STUDY OF THE DIELECTRIC AND MICROSTRUCTURE PROPERTIES OF (1-x) CaCu$_3$TI$_4$O$_{12}$ − (x) PbZr$_{0.65}$Ti$_{0.35}$O$_3$ COMPOSITE

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Abstract. In this paper, structural, dielectric and electrical properties of calcium copper titanate and PbZr$_{0.65}$Ti$_{0.35}$O$_3$ ceramic composite with composition (1-x) CaCu$_3$Ti$_4$O$_{12}$ − (x) PbZr$_{0.65}$Ti$_{0.35}$O$_3$ (where x = 0.00, 0.30, 0.50, 0.70 and 1.00) has been distinguished. The CaCu$_3$Ti$_4$O$_{12}$ sample was prepared by employing a high temperature solid state reaction technique and PbZr$_{0.65}$Ti$_{0.35}$O$_3$ synthesized by sol-gel route. X-ray diffraction (XRD), scanning electron micrograph (SEM), FT-IR spectrum (IR) was used to reach the structural properties of the studied compounds. The XRD and IR studies confirm the formation of pure phase for x = 0.00 and 1.00 concentrations i.e cubic and tetragonal, respectively. The SEM show change in the grain distribution, size and shape at addition of PbZr$_{0.65}$Ti$_{0.35}$O$_3$. Dielectric measurements were made by using an impedance analyzer, the results show that the dielectric constant of the CCTO/PZT composite is greater than that of pure CCTO and than that of pure PZT. The temperature dependence of the ac conductivity indicated that the conduction process is due to singly and doubly ionized, and frequency dependence of the ac conductivity of composites follows Jonscher's power law.

1. Introduction

Calcium Copper Titanate (CaCu$_3$Ti$_4$O$_{12}$, CCTO) based perovskite materials have been widely used for various applications, such as multilayer capacitor (MLCC), dynamic random access memory (DRAMs), microwave devices, electronic devices in automobiles and aircrafts such as multilayer capacitor and electronic devices, due to their excellent dielectric properties [1-3]. However, CCTO ceramic has high dielectric constant ($\varepsilon_r \sim 10^4 - 10^5$) independent of temperature (100-400K) which is desired for microelectronic applications. On the other hand, the CCTO ceramic has higher dielectric loss that limits its practical applications [4-6]. Recently, extensive studies of the formation of perovskite oxides of the systems Ca$_{1-x}$M$_x$Ti$_{1-x}$M$_x$O$_3$ (M = Cu, Y, Sr, Ba, Pb; M$\not\in$ = Co, Al, Fe, Cr) were performed. Almeida et al. [7] investigated the properties of the composite BaTiO3–CCTO film and its potential use as antennas and microdevices. In an analogous previous work, N. Hadi et al.[8] investigated the stability of the perovskite phase and the dielectric properties in the (1-x)CCTO-xBaTiO$_3$ ceramic (CCTO and BaTiO$_3$ perovskites), the value of dielectric constant was about 56,000

when x = 0.10. In this work, we report the effect of the presence of the PZT on the dielectric and microstructure properties of the CCTO. We compare these properties for the (1-x) $CaCu_3Ti_4O_{12}$–(x) $PbZr_{0.65}Ti_{0.35}O_3$ composites.

2. Experimental

The ceramic of (1-x)$CaCu_3Ti_4O_{12}$-x$PbZr_{0.65}Ti_{0.35}O_3$(where x = 0.00, 0.30, 0.50, 0.70 and 1.00) was synthesized by a modified solid-state route via three steps. **Firstly**, $CaCu_3Ti_4O_{12}$(CCTO) was synthesized by a solid state process using $CaCO_3CuO$ and TiO_2 were used as starting materials. In this route, stoichiometric ratios of the regents were mixed in agate motor for 1h, after that stirring in the medium of acetone for 3h. The mixed powder was calcined in air at 1050 ^0C for 4h. **Secondly**, $PbZr_{0.65}Ti_{0.35}O_3$ (PZT) ceramic powder was also synthesized by a Sol-Gel process using Lead (II) acetate trihydrate, $Pb(CH_3COO)_2.3H_2O$ zirconium acetate, $Zr(CH_3COO)_4$ and titanium isopropoxide, $Ti(OCH(CH_3)_2)_4$,. The metal acetate were dissolved in distilled water to obtain standard aqueous solutions of Pb^{2+} and Zr^{4+}, and mixed in separate beakers along with stoichiometric amounts of $Ti(OCH(CH_3)_2)_4$. The resulting dispersion was heated on a hot plate under stirring at 70–80 °C to evaporate the water and allow self-ignition. By controlling the hydrolysis condition of the complex solution, a PZT gel was formed. The dry gel was calcined at 700 °C for 4h in atmosphere PZT powders were obtained. **Finally**, the (1-x)$CaCu_3Ti_4O_{12}$-x$PbZr_{0.65}Ti_{0.35}O_3$ prepared of $CaCu_3Ti_4O_{12}$ and $PbZr_{0.65}Ti_{0.35}O_3$were carefully weighed in stoichiometric proportion and mixed thoroughly in agate motor for 1h then stirring in acetone for 2h. The powder was dried at 400 ^oC for 2h. The dried powder was then pressed into disks using polyvinyl alcohol (PVA) as a binder. The final sintering of the pellets was done at 1000 ^oC for 8h using a heating rate 3 ^oC/min.

3. Results and discussion

X-ray diffraction patterns of the CCTO and PZT powder are shown in **Fig. 1**.The CCTO and PZT powders show a single phase which is highly crystalline in nature where the main peaks of the ceramics are comparable to those of the standard ceramic XRD patterns of   CCTO (JCPDS 75-2188) and PZT (JCPDS 33-0784), which was identified to be cubic and tetragonal phase respectively.
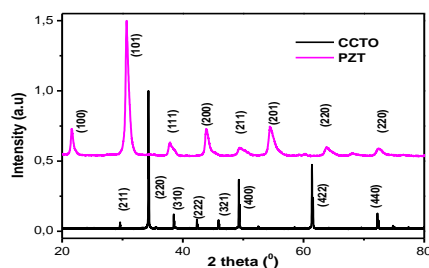

Fig. 1 X-ray diffraction pattern of CCTO and PZT pure

The phase formation of CCTO and PZT was further confirmed from FT-IR spectrum shown in **Fig.2.** The IR spectra of the CCTO ceramic in the region of 400–1200 cm^{-1} is dominated by three broad absorptions centered at 566, 516 and 447 cm^{-1} [7]. A similar spectrum is observed for the ceramic CCTO prepared in this work, with absorptions at 573, 523 and 451 cm^{-1} (see **Fig. 2**). The absorptions associated to CCTO are: 573 cm-1 related to Ca-O, 447 cm-1 related to vibrational mode

of the Ti-O-Ti and 523 cm^{-1} which is assigned to bending of Cu-O. For the PZT ceramic, two main absorptions were observed at 570 and 410 cm^{-1} which is consonant for the PZT ceramic, according to Singh et al. [6].
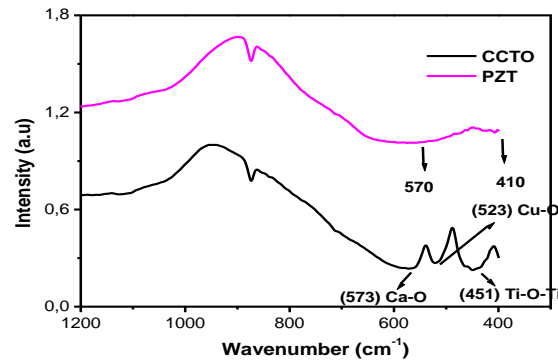

Fig. 2 FT-IR spectrum of CCTO and PZTpure.

The microstructure of CCTO, PZT and CCTO-PZT samples sintered at 1000 ^{0}C observed by SEM is shown in **Fig. 3.** It is found that the shape, the size and the distribution of grain of the microstructures of all the composites change with addition of PZT in CCTO. The size, distribution and shape of grain of the microstructures of all the samples confirmed the polycrystalline nature of the sample and well developed grains were observed in all the compositions. The grain size increases on increasing PZT contents compared with grains of pure PZT. The variation of average grain size with composition is shown in **Table 1**.
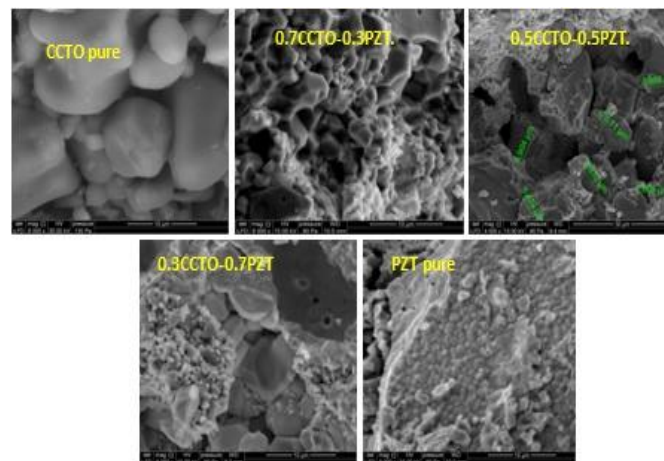

Fig. 3. SEM micrographs for CCTO, PZT and (1-x)CCTO-xPZT for *x* = 0.00, 0.30, 0.50, 0.70 and 1.00

Table 1: Variation average grain size of (1-x) CCTO–xPZT ceramics (x = 0.00, 0.30, 0.50, 0.70 and 1.00).

(1-x) CCTO–xPZT	grain size (μm)
x= 0.00	8.750
x= 0.30	5.747
x= 0.50	8.552
x= 0.70	5.000
x= 1.00	1.750

Fig. 4a and b show the behaviour of dielectric constant and dielectric loss of these ceramics as a function of temperature at 10 kHz. From Fig. 4a, the dielectric constant is almost constant up to 150, 200 and 300 °C for CCTO, CCTO-PZT and PZT, respectively. After this range, ε_r an increase gradually attaining a maximum value εmax at Curie temperature and thereafter it decreases with the further increase in temperature. This dielectric anomaly indicates a phase transition from ferroelectric to paraelectric phase at that particular temperature (Curie temperature, T_m). The Curie temperatures of CCTO, (1-x)CCTO-xPZT and PZT ceramics are 321, 337 (x = 0.30), 348 (x = 0.50), 360 (x = 0.70) and 370 °C (see table 2), respectively. The T_m shifts towards higher temperatures (T_m~360 °C) with increasing PZT content upon x=0.70. As can be noted from Fig. 4a and Table 2, the values of ε_r increased in the CCTO-PZT samples in temperature range of this study. The dielectric peak sharp around Tm, decreased with the increase of PZT content, which is one of the characteristics of the disordered perovskite structure with diffuse phase transition. The effect of the PZT content on the temperature dependence of CCTO dielectric loss or tan (δ) is shown in Fig. 4(b). The dielectric loss of pure CCTO is maximum with respect to other samples in the temperature range of this study. The PZT doped CCTO samples show small dielectric loss in which is dependent on PZT content. Variation of the values of dielectric loss at high temperature may be attributed to the conduction mechanism [10].
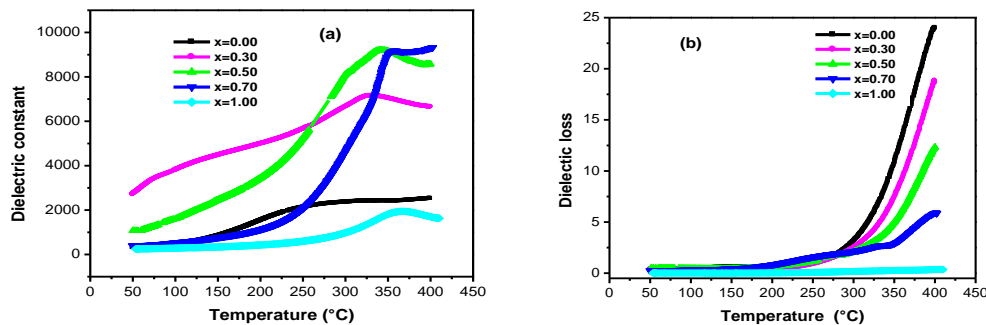
Fig. 4. Plot of real part of permittivity ε_r and dielectric loss tan (δ) of (1-x)CCTO-xPZT as a function of temperature at 10kHz (**a**) real part of permittivity ε_r (**b**) dielectric loss

Table 2: Variation of ε_r maximum and transition temperature (T_m) of (1-x) CCTO–xPZT ceramics.

(1-x) CCTO–xPZT	T_m	$\varepsilon_{r\ max}$
x= 0.00	321	1813.26
x= 0.30	337	5756.75
x= 0.50	348	6652.32
x= 0.70	360	6079.00
x= 1.00	369	1686.75

Fig. 5 shows the ac conductivity (σ_{ac}) as a function of frequency at 160 ^{0}C for all (1-x)CCTO-xPZT composites. The σ_{ac} is calculated from the dielectric data by using the relation [11];

$$\sigma_{ac} = \omega \varepsilon_0 \varepsilon'' \tag{1}$$

where σ_{ac} is the ac conductivity, ω is the frequency, ε_0 the permittivity of space free ($8.854.10^{-12}$ F/m), and ε'' is imaginary part of the dielectric constant. The frequency dependence of conductivity which obtained it in this study can be described by the Jonscher's universal power law [11, 12] given by:

$$\sigma_{ac}(\omega) = \sigma_{dc} + A\omega^n \tag{2}$$

where σ_{dc} is the frequency independent conductivity, A is the dispersion parameter and n is the dimensionless frequency exponent, with the values 0 and 1 which is a measure of the degree of interaction or an ideal Debye dielectric dipolar-type and an ideal ionic-type crystal respectively. The term $A\omega^n$ contains the ac dependence and characterizes all dispersion phenomenons. The plots showed a dispersive nature at 220 ^{0}C due to the typical RC network. Low frequencies region is dominated by conductive process in the ceramic while the high frequencies one is controlled by capacitive region [12]. The conduction difference between these compounds is due to the high defect concentration, mainly due to the oxygen vacancy resulting from the simple interaction between the components. The high conductivity in the composites at large frequencies is believed to be due to the hopping of the mobile species. Its proportionally to ω^n given in the equation 2, indicates that the electrical network (RC) response is qualitatively similar to the universal dielectric response (UDR) [9].
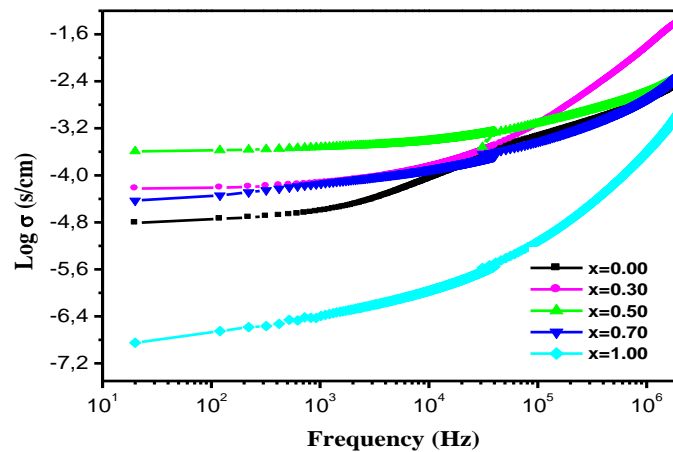

Fig. 5. Variation of ac conductivity with frequency at 220 ^{0}C of (1-*x*) CCTO–*x*PZT ceramics (*x* = 0.00, 0.30, 0.50 0.70 and 1.00).

4. Conclusion

In the present work, we have prepared the (1-x)CCTO-xPZT system with compositions of x = 0.00-1.00 by using solid state reaction route. X- ray diffraction pattern shows the formation of a pure phase for x = 0.00 and 1.00 compositions. The FT-IR studies confirm the formation of pure phase for CCTO and PZT powder and showed the presence of three and two main peaks, respectively. The dielectric study shows that, for CCTO-PZT, an enhanced of the dielectric constant compared with pure CCTO and PZT samples.

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