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Synthesis and characterization of $EuBa_2Ca_2Cu_3O_{9-x}$: The influence of temperature on dielectric properties and charge transport mechanism

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ABSTRACT

High dielectric constant materials have a crucial importance for various microelectronic applications such as memory devices, supercapacitors etc. Among other insulators, perovskite structured oxide materials attract great interest not only for their high dielectric constants but also their unique electrical and magnetic properties such as superconductivity etc. From this point of view, a new Europium based copper oxide layered material with perovskite structure ($EuBa_2Ca_2Cu_3O_{9-x}$ coded as Eu-1223) has been synthesized by solid state reaction method in this work. The physical and chemical properties of Eu-1223 have been determined by FTIR, SEM, XRF, XRD, TGA and DTA techniques. The influence of temperature on impedance and dielectric properties of Eu-1223 has been investigated by impedance spectroscopy measurements performed within the frequency interval of 5 Hz–13 MHz between 298 K and 408 K temperatures. It has been found that the Eu-1223 material has high dielectric constants at each temperature operated. In addition, Eu-1223 sample behaves as a colossal dielectric material up to 300 kHz for 408 K due to observation of dielectric constant values which are greater than 10^3. Furthermore, it has been revealed that Eu-1223 material can be used as thermally sensitive resistors in electronic circuits due to its decreasing resistance with increasing temperature. Moreover, it has been observed that the relaxation frequency of the system shifts from 46.5 kHz (low frequency radio wave band) to 1.57 MHz (mid frequency radio wave band) as the temperature increasing from 298 K to 408 K. According to dc conductivity investigations, the variation of dc conductivity with the inverse of temperature satisfies linear relationship that indicates a thermally activated nearest neighbor hopping conduction. On the other hand, it has been determined that ac conductivity has frequency dependent relation which obeys ω^s for the high frequency region. Furthermore, the frequency exponent, s, which takes values between 0.7 and 0.4, shows a decreasing behavior with increasing temperature. In conclusion, ac charge transport mechanism has been predicted as correlated barrier hoping for Eu-1223.

1. Introduction

In recent years, high dielectric constant i.e. colossal dielectric constant materials ($\varepsilon' \geq 10^3$) have been widely used in capacitive elements in microelectronic circuits such as memory and microwave devices. Especially, the minimization limit of the memory devices based on capacitive component strongly depends on the value of dielectric constant. From this point of view, scientists have focused on searching new oxide materials with high dielectric constant and low dielectric loss for technological purposes. Due to their high dielectric constant values, perovskites have been extensively utilized in these technological applications [1]. The materials with simple ABO_3 perovskite structure have many advantages such as ordered intergrowth structures which provides a long range order [2], oxygen deficient structures etc. During the search for new superconducting materials containing copper atoms, a number of oxides such as $LaBa_2Cu_3O_7$, $Bi_2Ca_{n-1}Sr_2Cu_nO_{2n+4}$, $Tl_mCa_{n-1}Ba_2Cu_nO_{n+m+2}$, $Hg_2Ca_{n-1}Ba_2Cu_nO_{2n+3}$, $Gd_2Ba_2Ti_2Cu_2O_{11}$, $La_2Ba_2Sn_2Cu_2O_{11}$, which do not exhibit superconducting properties, have been discovered [3–6]. Some of them have remarkable dielectric properties for memory device applications but their present abilities need to be developed for utilizing them in fast changing world of electronic devices. The dielectric properties of ceramic materials with contain titanium oxide such as $CaCu_3Ti_4O_{12}$, $Bi_{2/3}Cu_3Ti_4O_{12}$ etc. have also been investigated [7,8]. Lunkenheimer et. al. have been determined that dielectric constant value of $CaCu_3Ti_4O_{12}$ approximately equals to 2.10^3 at room temperature for 1 kHz [8]. On the other hand, the importance of copper oxide for next generation high dielectric constant materials has been revealed by Sarkar et. al. They showed that

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bulk copper (II) oxide (CuO) has temperature independent giant dielectric constant in the order of 10^4 within kHz frequency region above 230 K [9]. As is known, high dielectric constant materials with weak frequency and temperature dependent are very much desirable for device applications.

Europium based copper oxide layered material (Eu_2CuO_4) has a promising potential for microelectronics due to its high dielectric constants in the low frequency region [10]. The dielectric properties of polycrystalline nominal Eu_2CuO_4 ceramic samples have been investigated within 10^{-1}–10^6 Hz frequency domain from −100 to 150 °C temperature by Salame et al. [10]. The dielectric constant value of Eu_2CuO_4 has been determined as 2.10^3 at 50 °C for 1 kHz.

From this point of view, this work has been devoted to synthesize a new Europium based copper oxide layered material ($EuBa_2Ca_2Cu_3O_{9-x}$ coded as Eu-1223) with high dielectric constant and determine both its physical and chemical properties. In accordance with this purpose, in order to determine the performance of this new Europium based dielectric material for technological applications, the temperature and frequency dependences of dielectric and impedance properties have been investigated. Moreover, the frequency and temperature dependences of dc and ac conductivity mechanisms of Eu-1223 have also been investigated and discussed in terms of various conduction mechanisms.

2. Experimental

2.1. Synthesis of Eu-1223

In this study, $EuBa_2Ca_2Cu_3O_{9-x}$ has been synthesized by solid state reaction method by using Eu_2O_3(99.99%), BaO (99.99%), CaO(99.99%) and CuO (99.99%) powders as starting precursors. These precursor materials have been purchased from Sigma Aldrich. These powders have been mixed in appropriate stoichiometric ratios which give $EuBa_2Ca_2Cu_3O_{9-x}$ and then grinded in agate mortar for two hours. The resultant powder has been pressed into pellet under approximately 10^9 Pa pressure. The sample, which has 14.32 mm in diameter and 2.68 mm thickness, has been placed in Al_2O_3 crucible and heated at a rate of 1◦C/min to 900◦C for 24 h in atmospheric environment.

2.2. Characterization of Eu-1223

The chemical and physical properties of the Eu-1223 have been investigated by Fourier transform infrared (FTIR) spectroscopy, Scanning Electron Microscopy (SEM), X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD), thermogravimetric analysis (TGA), and differential thermal analysis (DTA).

Chemical analyze of Eu-1223 has been determined by X-ray fluorescence (XRF) measurements performed with the equipment model X-123SDD from Amptek, which carries an Au-target X-ray tube (30 kV, 100 μA). The system consists of an X-ray tube, a sample holder and a Silicon drift detector at a scattering angle of 90°. The geometry of the system has a distance of 12 mm from the sample to the X-ray tube with a collimation of 6 mm internal diameter and 15 mm length; a distance of 35 mm from the sample to the detector with a collimation of 25 mm length and 4 mm internal diameter. The XRF has been used in the laboratory in a bench top accessory stand and has been connected to a computer via USB and a remote trigger. The fluorescent peaks of Ca, Ba, Eu, and Cu were determined range from 3.68 keV (Ca-Kα) to 8.82 keV (Cu-L_β) as seen Fig. 1. The chemical composition of the sample has also been given in Table 1.

The FTIR spectrum has been determined by Spectrum 100 FTIR spectrometer (Perkin Elmer Inc., Waltham, MA, USA) operated in transmission mode with the spectral region from 4000 to 650 cm^{-1}. The FTIR spectrum of Eu-1223 has been given in Fig. 2. As seen Fig. 2, the minor peak at the wavenumber of 3640 cm^{-1} which can be assigned to the hydroxyl group stretching has also been found in the FTIR spectrum of the sample [11]. The band at 1406 cm^{-1} is commonly associated with ionic, bidentate or monodentate ligands on barium oxide [12]. The characteristic peaks observed at 873 cm^{-1} and 855 cm^{-1} in the spectrum exhibit the bending vibrations of the CaO crystal lattice [13,14]. The characteristic peak at 690 cm^{-1} in the spectrum also indicates the bending vibrations of the CuO crystal lattice [15]. The characteristic peak of Eu_2O_3 vibrations generally appears at 470 cm^{-1} [16]. Since the spectral measurement region of the spectrometer does not cover the wave numbers smaller than 600 cm^{-1}, the characteristic Eu_2O_3 vibration peak has not been observed in Fig. 2. However, the presence of Eu in the material has been confirmed by XRF results (See Fig. 1).

The lattice parameters of the Eu-1223 have been calculated from the XRD data taken by Cu (40 kV) (40 mA) Rigaku model XRD device. The related XRD patterns have been recorded at room temperature and given in Fig. 3. According to XRD patterns, the sample has tetragonal structure with the lattice parameters of a=b=7.36787A° and c=5.98287A°.

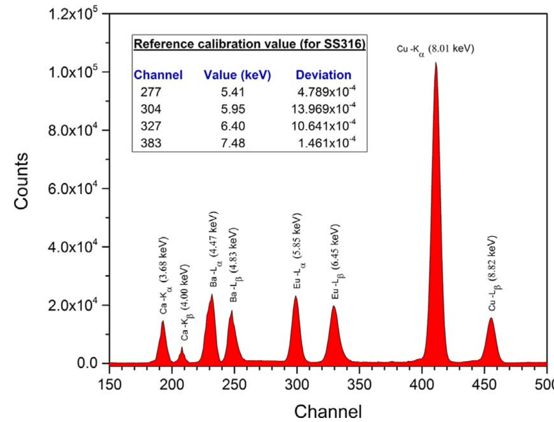

Fig. 1. XRF results of Eu-1223.

Table 1
Chemical composition of the sample.

Elements	Concentration (wt%)
Eu	18.234 ± 0.036
Ba	32.950 ± 0.066
Ca	9.602 ± 0.019
Cu	22.876 ± 0.045
O	16.336 ± 0.032

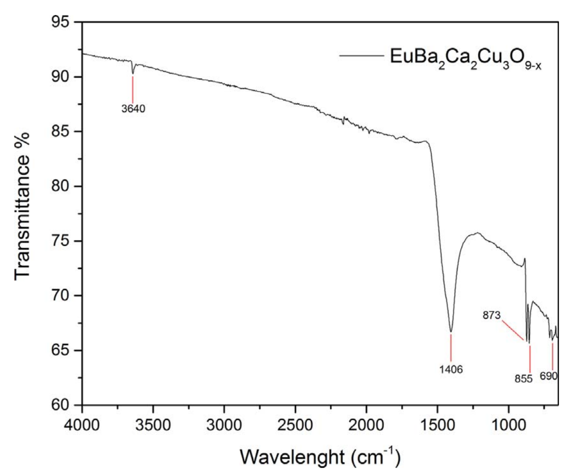

Fig. 2. FTIR spectrum of Eu-1223.