AC-conduction mechanism via dielectric measurements of (Cr)x/(CuTl)-
1223 nanoparticles-superconductor composites

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ABSTRACT

Chemical sol-gel route was opted for synthesis of chromium (Cr) nanoparticles (NPs) and solid-state reaction method was used to synthesize the superconducting (CuTl)0.5Ba2Ca2Cu3O10-δ {(CuTl)-1223} phase. The desired (Cr)x/(CuTl)-1223; x = 0–2.0 wt% nanoparticles-superconductor composites were obtained by the incorporation of Cr NPs in the host superconducting (CuTl)-1223 matrix. The crystal structure along with the phase purity was explored by X-rays diffraction (XRD) and the transport properties were studied by the dc-resistivity and dielectric measurements of these composites. The crystal structure of these composites was found un-altered, which indicated the presence of Cr NPs at the inter-granular regions of the host CuTl-1223 superconducting matrix. The suppression in superconducting transport properties of CuTl-1223 superconducting phase could be associated to the reduction of superconducting volume fraction after the inclusion of Cr NPs. The effects of Cr NPs on the ac-conduction process in (CuTl)-1223 phase were investigated via frequency dependent dielectric measurements at different operating temperatures.

1. Introduction

Many superconducting ceramic materials showed high dielectric properties, which is the need of modern age for technological practical applications [1–4]. These materials are the best candidates in different fields due to high dielectric constants and versatile synthesis techniques. The materials with both high and low dielectric constants are crucial in different fields of electronic industry [4]. Capacitive elements in electronic circuits make use of high dielectric constant materials, while electronic insulation devices generally utilize low dielectric constant materials [4]. Materials with dielectric constant greater than 10⁴ are known as colossal permittivity materials (CPMs) [5]. These CPMs with low dielectric loss can be considered as the best candidates for high energy-density storage applications [6,7]. Micro-cracks and inter-grain boundaries in polycrystalline superconducting ceramics are generally considered as dielectric media across which mobile charge carriers can be piled up and becomes the source of polarization in these materials [4]. Frequency and temperature are the crucial constraints in the study of ac-conduction process in superconducting materials [8,9].

The dielectric response of GdBa2CuO7-δ Superconductor added with single-walled carbon nanotubes was investigated at temperature 77 K and frequency ranging from 100 KHz to 5 MHz [10]. An enhancement in dielectric properties was observed after the addition of single-walled carbon nanotubes up to 0.06 wt% as a result of maximum reduction in defects and improvement in inter-grains connections. Real part of dielectric constant was increased at lower frequency regime and it was decreased with further increase in frequency. Two dispersion peaks were observed in imaginary part of dielectric constant due to space or interfacial polarizations. Negative value in tangent loss was observed in some samples due to permanent shift of space charge in the presence of applied electric ac-field. The dielectric study of Bi1.7Pb0.3Sr2Ca2Cu3O10-δ (Bi, Pb)-2223 superconductor with different concentrations of gold (Au) nanoparticles were executed [11]. The highest values of dielectric constant as well as tangent loss were observed at lower frequencies and these parameters got reduced with further increase in the values of external frequency. The pristine (Bi, Pb)-2223 superconducting sample...
showed higher values of dielectric parameters than Au nanoparticles added samples. The ac-conductivity showed its smaller values at lower frequencies, which were increased with the increase in the values of external frequency for all the Au nanoparticles added samples. The frequency dependent dielectric response of superconducting (CuTl)-1234 phase with different content of MgO nanoparticles at various temperatures were studied [12]. Real part dielectric constant was decreased with increasing concentration of MgO nanoparticles, while tangent loss and imaginary part showed Debye relaxation phenomena. The frequency dependent dielectric response of superconducting (CuTl)-1233 phase was investigated with different concentrations of MnFe2O4 nanoparticles at various temperatures [13]. The values of real and imaginary parts of dielectric constant and tangent loss were reduced with the increase of frequency, whereas the increasing contents of MnFe2O4 nanoparticles improved the values of these parameters and reciprocal response was observed in case of ac-conductivity for all the samples.

In present research work, we tried to find out the criterion for optimum dielectric properties by varying frequency and contents of Cr NPs in (CuTl)-1223 superconductor. The core objective of this project was to change the nature of material at the inter-granular regions of superconducting (CuTl)-1223 phase with the addition of antiferromagnetic Cr NPs. It is very obvious that the foreign elements or nanostructures can affect the inter-granular spaces, oxygen contents, grains’ size and weak-links among the grains, which ultimately influence the dielectric response of superconducting (CuTl)-1223 phase.

2. Experimental details

The powders of commercially available Copper Cyanide (Cu(CN)) (99%, BDH), Barium Nitrate (Ba(NO3)2) (99.50%, UNI-Chem) and Calcium Nitrate (Ca(NO3)2) (99%, Appi Chem) chemicals were mixed according to stoichiometric ratios and ground in an agate mortar and pestle for 3 h. The fine ground mixture was put into a quartz tube and placed in a pre-heated furnace for 24 h. The mixture was heat treated at a fixed temperature of 860 °C. This process of heat treatment was carried out twice following an intermediate grinding of one hour. The calculated temperature of 860 °C. This process of heat-treatment was carried out twice following an intermediate grinding of one hour. The calculated temperature of 860 °C. This process of heat-treatment was carried out twice following an intermediate grinding of one hour. The calculated temperature of 860 °C. This process of heat-treatment was carried out twice following an intermediate grinding of one hour. The calculated temperature of 860 °C. This process of heat-treatment was carried out twice following an intermediate grinding of one hour. The calculated temperature of 860 °C. This process of heat-treatment was carried out twice following an intermediate grinding of one hour. The calculated temperature of 860 °C. This process of heat-treatment was carried out twice following an intermediate grinding of one hour. The calculated temperature of 860 °C. This process of heat-treatment was carried out twice following an intermediate grinding of one hour. The calculated temperature of 860 °C.

The structure and phase purity of (Cr)x/(CuTl)-1223 composites were probed by X-ray diffraction (XRD) (D/Max IIIIC Rigaku with CuKα source of X-rays with wavelength 1.54056 Å). The dc-resistivity versus temperature measurements of these samples were carried out by conventional four-probe method with the help of commercial Physical Properties Measurement System (PPMS) manufactured by Quantum Design. Four low resistance contacts with silver paint were made on the surface of the slab shaped samples with dimensions of 1.2 × 1.0 × 4.0 mm3. The temperature stability was kept 2 mK during the transport measurements on these samples. The temperature dependent dielectric measurements of these composites were carried out by LCR meter (Hewlett-Packard 4294A) in frequency range 40 Hz–100 MHz at different operating temperatures from 77 to 298 K.

3. Results and discussion

3.1. X-ray diffraction (XRD)

The representative XRD spectra of pristine (CuTl)-1223 phase and (Cr)x/(CuTl)-1223 composites are given in Fig. 1. The majority of peaks in XRD spectra were properly indexed following the tetragonal crystal structure of the pristine superconducting (CuTl)-1223 phase. No prominent change in XRD spectra was observed with the addition of Cr NPs, which can be considered as the confirmation of the insertion of NPs at the inter-granular spaces of the host superconducting (CuTl)-1223 phase. Some un-indexed low intensity XRD peaks have also been observed that belong to undesired superconducting other phases and impurities [14,15].

3.2. Electrical dc-resistivity measurements

The variation of electrical dc-resistivity ρ (Ω-m) versus temperature T (K) of (Cr)x/(CuTl)-1223 composites is presented in Fig. 2. The zero-resistivity critical temperature Tc0 (K) of (Cr)x/(CuTl)-1223 composites are found 102, 100, 93, 92 and 90 K for x = 0, 0.5, 1.0 and 2.0 wt% contents of Cr NPs, respectively. The decreasing trend in Tc0 (K) with increasing contents of Cr NPs is most probably due to reduction of carriers’ concentration required for optimum superconducting properties. The enhanced potential barriers across the grain-boundaries due to presence of Cr NPs there, cause energy dissipation and ultimately Cooper pairs breaking takes place that reduces the carriers’ density and hence superconductivity [16]. The increase in normal state resistivity ρn (Ω-m) with increasing contents of Cr NPs in the host superconducting (CuTl)-1223 matrix is obviously due to enhanced spin scattering of normal electrons at the grain-boundaries across these antiferromagnetic NPs.
3.3. Dielectric measurements

The ac-conduction process in (Cr)x/(CuTl)1223 composites have been carried out via frequency dependent dielectric measurements at different temperatures from 77 to 298 K in frequency range 40–100 MHz. Any material can be chosen for dielectric applications on the basis of various parameters such as capacitance (C), conductance (G), complex dielectric constant ($\varepsilon_r = \varepsilon'_r - i\varepsilon''_r$), tangent loss (tanδ) and ac-conductivity ($\sigma_{ac}$). Mathematical expression for real part of the dielectric constant ($\varepsilon'_r$) is as under;

$$\varepsilon'_r = \frac{Cd}{\varepsilon_0 A}$$  \hspace{1cm} (1)

where C, d and A represent capacitance, thickness and area of electrode surfaces, respectively. The graph showing the change in $\varepsilon'_r$ with f (Hz) of (Cr)//(CuTl)-1223 composites at various temperatures is presented in Fig. 3(a–d). The maximal value of $\varepsilon'_r$ at lower frequency regime was increased with increasing temperature, while its value was decreased with increasing contents of Cr NPs. The variation in the value of $\varepsilon'_r$ with frequency can be explained in three different regimes. The maximum value of $\varepsilon'_r$ was obtained at lower frequencies, which was gradually decreased with increasing frequencies and showed almost constant values with further increase of frequencies. The polarization in the materials was reduced due to different time constants of applied ac-field and charge carriers. The charge carriers could not respond to applied ac-field at higher frequencies due to very short relaxation time constants. Therefore, the decreasing trend in values of $\varepsilon'_r$ with increasing applied frequency is associated with the less polarizability because the charge carriers cannot respond to externally applied ac-field [16,17]. The maximal values of $\varepsilon'_r$ at $T = 298$ K and $f = 40$ Hz are $1.3 \times 10^5$, $3.9 \times 10^3$ and $3.1 \times 10^3$ for (Cr)//(CuTl)-1223 composites with different concentrations of Cr NPs x = 0, 0.50, 1.00, and 2.00 wt %, respectively. The decreasing trend in values of $\varepsilon'_r$ can be associated with semiconducting nature of inserted Cr NPs in superconducting host (CuTl)-1223 phase. The maximal values of $\varepsilon'_r$ at 40 Hz frequency varied from $8.4 \times 10^3$ to $1.3 \times 10^4$, $2.2 \times 10^3$ to $4.3 \times 10^3$, $1.8 \times 10^3$ to $3.9 \times 10^3$ and $1.8 \times 10^3$ to $3.1 \times 10^3$ for (Cr)//(CuTl)-1223 composites with x = 0, 0.50, 1.00, and 2.00 wt% of Cr NPs contents, respectively. The insets of Fig. 3(a–d) specify the variation of maximum values of $\varepsilon'_r$ against the temperatures at lowest possible value of frequency $f = 40$ Hz. The highest value of $\varepsilon'_r$ increased with increasing temperature due to higher polarizability [18]. Koop's Theory along with Max Wagner Model has been utilized to explain characteristic dielectric response of cuprates and ferrites materials [19–21]. According to Koop’s theory, the bulk materials are supposed to be composed of two different regions i.e. grains as conducting regions and grain-boundaries as resistive regions. The charge carriers move from grain to grain-boundaries through hoping mechanism when external electric field is applied on the samples. The dielectric constant was decreased at high frequencies due to lagging of charge carriers across the grain-boundaries. A resonance and anti-resonance peak was observed in $\varepsilon'_r$ versus f (Hz) graphs around $10^6$ to $10^7$ Hz frequency, which was due to relaxation mechanism in the material. The charge carriers were transported from one place to another place due to multiple hoping processes. The energies of these charge carriers became extremely small to cross these potential barriers producing a peak in $\varepsilon'_r$ versus f (Hz) graphs around $10^6$ to $10^7$ Hz [22]. Another reason for this type of peak in $\varepsilon'_r$ versus f (Hz) graphs was the enhanced accumulation of charges at grain-boundaries or interior of the grains [23].

Fig. 3. (a–d) The variation of $\varepsilon'_r$ versus f for (Cr)//(CuTl)-1223; x = 0, 0.5, 1.0, and 2.0 wt% composites. In the insets, there are shown the variation of maximum values of $\varepsilon'_r$ versus temperature at lowest possible frequency f = 40 Hz.
In the dielectric constant measurements, the energy loss in any material subjected to external applied electric ac-field is represented by $\varepsilon''_r$, which is the imaginary part and it is denoted by;

$$\varepsilon''_r = \varepsilon_0 \omega (d)(G)/ A$$

Here $G$ denotes the conductance of the material. For $(\text{Cr})_x/(\text{CuTl})$-1223 composites, the variation in $\varepsilon''_r$ with $f$ (Hz) at various values of operating temperatures $T$ (K) is given in Fig. 4(a–d). At lowest possible applied frequency of 40 Hz, the highest values of $\varepsilon''_r$ are $3.80 \times 10^7$, $6.70 \times 10^6$, $2.00 \times 10^6$ and $7.80 \times 10^5$ at room temperature of 298 K for $(\text{Cr})_x/(\text{CuTl})$-1223 composites with $x = 0$, 0.50, 1.00, and 2.00 wt% Cr NPs contents, respectively. The values of $\varepsilon''_r$ are suppressed with the inclusion of semiconducting natured Cr NPs. The maximal values of $\varepsilon''_r$ at 40 Hz varied from $3.30 \times 10^7$ to $3.80 \times 10^7$, $6.00 \times 10^6$ to $6.70 \times 10^6$, $1.50 \times 10^6$ to $2.00 \times 10^6$ and $7.00 \times 10^5$ to $7.80 \times 10^5$ at different temperatures from 77 to 298 K for $(\text{Cr})_x/(\text{CuTl})$-1223 samples with $x = 0$, 0.50, 1.00, and 2.00 wt% Cr NPs contents, respectively. The graphs in the insets of Fig. 4(a–d) are showing the variation of highest values of $\varepsilon''_r$ against temperature at lowest possible frequency $f = 40$ Hz. The value of $\varepsilon''_r$ is observed to get increased with increasing temperature because of larger energy loss in the samples. Also, the values of $\varepsilon''_r$ were reduced with the increasing frequency and it became almost constant at higher frequency due to difference in time constants of charge carriers and applied ac-field [17]. Another reason for the suppression of $\varepsilon''_r$ with higher values of frequency was the reduction of orientational and space charge polarizations, which are the main sources of polarization in these materials [24,25].

The net energy loss in the material is commonly referred as loss tangent “tanδ”. It is obtained by taking the ratio of the $\varepsilon'$, and $\varepsilon''_r$, and is given as;

$$\tan \delta = (\varepsilon'_r)/(\varepsilon''_r)$$

The tanδ versus $f$ (Hz) plots for various temperatures ranging from superconducting state to normal state of these composites are given in the Fig. 5(a–d). The maximal values of tanδ at 40 Hz are $4.10 \times 10^4$, $5.30 \times 10^3$, $4.20 \times 10^3$ and $2.40 \times 10^3$ for $(\text{Cr})_x/(\text{CuTl})$-1223 composites with $x = 0$, 0.50, 1.00, and 2.00 wt%, respectively. The maximal values of tanδ at minimum frequency of 40 Hz varied from $2.10 \times 10^4$ to $4.10 \times 10^4$, $4.20 \times 10^3$ to $5.30 \times 10^3$, $3.10 \times 10^3$ to $4.70 \times 10^3$ and $1.40 \times 10^3$ to $2.40 \times 10^3$ at different temperatures from 77 to 298 K for $(\text{Cr})_x/(\text{CuTl})$-1223 composites with $x = 0$, 0.50, 1.00, and 2.00 wt% contents of Cr NPs, respectively. A decreasing tendency in the values of tanδ was observed in all the samples that owed to semiconducting nature of these Cr NPs present at inter-granular sites of host superconducting matrix. Insets of Fig. 5(a–d) show the graphs of variation of maximum tanδ versus temperature ranging from 77 K to 298 K. The suppression in tanδ value was observed with increasing temperature after inclusion of Cr NPs, which may be due to larger energy stored than energy loss [26].

The total conductivity ($\sigma_T$) of any material can be well explicated by two factors; (i) dc-conductivity ($\sigma_{dc}$) and (ii) ac-conductivity ($\sigma_{ac}$), which can be related as follows;

$$\sigma_T = \sigma_{dc}(T) + \sigma_{ac}(\omega, T)$$

where $\sigma_{dc}$ depends upon the temperature ($T$) and $\sigma_{ac}$ depends on temperature ($T$) as well as on frequency ($\omega$). The $\sigma_{ac}$ can also be written as;

$$\sigma_{ac} = \varepsilon'_r/\varepsilon_0 \omega \tan \delta$$

Fig. 4. (a–d) The variation of $\varepsilon''_r$ versus $f$ for $(\text{Cr})_x/(\text{CuTl})$-1223; $x = 0$, 0.5, 1.0, and 2.0 wt% composites. In the insets, there are shown the variation of maximum values of $\varepsilon''_r$ versus temperature at lowest possible frequency $f = 40$ Hz.
phenomenon in a material depends upon hopping of free charge carriers, mobility of charge carriers, grain-boundaries and space charge density. The increase in frequency may cause these conducting channels to hop more frequently, thereby facilitating the hopping mechanism of charge carriers [27]. The frequency dependent variation in $\sigma_{ac}$ of (Cr)$_x/(CuTl)$-1223; $x = 0, 0.50, 1.00, \text{ and } 2.00 \text{ wt%}$ samples at different temperatures of 77–298 K is given in Fig. 6(a–d). The very small constant values of $\sigma_{ac}$ at lower frequencies showed the enhanced polarization due to large accumulation of the charge carriers across the intergranular spaces. The value of $\sigma_{ac}$ started to increase exponentially at certain high frequency owing to small losses and increased hopping probability of charge carriers [28,29]. Similarly, a resonance and anti-resonance peak in $\varepsilon'_r$, was observed in $\sigma_{ac}$ versus $f$ (Hz) graphs, which was due to relaxation mechanism in the material [22]. These dispersion peaks also known as resonance/anti-resonance peaks between $10^6$ to $10^7$ frequency regions are observed in $\sigma_{ac}$ versus $f$ (Hz) of the host superconducting material as reported by other researchers [30,31]. This phenomenon is due to the interfacial polarization or space charge polarization. These dispersions are observed due to the complete alignment of the charges or dipoles with the field at certain frequency, which is known as natural frequency of the material. At this frequency, a great absorption of the applied signal occurs in the material leading to a peak in $\sigma_{ac}$ versus $f$ (Hz) graphs. The dispersion also takes place when the oscillation of the dipoles matches the oscillation of the applied field. The values of $\sigma_{ac}$ increase with the increasing values of temperature, which can be associated with the enhancement of hoping of mobile charge carriers due to enhanced thermal agitation [32,33].

4. Conclusion

The ac-conduction mechanism in (Cr)$_x/(CuTl)$-1223 composites was explored via frequency dependent dielectric measurements at various temperatures. Tetragonal crystal structure of the host (CuTl)-1223 superconducting phase remained unaffected, which indicated the presence of Cr NPs at the grain-boundary regions. The superconducting transport properties were suppressed with increasing contents of Cr NPs in superconducting (CuTl)-1223 matrix, which was attributed to the reduction of superconducting volume fraction and desired carriers’ density for optimum superconducting properties. The dielectric parameters ($\varepsilon'_r$, $\varepsilon''_r$, $\tan \delta$ and $\sigma_{ac}$) of superconducting (CuTl)-1223 phase were strongly influenced by the variation of frequency, temperature and contents of Cr NPs. The values of $\varepsilon'_r$, $\varepsilon''_r$, and $\tan \delta$ found maximum at lower frequency due to enhanced space charge polarization for all the samples. The value of $\tan \delta$ was decreased while the values of $\varepsilon'_r$, $\varepsilon''_r$, and $\sigma_{ac}$ were increased with addition of Cr NPs in superconducting (CuTl)-1223 matrix, which can be associated with the improvement of polarizability after the addition of these NPs. The dielectric properties of (CuTl)-1223 superconducting phase can be modified by varying the frequency, operating temperature and contents of Cr NPs. So, the ac-conduction process is strongly dependent on the frequency, temperature and contents of nanostructures in superconducting (CuTl)-1223 phase.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to
influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cryogenics.2019.103021.

References


Fig. 6. (a-d). The variation of \( \sigma \) versus f for (Cr)x/(CuTl)-1223; x = 0, 0.5, 1.0, and 2.0 wt% composites.
and charge transporting property of Te$_{90-x}$Se$_x$Ga$_x$ chalcogenides by a.c conductivity and dielectric analysis. Mater. Today Proceed. 2018;5:9041.


