Ceramics International 42 (2016) 11193–11200

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Tuning of dielectric properties of $(ZnO)_x$-(CuTl-1223) nanoparticles-superconductor composites

M. Mumtaz [a,*], Liaqat Ali [a], Abdul Jabbar [c], M.W. Rabbani [a], M. Naveed [a], M. Imran [a], Badshah Amin [a], M. Nasir Khan [b], M. Usman Sajid [b]

[a] Materials Research Laboratory, Department of Physics, FBAS, International Islamic University (IIU), Islamabad 44000, Pakistan
[b] Central Diagnostic Laboratory, Physics Division PINSTECH, P.O. Nilore, Islamabad 45500, Pakistan
[c] Department of Physics, Ghazi University, Dera Ghazi Khan 32200, Pakistan

ARTICLE INFO

Article history:
Received 14 November 2015
Received in revised form
6 April 2016
Accepted 6 April 2016
Available online 7 April 2016

Keywords:
$(ZnO)_x$-(CuTl-1223) nanoparticles-superconductor composites
Structural characteristics
Superconducting properties
Dielectric properties

ABSTRACT

Zinc oxide (ZnO) nanoparticles and $Cu_{0.5}Tl_{0.5}Ba_2Ca_2Cu_3O_{10-\delta}$ (CuTl-1223) superconducting phase were prepared separately by sol–gel and solid-state reaction, respectively. ZnO nanoparticles were mixed with CuTl-1223 to get $(ZnO)_x$-(CuTl-1223); $x=0$, 0.5, 1.0 and 1.5 wt% nanoparticles-superconductor composites, which were characterized by different experimental techniques. There was no change observed in crystal structure of host CuTl-1223 phase after addition of ZnO nanoparticles, which provide a clue about the occupancy of these nanoparticles at the grains-boundaries. The inclusion of ZnO nanoparticles was found to reduce the voids and to improve the inter-grains connectivity in the host CuTl-1223 phase. The zero resistance critical temperature $\{T_{c(R=0)}(K)\}$ was increased by increasing wt% addition of ZnO nanoparticles in CuTl-1223 matrix. The dielectric properties of these samples i.e. dielectric constants (ε_r' ε_r''), and dielectric loss (tan δ), were determined by experimentally measuring the capacitance (C) and conductance (G) as a function of frequency at different operating temperatures. The values of dielectric parameters were decreased with the increase of frequency and become constant at certain higher frequency values, while the values of these parameters were increased with the increase of operating temperature values. So, we can tune the dielectric properties of CuTl-1223 superconducting phase by varying the content of ZnO nanoparticles, frequency and operating temperature.

1. Introduction

The materials with giant dielectric constants can play a significant role for microelectronics growth due to desire of smaller and robust devices such as capacitor and memory devices [1]. High values of dielectric constants have also been observed in high temperature superconductors (HTSCs) [1–3]. There are four primary mechanisms of polarization in materials on basis of the frequency of external applied ac-field. Ions and electronic clouds of atoms can be shifted from their equilibrium positions, which can be observed in electronic polarization (α_e). This type of polarization has been observed in solids at very high frequencies of the order of 10^{15} Hz (i.e. in ultraviolet optical range). Atomic and ionic polarization (α_a), which can be originated from combined displacement of ionic charge and electronic charge distribution. This type of polarization can be observed at frequencies in the range of 10^{10} to 10^{13} Hz (i.e. in infrared optical range). Dipolar or oriental polarization (α_o) can occur in the range of frequencies from 10^3 to 10^6 Hz (i.e. in sub-infrared optical range). This type of polarization can normally be observed at lower frequencies due to shorter relaxation times. Interfacial polarization (α_i) is more sensitive in low frequency range of 10^3 Hz and may extend to few kHz [4–8]. A short-range motion of charges in all these polarizations contributes to the total polarization of the material. The dielectric properties of $Cu_{0.5}Tl_{0.5}Ba_2Ca_4Cu_3O_{12-\delta}$ (CuTl-1234) superconductor were investigated in frequency range from 10 kHz to 10 MHz at different operating temperatures from 78 K to 290 K and negative capacitance (NC) was observed. M. Mumtaz et al. [9] compared the dielectric constants of CuTl-1234 phase with those of Tl-2212 and Tl-2223 phases. They observed larger dielectric constant of double layered Tl-based HTSCs as compared to single layered CuTl-based HTSCs. The dielectric properties of (CuO, CaO_2 and $BaO)_y$/CuTl-1223; $y=0$, 5, 10, and 15 wt% nanoparticles-superconductor composites were also studied in frequency range from 10 kHz to 10 MHZ at different operating temperatures from 78 K to 300 K. The decrease in dielectric constant and increase in ac-conductivity was found at all operating temperatures with minimum frequency of 10 KHz [10]. It was observed a gradual

* Corresponding author.
E-mail address: mmumtaz75@yahoo.com (M. Mumtaz).

http://dx.doi.org/10.1016/j.ceramint.2016.04.029
0272-8842/

decrease in ac-conductivity (σ_{ac}) with the increase of frequency beyond certain values. The addition of ZnO, ZrO_2, Al_2O_3, MgO and SnO_2 nanoparticles improved oxygen contents to optimize the carriers concentration, inter-grains connectivity, grain-size and pinning mechanism in the bulk HTSCs [11–15].

In this article, we have reported the temperature and frequency dependent dielectric properties of $(ZnO)_x$-(CuTl-1223) nanoparticle-superconductor composites. The effect of all these factors was visualized in variation of dielectric parameters. Dipolar or oriental polarization and interfacial polarization mainly contribute to the dielectric parameters of these samples. The dielectric constants become saturated at high frequency for all operating temperatures from superconducting state to room temperature [4]. The mobile charge carriers pile up at the barrier producing a localized polarization in the materials [8]. The effects of dipolar polarization are weak and dielectric constant mainly originates from the electric and lattice polarization due to their short relaxation time. The conduction mechanisms of variety of electronic devices strongly depend upon the values of operating temperatures, frequency, fabrication conditions, surface charges, doping concentration and impurities. Therefore, the investigation of dielectric properties over the wide range of frequency and temperature is very important and can provide valuable information about conduction and polarization mechanisms [4,5].

2. Experimental details

2.1. Preparation of ZnO nanoparticles

We used sol-gel method to synthesize ZnO nanoparticles. First solution was prepared by mixing zinc nitrate and ethanol with appropriate ratios and second solution was prepared by mixing citric acid and distilled water in separate beakers. Second solution was mixed drop by drop in first solution. We also added ammonia drop by drop to maintain pH up to 5 during stirring process. Solution was stirred constantly at 85 °C till the formation of gel. The gel was placed in microwave oven for drying at 100 °C for 15 h. The dried material was ground in agate mortar and pestle to get powder. Then powder was placed in a furnace at 600 °C for 2 h. The material was again ground to get fine powder of ZnO nanoparticles after 2 h heat-treatment.

2.2. Preparation of $(ZnO)_x$-(CuTl-1223) nanoparticles-superconductor composites

$Cu_{0.5}Tl_{0.5}Ba_2Ca_2Cu_3O_{10-\delta}$ (CuTl-1223) phase was synthesized by solid-state reaction. $Cu_2(CN)_2$, $Ca(NO_3)_2$ and $Ba(NO_3)_2$ compounds were mixed in appropriate ratios and then ground for 2 h. The mixed material was loaded in quartz boats and heat-treated in pre-heated chamber furnace at 860 °C for 24 h followed by furnace cooling to room temperature. The firing process was completed in two steps each with 1 h intermediate grinding. Tl_2O_3 and ZnO nanoparticles with different wt% were mixed with precursor $Cu_{0.5}Ba_2Ca_2Cu_3O_{10-\delta}$ material and ground again for 1 h. The ground powder was pressed in the form of pellets under 3.8 t/cm^2 pressure. The pellets were wrapped in gold capsules and placed in pre-heated chamber furnace for sintering at 860 °C for 10 min followed by quenching to room temperature to get $(ZnO)_x$-(CuTl-1223); $x=0$, 0.5,1.0 and 1.5 wt% nanoparticles-superconductor composites.

Structure and phase purity of $(ZnO)_x$-(CuTl-1223) composites were determined by XRD (D/Max IIIC Rigaku with a CuK_α source of wavelength 1.54056 Å). The dc-resistivity versus temperature measurements were carried out by four points probe technique. The value of current during the dc-resistivity measurements was kept 1 mA. The dc-resistivity measurements were carried out during the heating cycle from 30 K to 290 K. The rate of heating was kept 1 K/min to 3 K/min during these measurements. The dimensions of slab-shaped samples were $1.2 \times 1.0 \times 4.0$ mm^3 and low resistive four contacts were made on the surface of the sample with silver paint. We have calculated the real part of dielectric constant (ε'_r), imaginary part of dielectric constants (ε''_r), and dielectric loss (tan δ) by experimentally measuring the capacitance (C) and conductance (G) with the help of Hewlett–Packard 4294A Multi-Frequency LCR Meter from 40 Hz to 100 MHz at various temperatures from 78 to 298 K.

3. Results and discussion

X-ray diffraction (XRD) peaks at $2\theta°=31.67°$, 34.31°, 36.14°, 47.40°, 56.52°, 62.73°, 66.28°, 67.91°, 69.03°,77.11° are indexed to (100), (002), (101), (102), (110), (103), (200), (112), (201), (202) planes of hexagonal wurtzite structure of zinc oxide nanoparticles as shown in the inset of Fig. 1. The average size of ZnO nanoparticles calculated by Debye Scherrer formula is 41 nm. No prominent diffraction peaks of impurity have been detected. XRD patterns of $(ZnO)_x$-(CuTl-1223) nanoparticles-superconductor composites with $x=0$, 0.5 and 1.0 wt% are shown in Fig. 1. These diffraction patterns show the dominance of CuTl-1223 phase as most of the diffraction peaks have been well indexed according to tetragonal structure of this phase following P4/mmm space group. The structure of host CuTl-1223 phase was unaltered after the addition of ZnO nanoparticles. Few un-indexed diffraction peaks of very low intensities may be due to presence of some other superconducting phases and unknown impurities [16].

The information about approximate particle size, distribution, morphological structure, and grain-size were obtained by scanning electron microscopy (SEM). SEM images and EDX spectra of $(ZnO)_x$-(CuTl-1223); $x=0$, 0.5 and 1.0 wt% nanoparticles-superconductor composites are shown in Fig. 2(a–c & a′–c′). SEM images show the presence of spherical and irregular nano-size shapes between the grains of host CuTl-1223 matrix, which have reduced the inter-grain voids after the addition of ZnO nanoparticles. There is no variation in structural chemistry of host CuTl-1223 matrix as observed by XRD analysis. Structure of CuTl-1223 phase remains preserved even after addition of ZnO nanoparticles, which clearly indicates the occupancy of theses nanoparticles at inter-

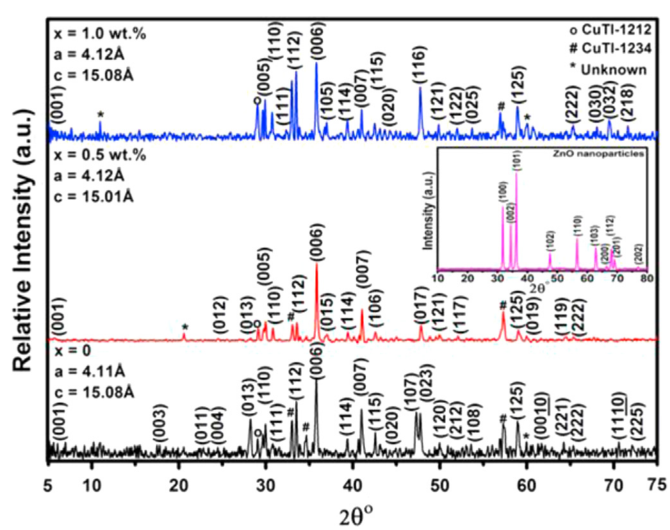

Fig. 1. XRD spectra of $(ZnO)_x$-(CuTl-1223); $x=0$, 0.5 and 1.0 wt% nanoparticles-superconductor composites samples. In the inset, there are shown XRD spectrum of ZnO nanoparticles.