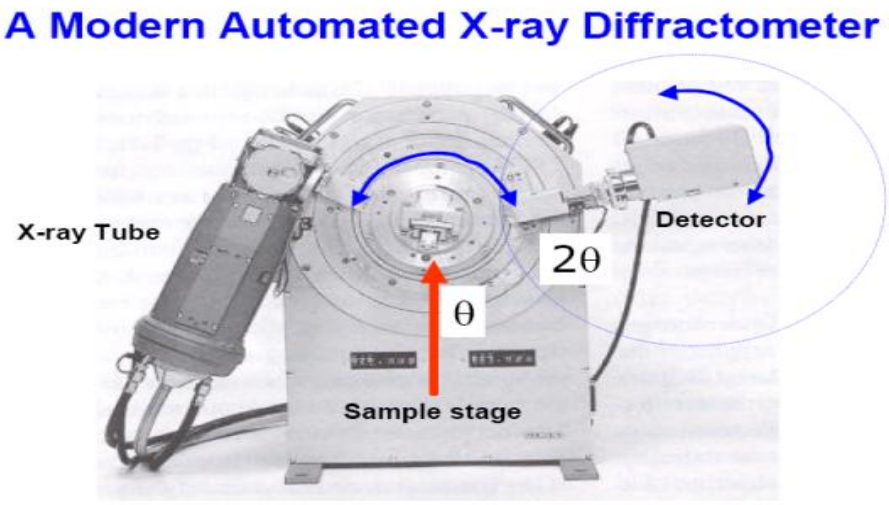

Fig 2 X-Ray Diffraction set up

3.1.2 Density Measurement

The density of the sintered pellets was measured using the Archimedes principle. In this method first the dry weight of the sintered pellets were taken using an electronic measuring machine. Then the pellets were immersed in water by putting in a suspended metallic wire in a beaker. Then the beaker is taken out from the desiccators and suspended weight of the immersed pellet was measured by the density measurement kit [10]. Finally the density was calculated as follows:

Density = Dry weight x density of water / (Dry weight – suspended weight) ---------- (3)

3.1.3 Dielectric Constant and Dielectric Loss Measurement

For the measurement of dielectric constant and dielectric loss were done by electroding the samples with silver paste. The coated samples were heated at 200 ^{0}C so as to dry the silver paste on the pellets completely. The HIOKI 3532-50LCR HiTester instrument were used for dielectric measurements. The frequency range was varied from 1Hz to 1MHz. The dielectric properties were also measured as a function of temperature starting from room temperature. Then the data were extracted and plotted using the origin software to get the desired graph for dielectric constant and dielectric loss [11].

3.1.4 Scanning Electron Microscope

Scanning electron microscopy is one of the high resolutions imaging technique to see the nanostructure of 5 nm size to micron size. In our project to observe the micrograph of $Sm_{2/3}Cu_3Ti_4O_{12}$ ceramic, we have taken the SEM images to understand the surface effect of $Sm_{2/3}Cu_3Ti_4O_{12}$ ceramic. Scanning electron microscopy is used to study the microstructure and topographies of the sample. It scans the surface of the sample to build a 3-D image of the specimen with the help of electron beam. The magnification power of SEM is of nanometre scale range. It has the basic principle i.e, the interaction of the electron beam generated from x-ray

tube and the sample surface. This interaction generates a variety of signals and these signals include secondary electron, X-rays, backscattered electron, photons, heat and transmitted electrons. Backscattered electrons and secondary electrons are used for the imaging of the sample. Secondary electrons are used to study the topography and morphology of the sample whereas the back scattered electrons help to illustrate the contrast in the composition of multiphase samples. SEM most commonly comes in conjunction with EDAX [12]. SEM has a wide range of applications ranging from the ceramic industry to the forensic lab. Through SEM observations can be done in macro and submicron ranges. It can be used in the forensic lab to investigate the gun shot residues and due to its ability of combining imaging with elemental analysis this is possible [13]. When it is coupled with EDAX it can be used to determine the percentage compositions of different elements present in the compound.

Chapter 4

4.1 Results and Discussion

TGA-DSC

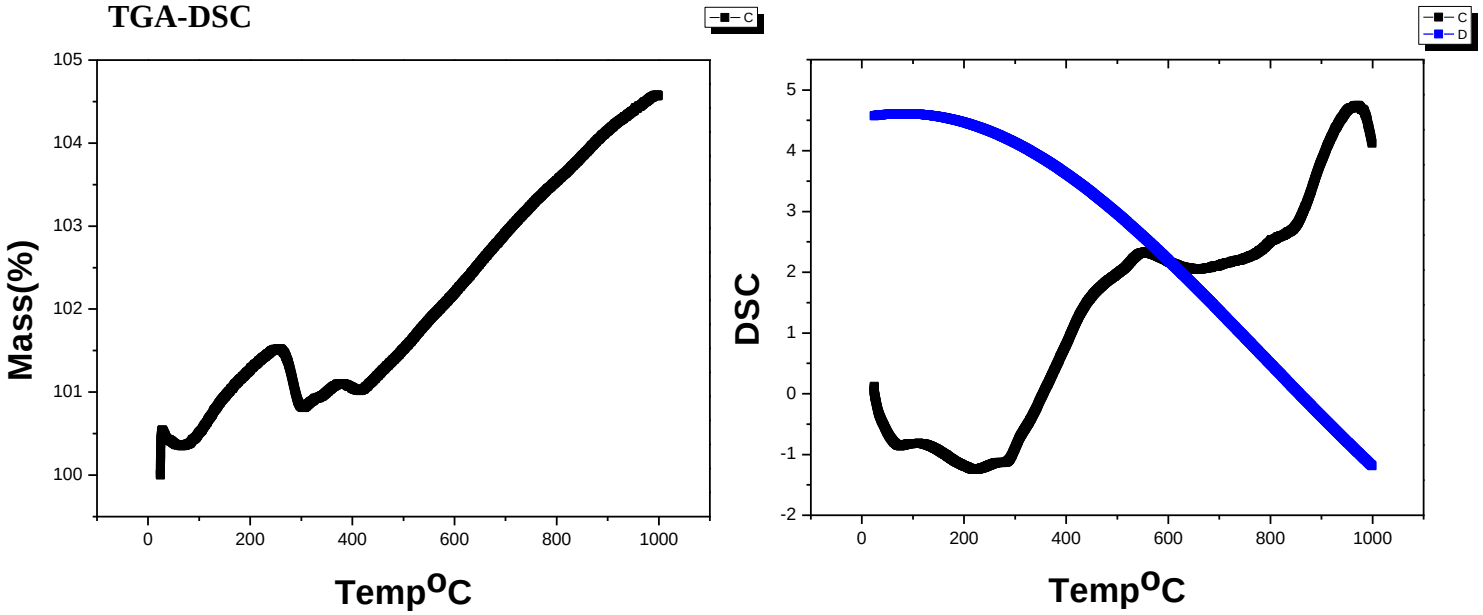

Fig. 3 TGA-DSC curve of $Sm_{2/3}Cu_3Ti_4O_{12}$ raw powder

Fig 3 shows the TGA-DSC data of $Sm_{2/3}Cu_3Ti_4O_{12}$ sample respectively. It is shown in this graph that mass increases with increase in temperature. The weight gain in the temperature range of ~700°C to 1100°C may be due to the contact with atmospheric oxygen.

X-Ray Diffraction Study

Fig- 2 shows the XRD patterns of $Sm_{2/3}Cu_3Ti_4O_{12}$ ceramics calcined at 1000 °C for 15 and 30 minutes confirming the formation of perovskite phase with cubic structure in the $sm_{2/3}Cu_3Ti_4O_{12}$ ceramic samples.

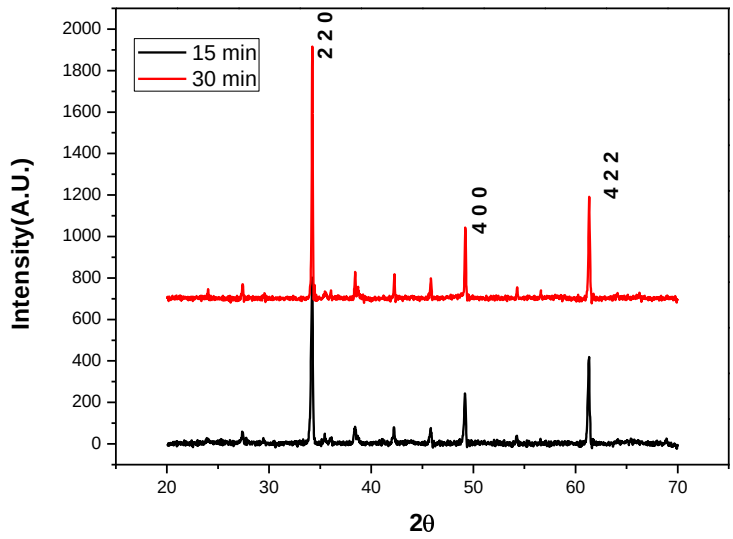

Fig.4 XRD peaks of $Sm_{2/3}Cu_3Ti_4O_{12}$ sample calcined at 1000^0C for 15 and 30 minutes

The phase of SmCTO is detected in all XRD patterns. The maximum intensity was obtained at 32.24. The surface morphologies of the $Sm_{2/3}Cu_3Ti_4O_{12}$ ceramics are demonstrated. The above figure shows the XRD patterns of $Sm_{2/3}Cu_3Ti_4O_{12}$ ceramics calcined at 1000 °C for 30 minutes confirming the formation of well $Sm_{2/3}Cu_3Ti_4O_{12}$ phases. Slight changes in the microstructure of the $Sm_{2/3}Cu_3Ti_4O_{12}$ ceramics are observed. The peaks which are calcined at 1000 °C for 30 min. better than the sample calcined for 15 minute. So we took SmCTO ceramics which is calcined at 1000 °C for 30 min. as consideration and do next measurements of those samples.

Table 1 Density Measurement

Sample sintered	Dry weight (g)	Suspended weight (g)	Density in g/cm3
20 MINUTES	**0.3828**	**0.3108**	**5.31**
40 MINUTES	**0.4778**	**0.3858**	**5.19**
60 MINUTES	**0.3914**	**0.3159**	**5.18**

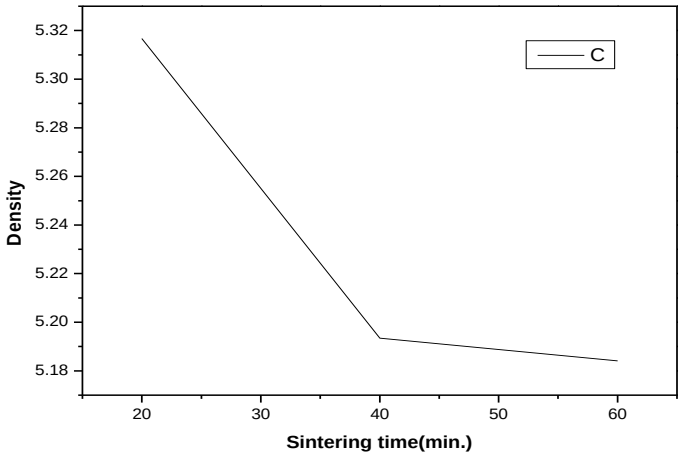

Fig.5 Density vs. sintering time of $Sm_{2/3}Cu_3Ti_4O_{12}$ sample sintered at 1050^0C for 20, 40 and 60 minutes.

Fig 5 shows the density measurement of $Sm_{2/3}Cu_3Ti_4O_{12}$ sample. The highest density for $Sm_{2/3}Cu_3Ti_4O_{12}$ was obtained to be 5.31g/cm3. The density in microwave method was found to be highest for the sample sintered at 1050 ^{0}C for 20 min followed by the samples for 40 and 60 min. And for microwave method the highest density was found for sample sintered at 20 minutes followed by 30 minutes and 40 minutes.

Scanning Electron Microscope

The SmCTO sample calcined at 1000^0C for 30 minutes has been optimized for the sintering condition in the microwave furnace. Therefore, the SmCTO samples are sintered at 1050^0C for 20, 40, and 60 minutes

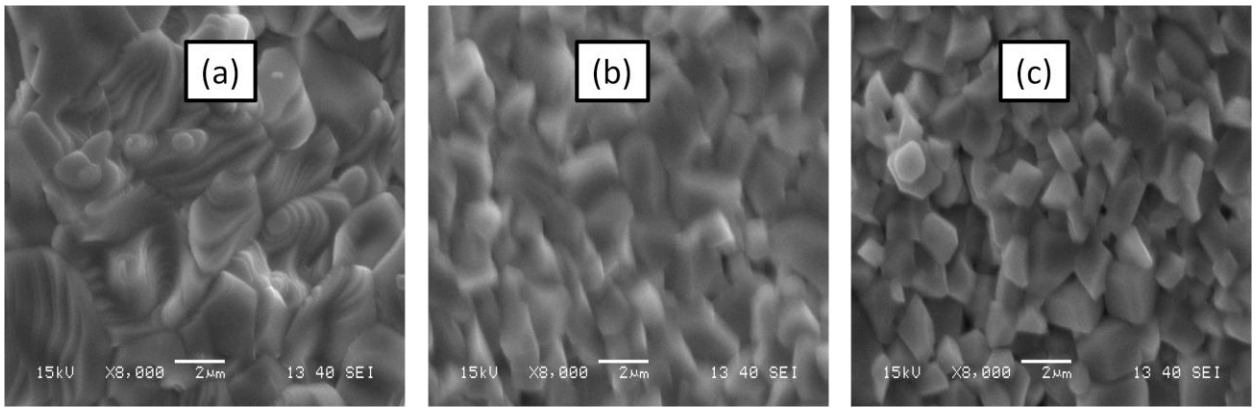

Fig.6 SEM micrograph of $Sm_{2/3}Cu_3Ti_4O_{12}$ sample sintered at 1050^0C for 20, 40 and 60 minutes

The above figure represents the SEM of $Sm_{2/3}Cu_3Ti_4O_{12}$ sample sintered at 1050 ^{o}C for 20, 40 and 60 minutes respectively. This figure shows that the grains are with less porosity and with uniformly distributed grains.

Table 2 Grain size measurement

Sintering time	Grain size(μm)
20 min	1.7
40 min	1.4
60 min	1.5

Dielectric Measurements

Dielectric constant & dielectric loss vs. frequency is measured by HIOKI LCR 3532-50 Hi Tester for the $Sm_{2/3}Cu_3Ti_4O_{12}$ systems synthesized by microwave processing.

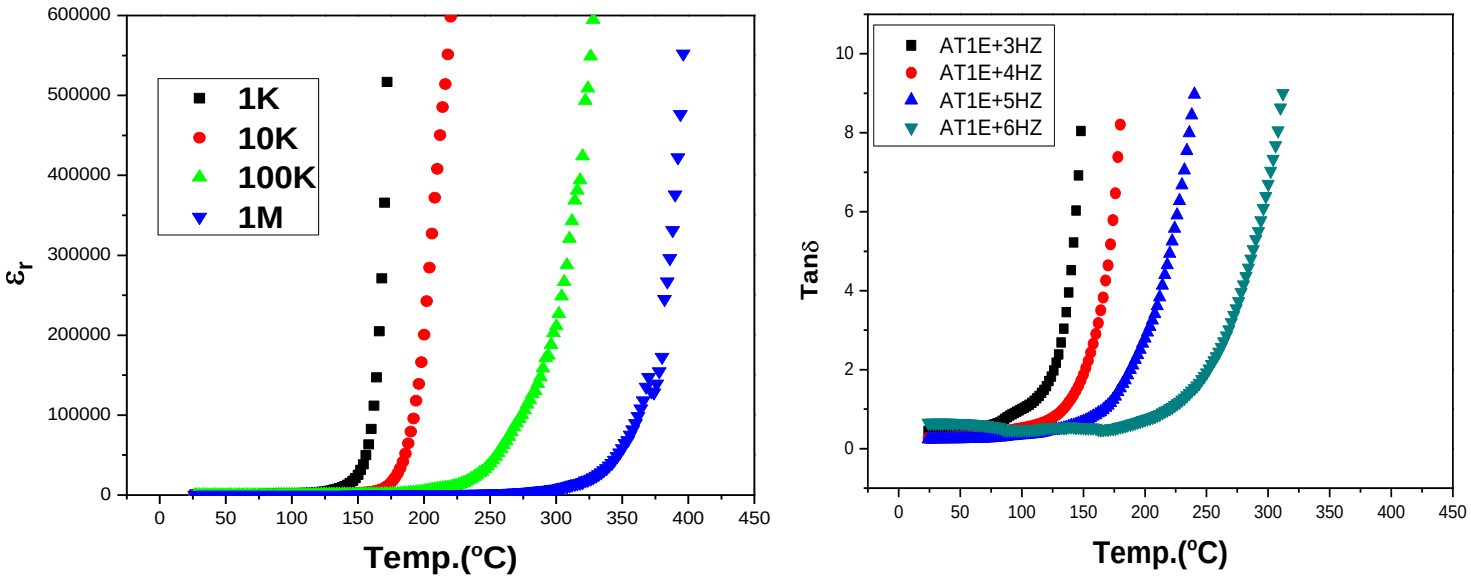

Fig.7 ε_r and tanδ vs. temperature at different frequencies of $Sm_{2/3}Cu_3Ti_4O_{12}$ sample sintered at 1050^{0}C for 60 minutes

The above figure shows the dielectric constant and dielectric loss of 60 min sintered SmCTO sample.

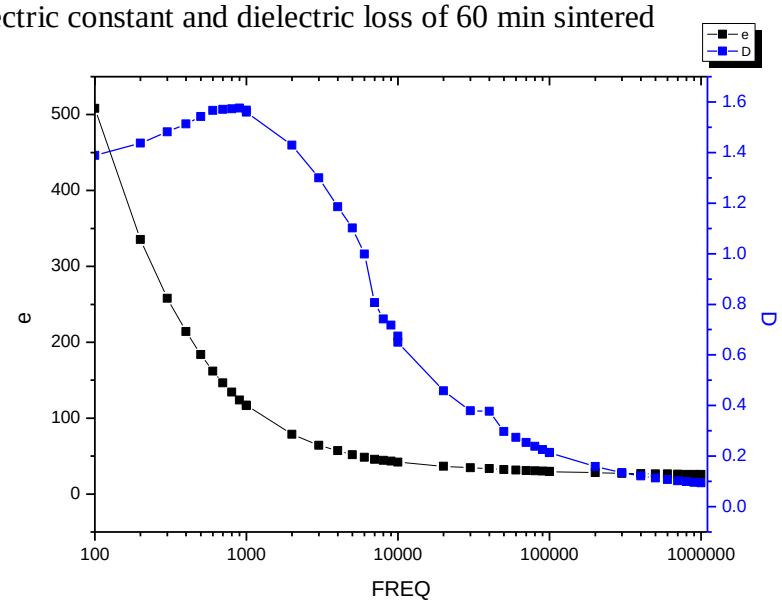

Fig.8 Room temperature ε_r and tanδ plots at different frequencies of $Sm_{2/3}Cu_3Ti_4O_{12}$ sample sintered at 1050^0C for 60 minutes

Fig 8 represents the dielectric constant and dielectric loss of 60 min sintered SmCTO sample at room temp.

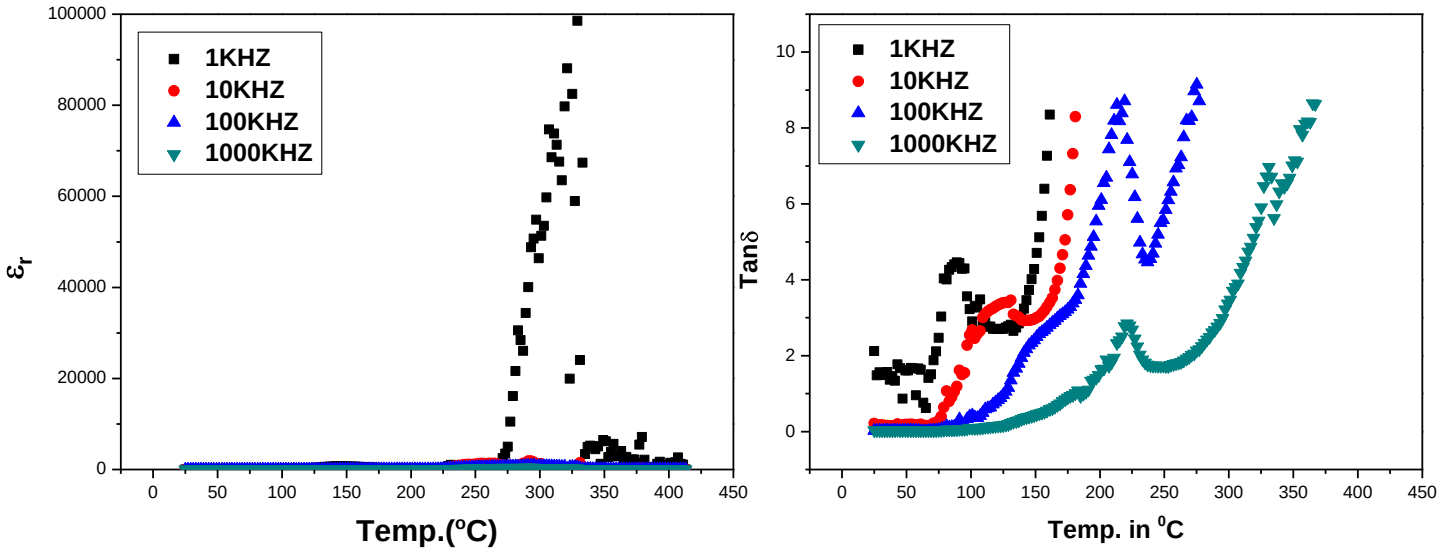

Fig.9 ε_r and tanδ vs. temperature at different frequencies of $Sm_{2/3}Cu_3Ti_4O_{12}$ sample sintered at 1050^0C for 40 minutes

Fig-9 represents the dielectric constant and dielectric loss of 40 min sintered SmCTO sample respectively.

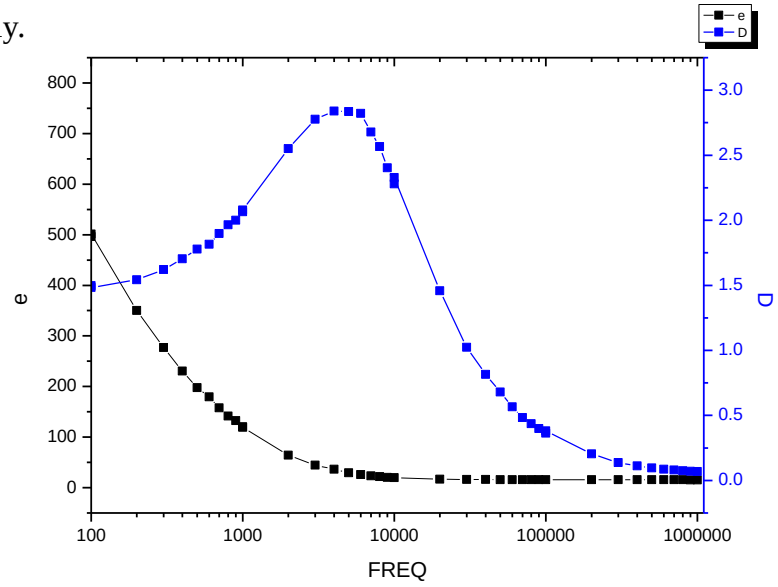

Fig 10 Room temperature ε_r and tanδ plots at different frequencies of $Sm_{2/3}Cu_3Ti_4O_{12}$ sample sintered at 1050^0C for 40 minutes

Fig 10 is the dielectric constant and dielectric loss of 40 min sintered SmCTO sample at room temperature.

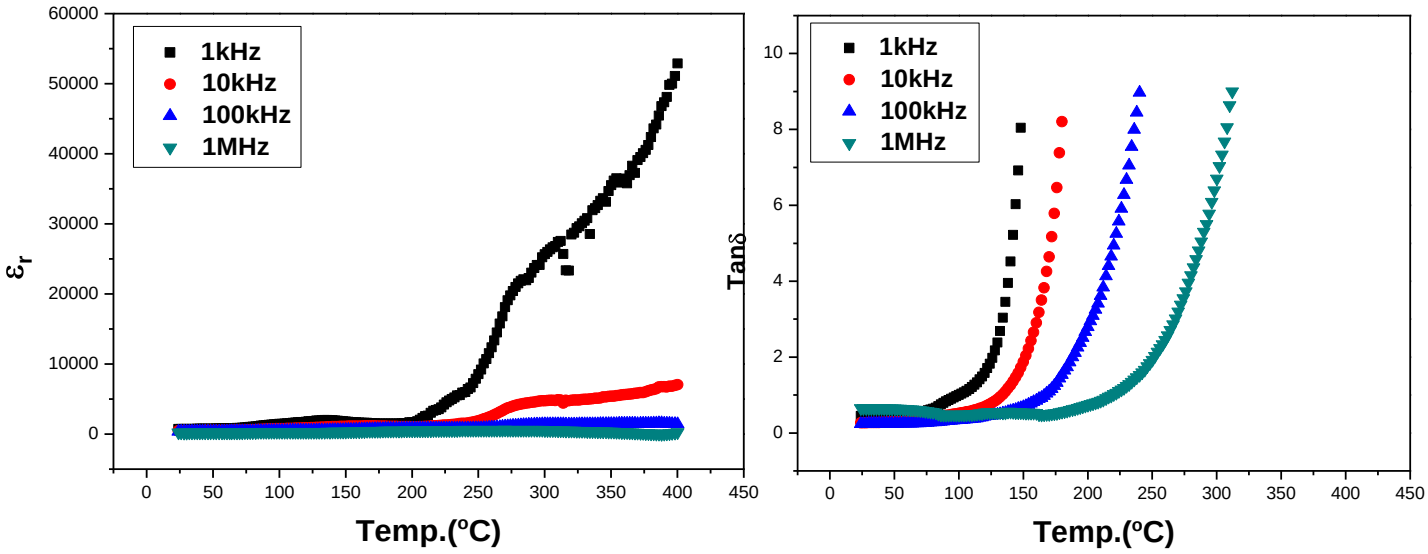

Fig 11 ε_r and tanδ vs. temperature at different frequencies of $Sm_{2/3}Cu_3Ti_4O_{12}$ sample sintered at 1050^0C for 20 minutes

Fig 11 represents the dielectric constant and dielectric loss of SmCTO sample sintered at 20 min respectively.

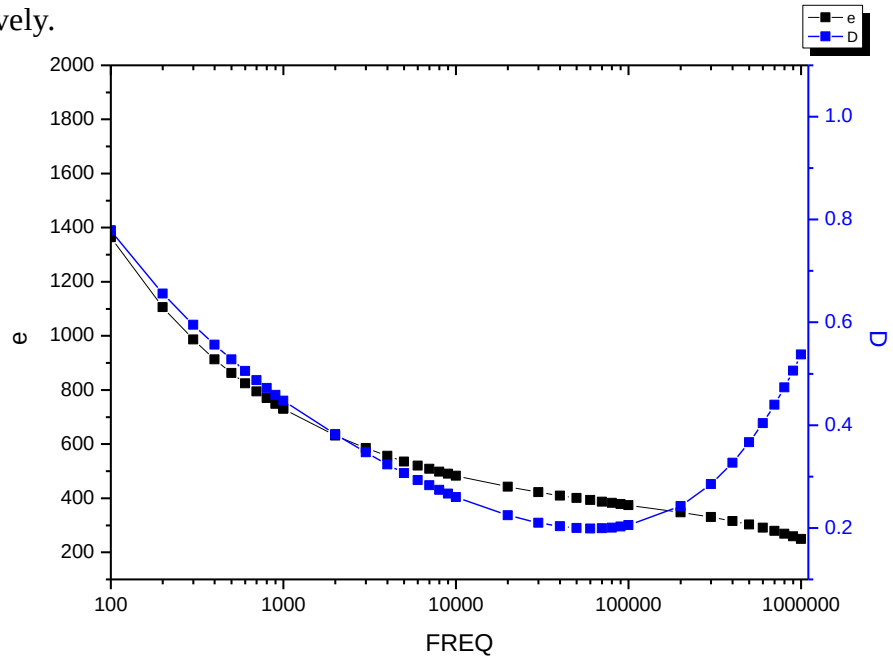

Fig 12 Room temperature ε_r and tanδ plots at different frequencies of $Sm_{2/3}Cu_3Ti_4O_{12}$ sample sintered at 1050^0C for 20 minutes

Fig 12 is the dielectric constant and dielectric loss of 20 min sintered SmCTO sample at room temperature.

In each case, ε_r decreases with frequency. The fall in ε_r is due to the fact that polarization does not occur instantaneously with the application of the electric field,it is due to the inertia of dipoles and the delay in response towards the impressed alternating electric field leads to dielectric loss and decline in ε_r. At low frequencies, all types of polarization contributes and as the frequency is increased and hence the decrease in ε_r. At lower frequencies ε_r is maximum because the contributions from the space charge polarization is large. At higher frequencies, contributions from the polarizations having high relaxation time cease resulting in the decrease in ε_r [14].

Table 3 Dilectric Measurement

samples	**20 min sintered pellets**	**40 min sintered pellets**	**60 min sintered pellets**
€r at 1 KHz at room temp.	721.63	17.54	649.28
tan2 at 1 KHz at room temp.	0.45042	2.11816	0.45042

4.2 Conclusions

The sample $Sm_{2/3}Cu_3Ti_4O_{12}$ was prepared using the microwave synthesis route. At lower calcination temperature of 1000 ^oC pure phase can be prepared. XRD pattern of $Sm_{2/3}Cu_3Ti_4O_{12}$ ceramic indicates the perovskite phase with very small or negligible impurity phases. Density and dielectric properties were measured for $Sm_{2/3}Cu_3Ti_4O_{12}$ ceramics. Density was highest for the sample sintered at 1050 ^oC in case of microwave route for 20 minutes. For the capacitor application these ceramics are potential candidates. The average grain size is in between 1.5-2μm.

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