Structural and Dielectric Properties of Bi-Zn Substituted Calcium Copper Titanate (CCTO)

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Abstract

Calcium copper titanate (CCTO), an electroceramic with giant dielectric constant is useful in supercapacitor, microwave absorption, shielding of electromagnetic interference, and high frequency application. Bi3+-Zn2+ substituted CCTO with chemical composition Ca1-xBixCu3Ti4-xZnxO12 (0.0<x<0.2) was fortified using sol-gel auto combustion technique and were characterized using XRD, FESEM, and impedance analyser. XRD confirms the formation of CCTO phase with some traces of CuO and CaTiO3 phase. FESEM micrograph shows particles shapes close to cubic shape.

Keywords: CCTO, dielectric constant, dielectric loss, Cole-Cole plot

1. Introduction

The desire for high performance and miniaturization devices has driven scientist on a quest for nanomaterials with excellent properties [1][2][3][4][5][6]. The CCTO belongs to the group of materials having high dielectric constant having general formula ACu3Ti4O12 (A=Ca, La2/3, Bi2/3, or Pr2/3) with CaCu3Ti4O12 showing much higher dielectric constant as compared with the rest [7]. Several approaches have been employed in the synthesis of CaCu3Ti4O12. However, sol-gel method due to low reaction time, homogeneity, low sintering time and easy synthesis procedure is most suitable one and hence used for the synthesize Bi-Zn substituted CCTO.

2. Experimental details

Bi-Zn substituted CCTO having chemical composition Ca1-xBixCu3Ti4-xZnxO12 (0.0<x<0.2) have been synthesized via sol-gel method. Analytic reagent (AR) material such as Ca(NO3)2·4H2O (CDH), Bi(NO3)3·5H2O (CDH), Cu(NO3)3·3H2O (Loba Chemie), Zn(NO3)2·6H2O (Loba Chemie), TiO2 (Loba Chemie) and citric acid (Loba Chemie) were weighed in stoichiometric ratios and dissolved in double distilled water. Citric acid was weighed in molar ratio of 1:1 respectively for cations and citric acid. Then it was heated at 85-100 °C on a magnetic stirrer to obtain a gel which was further heated on hot plate at 270-300 °C. A black precursor substantial was attained and grinded with mortar and pestle resulting fine CCTO which was pre-sintered at 800 °C for 6 hours to eliminate impurities and then sintered at 900 °C for 6 hours.
3. Characterization techniques

The structural properties, morphology and dielectric properties were investigated using X-ray diffraction, FESEM and impedance analyser, respectively.

4. Results and discussions

4.1 Phase study

Fig. 1 dowries the XRD patterns of Ca$_{1-x}$Bi$_x$Cu$_3$Ti$_{4-x}$Zn$_x$O$_{12}$ (x=0.0, 0.1, 0.2). The observed diffraction peaks were indexed according to JCPDS 75-2188. It was observed the peaks are identical to pure CCTO through cubic perovskite assembly and space group $Im\bar{3}$, small traces of CaTiO$_3$ and CuO [8].

![XRD patterns](image)

The various lattice constant ($a$) and unit cell volume ($V_{cell}$) were premeditated using

$$a = d\sqrt{h^2 + k^2 + l^2}$$

$$V_{cell} = a^3$$

The values of lattice constant ($a$) was found to be 7.36, 7.38, and 7.37 for (0.0<x<0.2), respectively. Similarly, the volume of unit cell ($V_{cell}$) observed to be 398.98, 402.97, and 401.23 respectively for x=a(0.0), b(0.1), c(0.2). The variation in “a” and “$V_{cell}$” might be due lattice falsification tempted as a consequence of the occupancy of the replaced cations.

4.2 Morphology analysis

Fig 2 displays the FESEM micrograph and particle size dispersal of Ca$_{1-x}$Bi$_x$Cu$_3$Ti$_{4-x}$Zn$_x$O$_{12}$ (x=0.0). Clearly, well-defined grains with absence of agglomeration and shapes close to cubic shapes can be seen in the micrograph. The middling particle size was institute 0.265 µm.
4.3 Dielectric and impedance spectroscopy

Fig 3 (a) and (b) respectively present the disparity of dielectric constant and dielectric loss with frequency for \( \text{Ca}\!_{1-x}\!\text{Bi}_x\!\text{Cu}_3\!\text{Ti}_{4-x}\!\text{Zn}_x\!\text{O}_{12} \) \((0.0<x<0.2)\). The values of \( \varepsilon' \) and \( \tan \delta \) for the were estimated using the relation

\[
\varepsilon' = \frac{Z''}{2\pi \omega C_0 \sigma^2}
\]

(3)

\[
\tan \delta = \frac{Z''}{\varepsilon'}
\]

(4)

Where \( Z'' \) denotes impedance imaginary part, \( \omega \) frequency, \( C_0 \) geometrical capacitance, \( Z \) is the impedance. The dielectric behaviour of the arranged samples is typical of CCTO electroceramic. There is a sharp decrease at much lower frequencies as well as intermediate and higher frequencies. Dielectric response at lower frequencies is usually attributed to Maxwell-Wagner (interfacial) polarization. The dielectric response observed at intermediate frequencies is a consequence of atomic and dipolar polarization whereas that observed at higher frequencies are due to electronic polarization. The \( \tan \delta \) found to be almost independent of frequency at below and transitional frequencies. However, at advanced frequencies sudden increase in \( \tan \delta \) was observed, this could be ascribed to resonance upshot subsequent from abandoned conductance of the contacts and leads [9].

Fig 4 (a), (b), and (c) shows the plot of AC conductivity, variation of \( \ln \sigma_{AC} \) with \( \ln \omega \), as well as Cole-Cole plot for \( \text{Ca}\!_{1-x}\!\text{Bi}_x\!\text{Cu}_3\!\text{Ti}_{4-x}\!\text{Zn}_x\!\text{O}_{12} \) \((0.0<x<0.2)\). From Fig 4 (a), we can see that the conductivity remains frequency independent from lower to intermediate frequencies after which an abrupt increase was detected at much higher frequency as a result of electronic polarization. The total conductivity \( (\sigma_{total}) \) of solids can be expressed with Jonscher’s law

\[
\sigma_{total} = \sigma_{AC} + \sigma_{DC}
\]\n
(5)

\[
\sigma_{AC} = A\omega^S
\]\n
(6)
Fig 3. (a) Dielectric constant and (b) dielectric loss of Ca$_{1-x}$Bi$_x$Cu$_3$Ti$_{4-x}$Zn$_x$O$_{12}$ (x=0.0, 0.1, 0.2)

Fig 4. (a) AC conductivity, (b) variation of ln$\sigma_{AC}$ with ln$\omega$, and (c) Cole-Cole plot for Ca$_{1-x}$Bi$_x$Cu$_3$Ti$_{4-x}$Zn$_x$O$_{12}$ (x=0.0, 0.1, 0.2) (a) x=0.0, (b) x=0.1, and (c) x=0.2
Where $\sigma_{AC}$ represents the frequency dependent, $\sigma_{DC}$ is the frequency independent, $A$ temperature dependent constant $\omega$ is the frequency, and $S$ is the exponential term where $s$ lies among 0 (frequency independent) and 1 (frequency dependent). From Fig 4 (b), a linear relationship can be observed between $\ln\sigma_{AC}$ and $\ln\omega$. Clearly, $\ln\sigma_{AC}$ increases steadily with increase in $\ln\omega$. The slope of this linear graph gives the values of the exponent “$S$” in eqn. 6 whose value usually lies amongst 0 and 1. When $s = 0$, the conducting nature is frequency independent (i.e. DC conductivity) and when $s \leq 1$ the conducting nature of the sample is frequency dependent (i.e. AC conductivity) [10][11]. The slope of the linear plot for $0.0 < x < 0.2$ was found to be approximately 0.88, 0.90, and 0.92 respectively (Fig 4 (b)). Hence, AC conductivity is the dominant conduction mechanism present in the samples.

Fig 4 (c) dowries the Cole-Cole design of the prepared samples. In general, the plot of $Z''$ versus $Z'$ gives a semi-circle arc. The fragment of the semi-circle arc at the advanced frequency region of the plot shows contribution from the grains (grain resistance ($R_g$)) while that at the inferior frequency region shows influence of the grain boundaries (grain boundary resistance ($R_{gb}$)). Hence, utmost of the charities to dielectric constant of the CCTO ceramics instigate from $R_{gb}$ [7].

5. Conclusion

We have successfully synthesized Bi$_3^{3+}$-Zn$_{2+}$ substituted CCTO and studied its structural and dielectric properties. The dielectric response of the prepared CCTO electroceramic was found to be typical of a dielectric material. Maxwell-Wagner, atomic, dipolar as well as electronic polarization occurring at various frequencies are the reason behind the dielectric response of the material.

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