Dielectric and optical study of high dielectric CCTO ceramics

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Abstract. $CaCu_3Ti_4O_{12}$/CCTO ceramic was synthesized by conventional solid state reaction route. The structural, microstructural, optical, and dielectric properties of the CCTO ceramics, sintered at different temperatures, have been investigated and discussed in detail. XRD analysis confirmed the formation of single perovskite phase at 1050 ^{o}C for 4 h. The CCTO ceramic samples, sintered at 1100 ^{o}C showed better microstructural and dielectric properties. The RT values of ε_r and $\tan\delta$ at 1 kHz frequency of the CCTO ceramic samples sintered at 1100 ^{o}C were found to be ~ 11,537 and 0.21, respectively.

1. Introduction

Lead based ceramics have been potential candidates for many electrical applications due to their high dielectric constant (ε_r) [1]. However, recently lead free ceramics with dielectric constant comparable to their lead based counterparts have been in use due to the environmental issues [2,3]. Normally, ferroelectric or relaxor based perovskite materials show dielectric constants higher than 1,000 at room temperature (RT). In these materials, the dielectric constant increases with the increase in temperature and becomes maximum at Curie transition temperature (T_c). This temperature dependence of dielectric constant in the ferroelectric and relaxor materials is undesirable for many applications. The drive for ultra miniaturization of the electronic devices in automobiles and air craft requires the development of high ε_r materials that are stable over a wide range of temperatures. Calcium copper titanate ($CaCu_3Ti_4O_{12}$)/CCTO is has attracted the attention of many researchers because of its high ε_r at RT (up to 10^5) in the

frequency range between 100 Hz and 1 MHz [4]. Also, this high value of ε_r was found to be independent in the temperature range of 100-600K [5]. CCTO was first discovered by Subramanian *et al*. in the year 2000 [6]. It is an oxide based cubic perovskite like ceramics ($AA'_3B_4O_{12}$).

In this paper, CCTO ceramics have been synthesized by the conventional solid state reaction route. The structural, microstructural, optical, and dielectric properties of the CCTO ceramics, sintered at different temperatures, have been investigated and discussed in detail.

2. Experimental

CCTO samples were prepared by conventional solid state reaction route. To synthesize CCTO samples, Calcium Carbonate ($CaCO_3$, 98.5% purity), Copper (II) oxide (CuO, 99% purity) and Titanium Dioxide (TiO_2, 99% purity), all Merck (India), were used as the starting materials. Stoichiometric weights of all the powders were mixed and ball milled with acetone for 10 h, using zirconia balls as the grinding media. After ball milling, the mixture was dried in an agate mortar and grinded for the homogeneous mixing of the powders. After grinding of the starting powders, the thermal decomposition and crystallization of the powder sample was investigated by differential scanning calorimeter (TGA–DSC, STA449C, NETZSCH). Then calcination of the samples was carried out at 900, 1000, 1050 and 1100 $^{\circ}$C for 4 h, respectively. Single perovskite phase was found at 1050 $^{\circ}$C for 4 h. The phase formation of the calcined CCTO powder was confirmed from the XRD study, performed on a Philips X'PERT System X-Ray Diffractometer (PW 3020, Phillips, Eindhoven, The Netherlands) with Cu K_{α} radiation ($\lambda = 1.5405$ A°). The calcined powder was then mixed thoroughly with 2 wt.% polyvinyl alcohols (PVA) binder solution and pressed into disks of diameter ~10 mm and a thickness ~1.5 mm under ~60 MPa pressure. Then sintering of the samples was carried out at 1050 and 1100 $^{\circ}$C for 8 h with a heating rate of 5 $^{\circ}$C/min. The microstructure analysis of the sintered sample was carried out using a JEOL JSM-6480LV scanning electron microscope (SEM). The experimental densities (d_{ex}) of the samples were measured by the Archimedes method. The UV-Visible optical absorption spectra of CCTO ceramic powders was taken out by using UV visible spectrometer (Model: Shimadzu UV, 2250) in the wavelength ranges from 200 to 800 nm at RT. Then silver paste was applied on both the sides of the sintered samples for different electrical measurements. ε_r and tanδ were measured as a function of frequency using a computer interfaced HIOKI 3532-50 LCR-HITESTER.

3. Result and Discussion

Figure 1 shows TG-DSC curves of uncalcined CCTO powder sample. TGA curve shows overall weight loss ~ 11% RT to 1100 ^{o}C. The weight loss processes in the TGA curve are divided into three major steps. The first major step of weight loss, which is ~ 7%, is observed between 600-750 ^{o}C. This weight loss can be associated with the decomposition of the thermally unstable organic compounds [7]. In the same temperature range, the DSC curve shows an exothermic peak. The second major step in TGA curve of the weight loss, which is ~ 4 %, is observed between 750-950 ^{o}C. The last step of major weight loss is observed after 950 ^{o}C. In the same temperature range, the DSC curve shows a major exothermic peak. The appearance of exothermic peak in the DSC curves at ~ 950 ^{o}C can be correlated with the crystallization process in the CCTO powder. No further significant weight loss is observed above 950 ^{o}C temperature, indicating an absence of further decompositions beyond this temperature. Hence, from the TG-DSC study, it can be concluded that for the single perovskite phase formation, the calcination of the CCTO ceramic samples can be carried out above 900 ^{o}C.
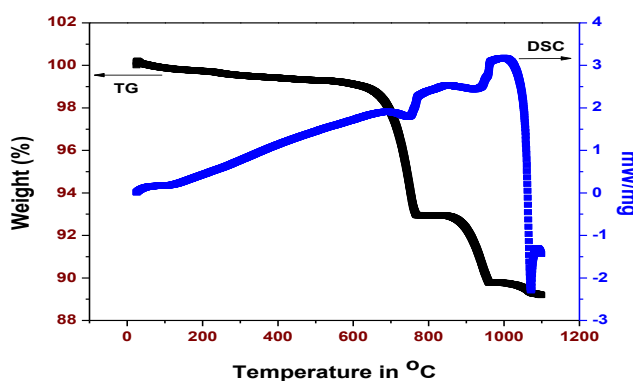

Fig. 1 TG-DSC curves of the uncalcined CCTO powders.

Figure. 2(a) shows the RT XRD patterns of the CCTO samples calcined at 900, 950, 1000 & 1050 ^{o}C for 4 h, respectively. Single perovskite phase is formed at 1050 ^{o}C for 4 h. Sintering of the CCTO ceramic samples has been carried out at 1050 & 1100 ^{o}C for 8 h, respectively as shown in Fig. 2(b). The optimum sintering temperature is found to be 1100 ^{o}C, for 8 h.
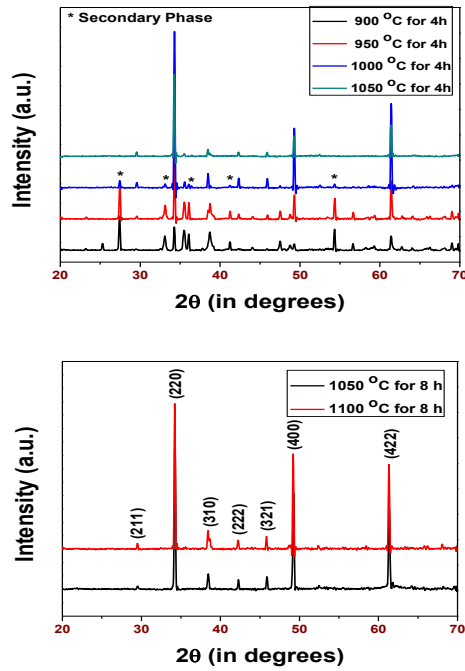
Fig. 2 XRD patterns of **(a)** calcined and **(b)** sintered CCTO ceramics.
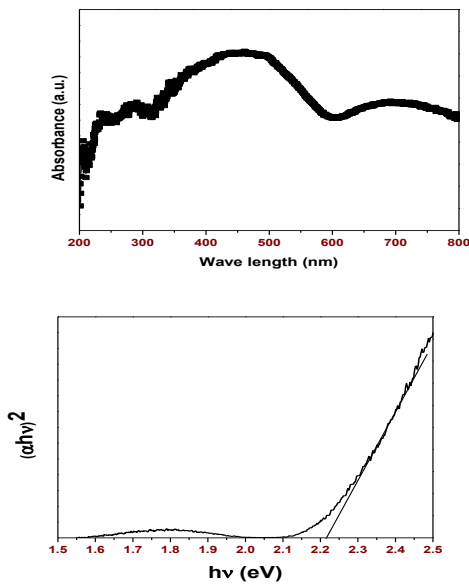

Fig. 3(a) UV-Visible absorption spectra and **(b)** $(\propto h\nu)^2$ vs hν curve of CCTO ceramics.

Figure 3(a) shows absorption spectrum of the CCTO sample recorded in the 200 to 800 nm wavelength range. The absorption spectra of the CCTO samples show two broad bands: (i) around 220-550 nm and (ii) around 700 nm. The first band can be resolved by curve-fitting into 3-components with the maxima around 330, 370 and 470nm. The intensity of these components is much higher than that of the 700 nm band. E_g value of CCTO ceramic is calculated by plotting the $(\propto h\nu)^2$ vs hν curve (shown in Fig. 3(b)) and by extrapolating the linear portion of the absorption edge to find the intercept with energy axis. The value of E_g of the CCTO ceramic samples is found to be ~ 2.22 eV.

Figure 4 shows the SEM of CCTO ceramic samples, sintered at 1050 and 1100 ^{o}C for 8 h, respectively. CCTO ceramic samples, sintered at 1100 ^{o}C for 8 h, exhibit a reasonably uniform microstructure with clear grain boundaries. The average grain size of the CCTO ceramic samples, sintered at different temperatures, is calculated by linear intercept method and is found to be in between 10-20 μm. SEM of the CCTO samples sintered at 1050 ^{o}C shows incomplete grain growth.
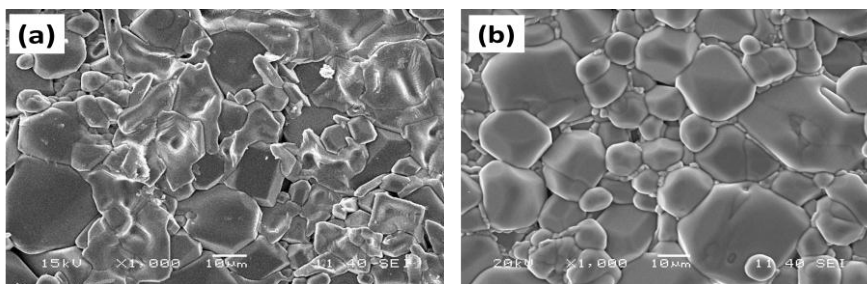

Fig. 4 SEM micrographs of CCTO ceramics sintered at **(a)** 1050 and **(b)** 1100 ^{o}C, respectively.

The experimental densities (d_{ex}) of the CCTO ceramic samples, sintered at different temperatures, are measured by Archimedes' method. The density increases with the increase in sintering temperature [8]. The values of the experimental density and porosity of the CCTO ceramic samples is listed in Table – 1.

Table 1. Different Parameters of the sintered CCTO ceramics

Different Parameters	Sintering Temperatures in ^{o}C	
	1050	**1100**
d_{ex} in gm/cc	4.64	4.76
Porosity in %	4.05	2.49
ε_r at RT	11498	11537
tanδ at RT	0.181	0.213

The frequency dependence of both ε_r and tanδ of CCTO ceramic samples sintered at 1050 and 1100 ^{o}C is shown in Fig. 5. ε_r values of the sintered CCTO ceramic samples are found to decrease with the increase in frequency. The highest value of $\varepsilon_r \sim 11537$ at RT and at 1 kHz frequency is observed in the CCTO ceramic samples, sintered at 1100 ^{o}C for 8 h. The reason for the highest ε_r can be explained by considering that the charge carriers accumulate at the interface between the semiconducting grains and the insulating grain boundary, which results in interfacial space charge polarization and hence large ε_r [9]. The tanδ value of the CCTO sample is obviously frequency dependent and begins to increase quickly above 10^5 Hz. The variation of tanδ above 10^5 Hz signifies that the relaxation process does not lie within the studied frequency range.
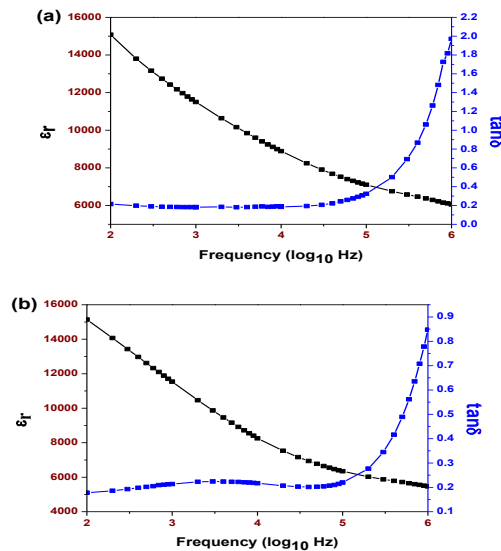

Fig. 5 RT frequency dependence of ε_r and tanδ of the CCTO ceramics sintered at (a) 1050, and (b) 1100 ^{o}C, respectively.

4. Conclusion

CCTO ceramic samples were synthesized by conventional solid state reaction route. XRD showed the formation of single perovskite phase at 1050 ^{o}C for 4 h. CCTO ceramic samples, sintered at 1100 ^{o}C showed better microstructural and dielectric properties. The RT values of ε_r and tanδ at 1 kHz frequency of the CCTO ceramic samples sintered at 1100 ^{o}C were found to be ~ 11,537 and 0.21, respectively.

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