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Synthesis and Characterization of Zirconium Tin Titanate ($Zr_{0.8}Sn_{0.2}TiO_4$)

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Abstract: This study is part of a new approach towards the development of the of low frequency dielectric properties of the microwave dielectric ceramics zirconium tin titanate ($Z_{0.8}Sn_{0.2}TiO_4$). The Zirconium Tin Titanate (ZST) sample was prepared by the sol-gel technique. The precursor gel powder weight loss and thermal decomposition temperature were analysed by the TGA/DSC and DTA. The Fourier Transform Infrared Spectra (FTIR) was taken for confirming the bonding characteristics of Zro_2 ,TiO_2 with Sno_2. The gel powder was calcined at 800°C for 3 h using the X-ray diffraction the calcined ZST powder crystalline phase formation was found to be orthorhombic and the obtained grain size was less than 1µm. The calcined powder was pelletized by uni-axial press 40MPa and sintered at 1400°C for 3 h. The surface morphology of the sintered sample was analysed by the scanning electron microscope (SEM). The dielectric properties, including dielectric constant and dielectric loss, and conductivity of the sample was measured by the LCR meter as a function of different temperatures, in the frequency range of 50Hz to 5 MHz. This study confirmed that zirconioum tin titanate can be used for low frequency microwave dielectric applications.
Keywords: ZST, Sol-gel method, X-ray diffraction, Scanning electron microscopy,Dielectric properties .conductivity.

1. Introduction

Recently great interest has been paid to Zirconium tin titanate ($Z_{0.8}Sn_{0.2}TiO_4$) for its low dielectric loss and high dielectric constant, high quality factor almost zero temperature coefficient and strong temperature stability leading to its specific applications in devices such as frequency discriminator. In order to accommodate the rapid growth of the wireless communication industry, ZST materials were used as dielectric resonators ranging from cellular phones to global positioning systems, microwave filters and oscillators [1-8]. Already, many research groups have reported the different synthesis routes to prepare ZST materials: viz Co-precipitation [9], Hydro thermal synthesis [10-11] and so on.. In this paper zirconium tin titanate was prepared by the sol-gel method [12]. Many researchers have already reported the dielectric properties of ZST in microwave frequency region at GHz [13], but, so far, the low frequency range (50 Hz to 5 MHz) dielectric properties of ZST have not yet been reported. In this study the microwave dielectric ceramic material ZST was prepared by sol-gel method, and its low frequency dielectric properties and conductivity, were studied.

2. Materials and methods

The $Zr_{0.8}Sn_{0.2}TiO_4$ ceramics materials were prepared by the sol-gel technique. Zirconium oxychloride ($ZrOCl_28H_2O$), Titanium isopropoxide, ($C_{12}H_{28}O_4Ti$) and Tin nitrate $Sn(NO_3)_2$ were used as the starting materials. Initially, Titanium isopropoxide was mixed with acetyl acetone and 2-isoproponal solutions. Then, the second solution was prepared with zirconium oxy chloride and methanol. Finally, tin nitrate was dissolved in an acetic acid and HNO_3 mixed solution. Under vigorous stirring conditions these three solutions were mixed together until a yellow coloured sol was obtained. Then the sol was slowly evaporated at 90°C for 2 h till yellow colour gel was obtained. The gel was dried in a hot air oven at 45°C for a few days. The precursor gel powder was analysed in the temperature range of 50°C-1000°C, by simultaneously by using the DSC/TGA, and DTA,(PERKIN ELMER, PYRIS DIAMOND) model. The obtained gel powder was calcined at 800°C for 3 h and its particle size was calculated by the particle size analyzer. The FTIR spectra were taken by the MIR 8300 spectrometer, operating in the range of 400–4000 cm^{-1} for characterizing the stretching of the molecules in the gel and the calcined ZST powder. The calcined ZST powder was studied by powder X-ray diffraction (Seifert, model 3000P), and it was mixed with the Poly Vinyl Alcohol (PVA) binder, using a pestle and mortar, then pelletized in to 10 mm dia and 1.5 mm thick disks under 40 Mpa pressure using the uni axial press. These pellets were sintered in a conventional furnace at 1400°C for 3 h holding time at a heating/cooling rate of 10°C/min. The density measurements of the sintered samples were carried out using the Archimedes principle. The scanning electron microscope images were captured using the HITACHI model S-3400 JAPAN. The dielectric properties and conductivity of the zirconium tin titanate sintered sample were measured in the low frequency region (50 Hz - 5MHz) as a function of different temperatures ranging from 40°C to 550 °C using the LCR meter (HIOKI 3532 LCR HITESTER.)

3. Results And Discussion

The FTIR analysis spectrum of zirconium tin titanate gel is shown in figure 1(a). The FTIR spectra were measured in the range of 400 cm^{-1} to 4000 cm^{-1}. The small and broad peaks at 3868 cm^{-1} and 3403 cm^{-1} were assigned to the OH functional group. The broad and sharp envelop at 1674cm^{-1}, is due to the water mode (H_2O) of the bending vibration. The bands at 1428cm^{-1}, 1307cm^{-1}, 1352 cm^{-1} indicate the presence of the nitrate groups. The sharp peak at 992 cm^{-1} is assigned to SnO_2 stretching vibration and the strong and sharp absorption bands at 901 cm^{-1} and 812 cm^{-1} are related to (Zr-O) +δ. The broad intense peaks around 686 cm^{-1} and 514 cm^{-1} may be attributed to Zr-O and Zr-O-Ti (i.e due to the metal stretching with oxygen) respectively. The FTIR spectra of the ZST sample calcined at 800°C for 3h is shown in figure 1(b). Due to the calcination effect the peaks intensity decreases. The peaks at 455, 619 cm^{-1}, 992cm^{-1} confirmed the presence of Ti-O, Zr-O-Ti and SnO_2 (metal oxide) respectively.

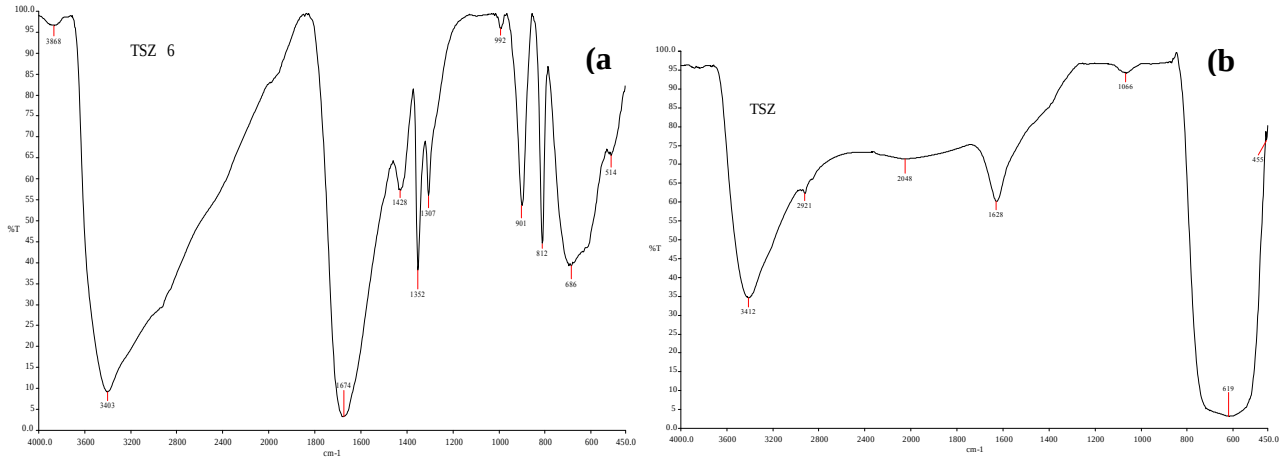

Fig.1 FTIR spectra of Zirconium Tin Titanate ($Z_{0.8}Sn_{0.2}TiO_4$): (a) gel powder, and (b) Calcined powder.

Figure (2) shows the simultaneous thermo gravimetric analysis and differential scanning calorimeter (TGA/DSC) spectrum of zirconium tin titanate precursor gel. The TGA graph shows a slight weight loss in the temperature range of 53.17°C – 113.43°C (15.84% = 0.805mg), that is due to the evaporation of water. The major drastic weight loss was observed in the temperature range between 319.5 and 368.10°C (25% = 1.270 mg), which is due to decomposition of nitrate. The TGA results matched exactly with the DSC spectrum of exothermic peaks at 71.65°C and 345.67°C respectively. It is confirmed that the decomposition as well as endothermic reaction appeared in the temperature range of 242.69 °C and 384.13°C, and an endothermic peak was observed at 354.43 °C in the DTA analysis, as shown in fig.3.

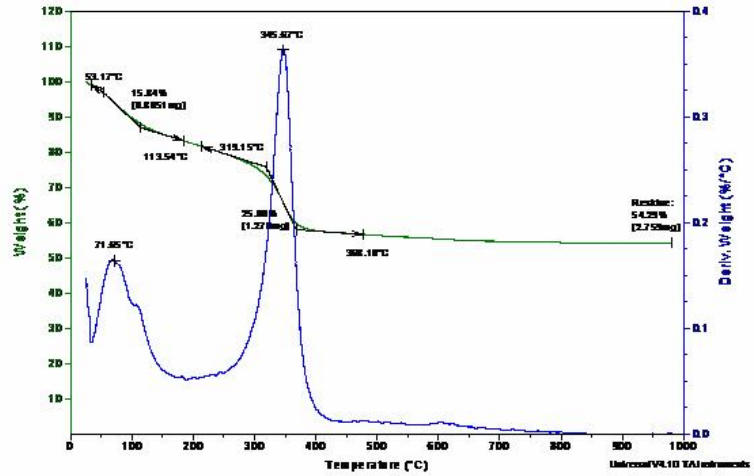

Fig.2 Combined TGA/DSC analysis of ZST precursor gel

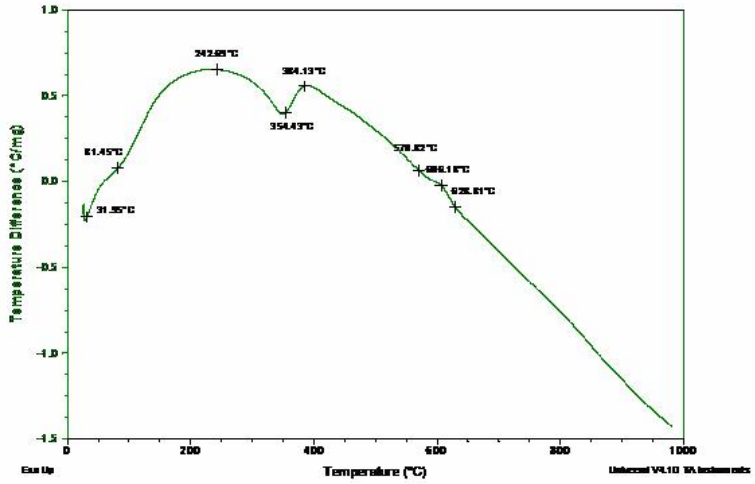

Fig.3. DTA Trace of ZST precursor gel sample

Figure (4) shows the XRD patterns of zirconium tin titanate ($Z_{0.8}Sn_{0.2}TiO_4$) powder calcined at 800°C for 3 h. The phase identification was carried out with the help of the standard JCPDS data base (File No.81-2214). Eight major diffraction intensity peaks from planes (1 1 1) [2^{-} = 30.083°, d = 2.9762 Å], (0 2 0) [2^{-} = 32.354 °, d = 2.7640 Å], (2 0 0) [2θ = 37.612º, d = 2.3896 Å], (1 1 2)[2θ =43 .830º, d = 2.0639Å], (2 0 2)[2θ =52 .700º, d = 1.735Å], (1 3 1)[2θ =56 .480º, d = 1.627Å], (1 1 3)[2θ = 60 .650º, d = 1.520Å], and (3 1 2)[2θ =72 .105º, d = 1.3088Å] were identified and they could be indexed to the orthorhombic structure with

lattice parameters a = 4.837 Å, b = 5.417 Å , and c = 5.267 Å. The 100 % intensity peak crystalline size of zirconium tin titanate has been calculated using the Debye- Scherer relation given by (1)

$$D = (0.98\ \lambda)/ [\beta \cos (\theta)] \text{ ---------- (1)}$$

where 'D' is the average particle size in nm, ' β' is the full width at half maximum (FWHM) of X – ray reflection expressed in radians and θ is the position of the diffraction peaks in the diffractogram. The average grain size of the ZST sample was found to be less than 1μm.

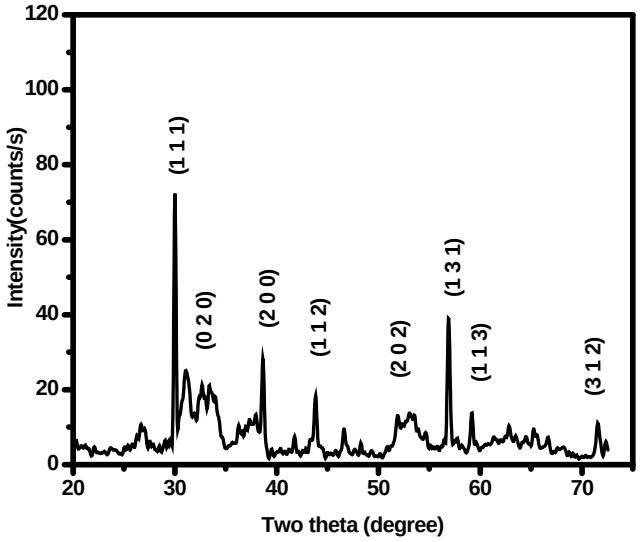

Fig. 4 XRD Patterns of ZST Powders Calcined at 800°C

Fig.5 shows the particle size analysis result of the prepared ZST sample, which confirmed that the particle size was less than 1μm.The SEM images and fracture surface images of the zirconium tin titanate sample sintered at 1400°C for 3 h are depicted in fig 6. Pentagonal and tetragonal uniform sized grains are present in the SEM images 6(a-b) and the grains are arranged on the surface without any pores as well as any cracks, which conclude that the ZST samples were sintered fully with a density >96%.

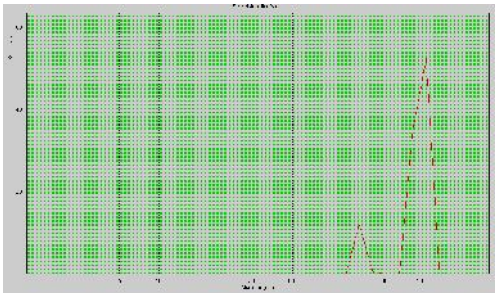

Fig 5. Particle size analysis of Zirconim Tin Titanate powder synthesised by sol –gel technique.

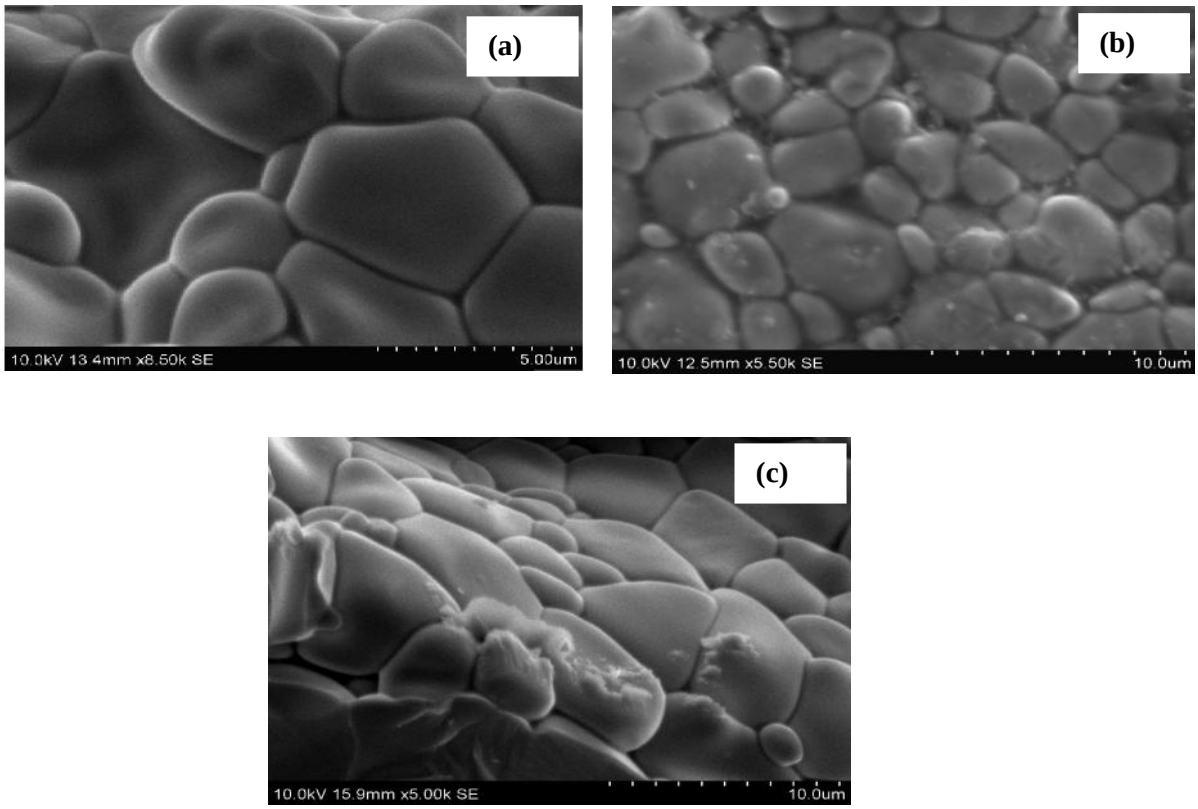

Fig.6. SEM Morphologies of ZST sample sintered at 1400°C for 3 hrs

Dielectric constant

In general, the dielectric constant study of a ceramic material gives an outline about the nature of atoms, ions and their bonding in the material. From the analysis of the dielectric constant and dielectric loss as a function of frequency and temperature, the different polarization mechanisms in solids can be understood. Here, the dielectric constant was measured as a function of frequency (50Hz-5MHz) at temperatures ranging from 40°C, 100°C,200°C, 300°C 400°C 500°C and 550°, and is shown in Fig.7. The dielectric constant was evaluated by using the following relation,

$$£_r = \frac{Cd}{£_0 A} \qquad (2)$$

Where C- is the capacitance, *d* is the thickness of the sample, and *A*, is the area of the sample.ε_0 is the relative permittivity of free space. From this plot, it was observed that the value of the dielectric constant was high in the lower frequency region for all the temperatures, and then it decreased with an increase in the frequency. The high value of the dielectric constant at a low frequency region is attributed to space charge polarization due to charged lattice defects. [14]

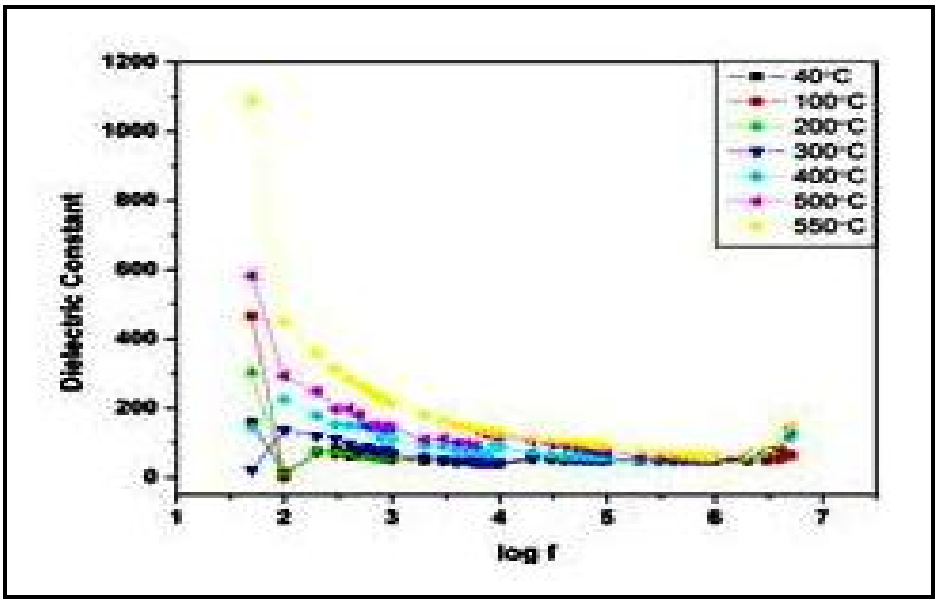

Fig.7. Dielectric constant versus frequency

The dielectric constant in ceramics was attributed to four types of polarizations: interfacial, dipolar, atomic and electronic, at lower frequencies as well as lower temperatures as all the four types of polarization are involved, the, dielectric constant and the dielectric loss are very high. The dielectric constant and the dielectric loss gradually decrease due to the increase in the frequency and the temperature, which is due to the presence of polarizations (interfacial and dipolar) and the disappearance of the other two types. This proves that the dielectric constant and dielectric loss strongly temperature dependent. Beyond a certain temperature (350°C) the charges acquire adequate thermal energy to overcome the resistive barrier at the grain boundary and conduction takes place in a resulting in a decrease in the polarization. The interfacial polarization occurs up to frequencies of around 3 MHz as well as above 500°C, with possibly some contribution from the dipolar polarization also which slightly increases with the temperature. With further increase in the temperature above 500°C the dielectric constant as well as dielectric loss would be saturated because the electronic exchange can't follow the a.c field beyond a certain critical frequency. At low frequency the dielectric constant of the ZST ceramics decreased slightly with increasing frequency this agrees very well with the results reported in the literature [14].

Dielectric loss

The dielectric loss of zirconium tin titanate was measured as a function of frequency at different temperatures ranging from 40°C, 100°C,200°C, 300°C 400°C, 500°C and 550°C and shown in fig 8. The low value of the dielectric loss at high frequency suggests that the materials possess good optical quality. Figure 9 shows the conductivity versus temperature graph. From this measurement, it is seen that the when ever there is an increase in temperature, the conductivity also increases.

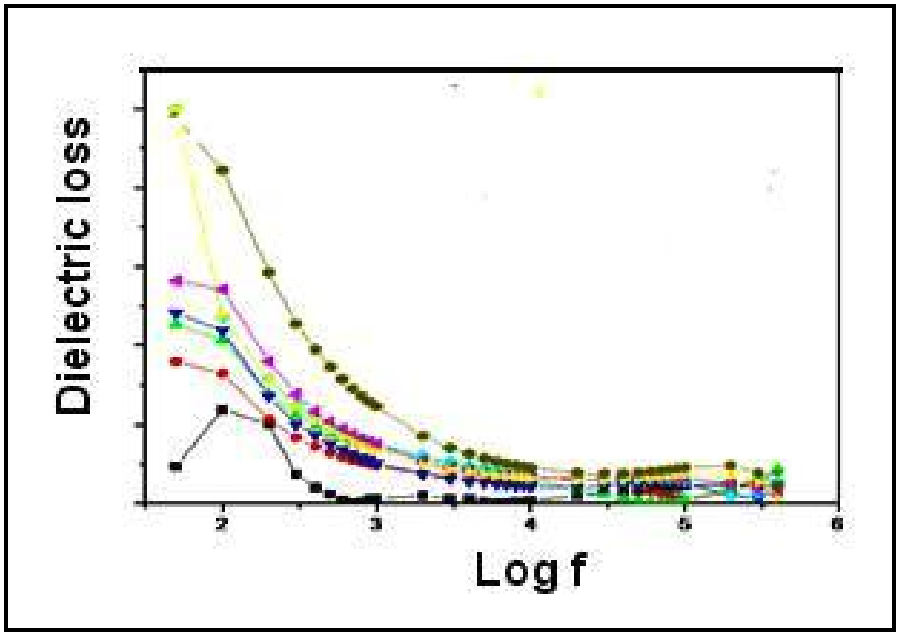

Fig.8.Dielectric loss versus log f

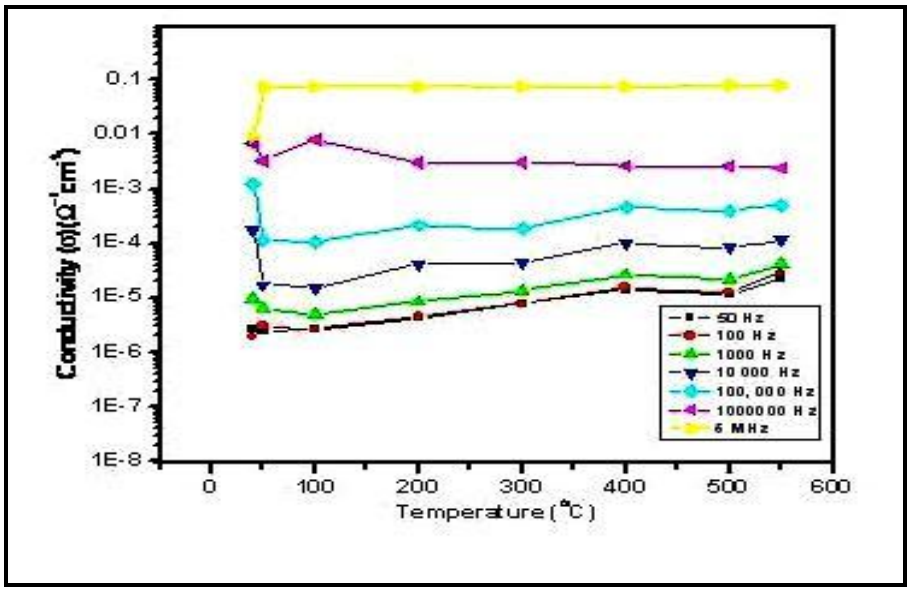

Fig.9. Temperature variation versus conductivity of the ZST sintered at 1400°C for 3 h

4 Conclusion

In this study the ZST sample was successfully synthesised by the sol gel technique and the prepared samples were characterised by using the FTIR, XRD, TGA/DSC, DTA, SEM and LCR meter. The phase formation of the powder was confirmed as orthorhombic and the grain size obtained was less than 1μm as found from the XRD. Weight loss was observed in the TGA results and compared with the DSC studies. The decomposition temperature of the ZST sample's DTA results matched well with the TGA trace. From SEM images it is seen that the grains do not have any pores or cracks and pentagonal and tetragonal shapes are obtained. The electrical conductivity and dielectric properties of the ZST samples were obtained. The dielectric study confirmed that the ZST is the best low frequency microwave material, and is suitable for many low frequency microwave applications.

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