March 2024, Vol:2, Issue:1

International Journal of New Findings in Engineering, Science and Technology

journal homepage: *https://ijonfest.gedik.edu.tr/*

Dielectric and Optical Properties of $Eu_x(Bi_{1-x})Sr_2CaCu_2O_{6.5}$ (x=0.3 and 1) Samples

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Abstract

Eu-based copper oxide layered ceramics have some interesting dielectric properties depending on its stoichiometric ratios and elements used in ceramics. In this study, optical properties of $EuSr_2CaCu_2O_{6.5}$ and $Eu_{0.3}Bi_{0.7}Sr_2CaCu_2O_{6.5}$ samples and dielectric property of $EuSr_2CaCu_2O_{6.5}$ sample were investigated for the first time. Negative real permittivity for $EuSr_2CaCu_2O_{6+x}$ sample was observed at temperature with 373 K and higher temperatures and below than the cross over frequency with 14 Hz. Moreover, it is determined that Eu^{3+} concentration in the material affects the relative emission intensity.

Keywords Eu-based ceramics; Optical properties of Eu-based ceramics; Dielectric properties of Eu-based ceramics.

1. INTRODUCTION

Materials with negative or colossal ($\varepsilon' \geq 10^3$) dielectric constant attract the attention of the scientific world due to the next generation technological applications. The variation the dielectric properties of the material by changing its stoichiometric ratio or elements in the materials make the material interesting for scientist. In the literature, dielectric properties of some materials doped with europium such as europium trioxide doped lead boro-tellurite glasses [1], $(Eu,Ca)Cu_3Ti_4O_{12}$ ceramics [2], Eu_2O_3-doped calcium copper titanium oxide samples [3] having with giant and positive real dielectric constant were investigated by researchers. Z.Güven Özdemir and her research group were studied dielectric properties of $Eu_x(Bi_{1-x})Sr_2CaCu_2O_{6.5}$ ceramics (where x=0, 0.3, 0.5, 0.7) between 1 Hz and 40 MHz from room temperature to 433 K for the first time[4,5]. Also, the research group determined the dielectric properties of $EuBa_2Ca_2Cu_3O_{9-x}$ (Eu-1223) and $EuBa_2Cu_3O_{7+x}$ (Eu-123) samples [4,5]. In this article, real dielectric constants of the materials investigated by Güven Özdemir and et al. were reviewed in details. Also, this paper reports the measurements of the optical properties of $EuSr_2CaCu_2O_{6.5}$ coded as (Eu_1Bi_0)-212 and $Eu_{0.3}Bi_{0.7}Sr_2CaCu_2O_{6.5}$ coded as $(Eu_{0.3}Bi_{0.7})$-212 and dielectric property of the (Eu_1Bi_0)-212 sample for the first time. It was reported that negative real permittivity for $EuSr_2CaCu_2O_{6+x}$ sample was observed at temperature with 373 K and higher temperatures and below than the cross over frequency with 14 Hz.

The rare earth ions are very effective ions in many optical materials due to a large number of the absorption and

https://doi.org/10.61150/ijonfest.2024020103

emission bands arising from the transitions between the energy levels [6]. For this reason, many researchers interested in trivalent Eu ions as a luminescence centers in intense red emission which comes from its $^5D_0 \rightarrow {}^7F_2$ transition [7,8]. Luminescent materials (or phosphors) as Eu ions and doped Eu ions are good canditates for many technological applications such as fluorescent lightings [9], computer screens [10], lasers [11], temperature sensors [12], solar cells [13], fingerprint detections [14] and biological fluorescence probes [15]. White light can be produced by appropriate combination of the primary colors (red, green and blue). Eu-doped luminescent materials are commercially used as red phosphors for white light production in LEDs due to the intense red emission of Eu^{3+} [16,17]. In the study, the optical properties $(Eu_{0.3}Bi_{0.7})$-212 and (Eu_1Bi_0)-212 samples were investigated for the first time and it was determined that the higher luminescence intensity occurs due to the higher mole concentration of the europium

2. DIELECTRIC PROPERTIES OF Eu- BASED CuO_2 LAYERED MATERIALS

The substances with negative dielectric constant (NDC) [18,19] can be utilized as electromagnetic shielding, optical power limiting, perfect absorber, microelectronic implements such as capacitors, memory devices etc. Also, the materials with NDC have a promising potential for metamaterials applications. The importance of metamaterials (MMs) is to have a negative index of refraction [6,20]. In this context, Eu-based copper oxide materials have not only negative dielectric constant (NDC) but also high dielectric constant depending on mole ratio of Eu elements in the sample and temperatures operating. Eu-123 [21] and $(Eu_{0.7}Bi_{0.3})Sr_2CaCu_2O_{6.5}$ coded as $(Eu_{0.7}Bi_{0.3})$-212 [4] ceramics belonging to the Eu-based copper oxide family have the NDC. Eu-123 sample was investigated at room temperature under the magnetic field varying from 0–0.4 T as shown in Figure 1[21].

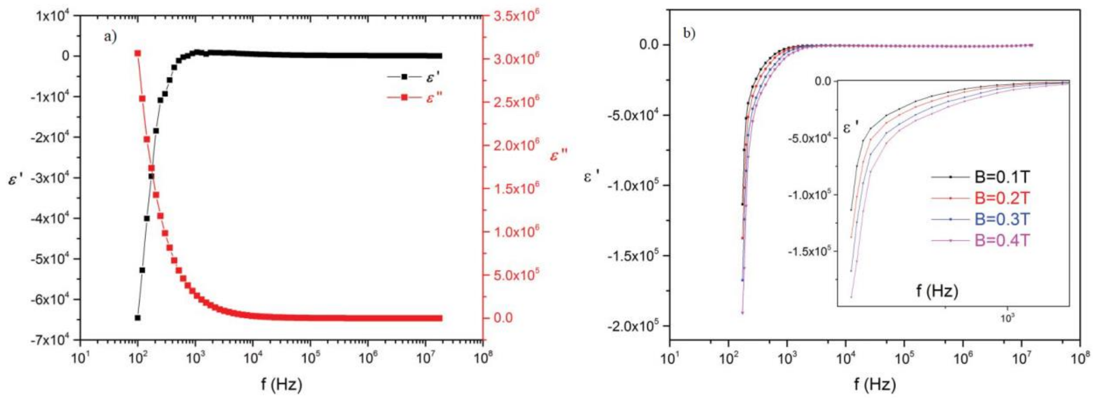

Figure 1. a) The real and imaginary components of complex dielectric function. b) The effect of magnetic field on the real part of complex dielectric function of Eu-123[21].

As is seen Figure 1 that the real part of complex dielectric function (ε′) of the Eu-123 sample has negative values for low frequencies up to 1 kHz. On the other, when the magnetic field is applied to the sample, the magnitude of ε′ increases and NDC property extends to 10 kHz at room temperature [21].

$(Eu_{0.7}Bi_{0.3})$-212 sample displays the negative real permittivity (NRP) which was observed at 353 K and the higher temperatures as shown in Figure 2 [4].

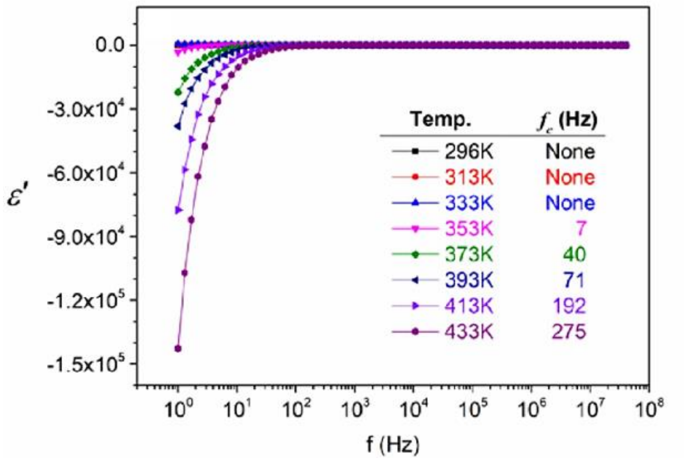

Figure 2. The frequency dependence of the real part of complex permittivity of (Eu0.7Bi0.3)-212 material at all temperatures operated [4].

Güven Özdemir and et al. determined that Eu-1223 [22] and $(Eu_{0.5}Bi_{0.5})$-212 [5] samples have very high dielectric constant ($\varepsilon' \geq 10^3$), and they suggested that the materials investigated can be good candidate for next generation electronics and large scale integrated microelectronics technology (Figure 3). The effect of temperature on dielectric properties of Eu-1223 was investigated within the range of 5 Hz–13 MHz frequencies and 298 K-408 K temperatures. It was determined that at each temperature, the Eu-1223 sample has high dielectric constants. Also, Eu-1223 material acts as a very high dielectric material, which are greater than 103, up to 300 kHz for 408 K [22].

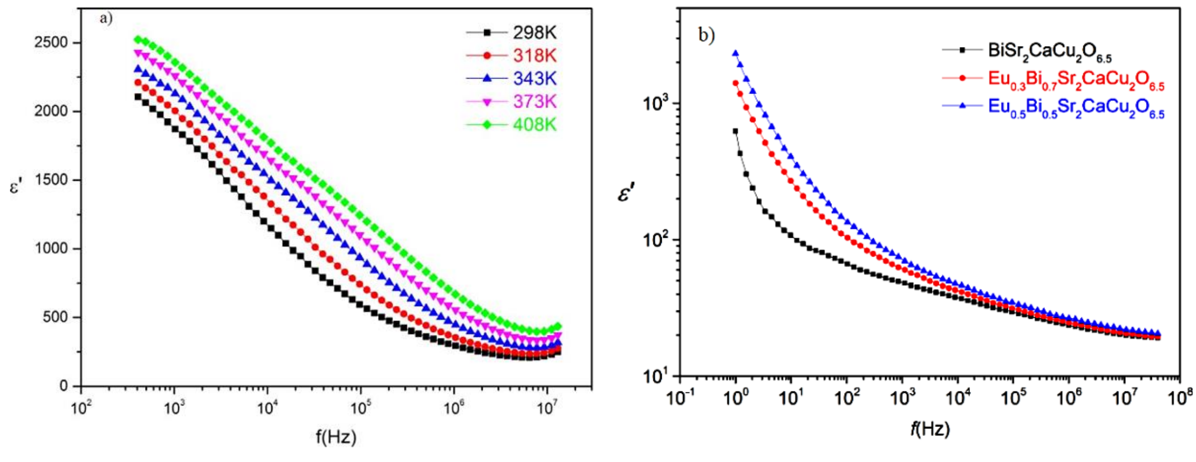

Figure 3. a) Frequency dependence of the real components of the complex dielectric functions at different temperatures for Eu-1223 material [3]. b) for the (Eu_xBi_{1-x})-212 samples (x=0, 0.3, 0.5) at room temperature [2].

It was determined by dielectric measurements that $(Eu_{0.5}Bi_{0.5})$-212 sample exhibits a higher dielectric constant and lower dielectric loss relative to (Eu_0Bi_1)-212. In this context, partial europium substitution into $BiSr_2CaCu_2O_{6.5}$ system was proposed as an effective dopant for producing better dielectric material with the lower dielectric loss.

3. SYNTHESIZES OF $Eu_X(Bi_{1-X})Sr_2CaCu_2O_{6.5}$ SAMPLES

To prepare of Eu substituted Bi based materials ($Eu_xBi_{1-x}Sr_2CaCu_2O_{6.5}$ where x=0.3 and 1) which were synthesized by conventional solid-state reaction, Eu_2O_3(99.99%), Bi_2O_3(99.99%), SrO (99.99%), CaO (99.99%) and CuO (99.99%), powders supplied from Sigma Aldrich were used. Powders in appropriate stoichiometric ratios were ground in an agate mortar for 2 h. The pressure of approximately 10^9 Pa was applied for pressing the resultant powder and the pellet obtained was place in Al_2O_3 crucible and heated at a rate of 1 °C/min to 950 °C for 24 h in an atmospheric environment. For fine powder mixture, the material was ground for 15 min and then it was again pressed. At the end of process, the pellet was sintered at 950 °C for 24 h in an atmospheric environment [5].

4. RESULTS AND DISCUSSION

4.1.Dielectric Property of (Eu_1Bi_0)-212 material

NOVO Control Broadband Dielectric/Impedance analyzers with Quatro Cryo system in the temperature interval between 296–433 K within frequency range 1 Hz and 40 MHz was used to take impedance measurements. In the study, dielectric property of the (Eu_1Bi_0)-212 sample was measured by impedance analyzer for the first time. Negative real permittivity for (Eu_1Bi_0)-212 material was observed at temperature with 373 K and higher temperatures and below than the cross over frequency with 14 Hz as shown in Figure 4.

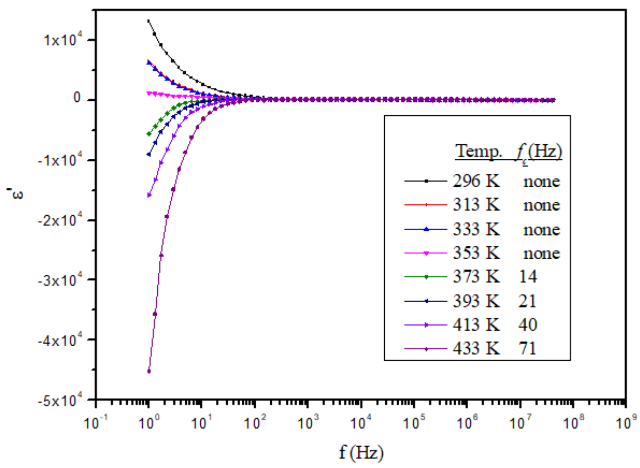

Figure 4. Frequency dependence of the real components of the sample at different temperatures for (Eu_1Bi_0)-212 material.

It was determined that substitution of europium for bismuth in the stoichiometric ratio higher than 0.5 enables negative real permittivity at temperatures of 353 K and above [4].

4.2.Optical Properties of (Eu_1Bi_0)-212 and ($Eu_{0.3}Bi_{0.7}$)-212 Samples

The optical properties of (Eu_1Bi_0)-212 and ($Eu_{0.3}Bi_{0.7}$)-212 samples were investigated in the article for the first time. The emission spectra were collected using a monochromator (Princeton Instruments - model SP2500i) and Silicon detector (Acton series: SI-440) for the detection of the optical region luminescence. The samples were excited with a continuous wave (CW) laser operating at 485 nm. All measurements were performed at room temperature.

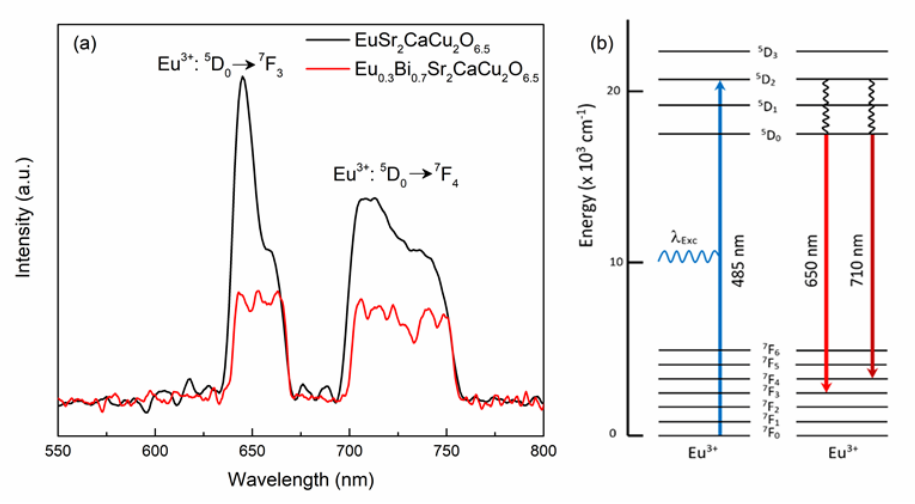

Figure 5. (a) The luminescence spectra of the (Eu_1Bi_0)-212 (black line) and ($Eu_{0.3}Bi_{0.7}$)-212 (red line) samples under 485 nm laser excitation with CW laser, (b) the energy level diagram of Eu^{3+} and possible paths.

Figure 5 (a) shows the luminescence spectra of the(Eu_1Bi_0)-212 and ($Eu_{0.3}Bi_{0.7}$)-212 samples under 485 nm laser excitation with CW laser. The red emission of Eu^{3+} is located at around 650 nm associated with $^5D_0 \rightarrow {}^7F_3$ transition. The dark-red emission located between 700 nm and 750 nm due to the $^5D_0 \rightarrow {}^7F_4$ transition. The energy level diagram of Eu^{3+} and possible paths under 485 nm excitation is also given in Figure 5 (b). Eu^{3+} ions are first excited to $^5D_2$ level under 485 nm laser excitation and then decay into $5D_0$ level by non-radiative relaxation process. The electrons decay radiatively from $^5D_0$ level to the $^7F_3$ and $^7F_4$ level to produce red and dark-red emissions, respectively. The reduction of the relative emission intensity of $^5D_0 \rightarrow {}^7F_3$ and $^5D0 \rightarrow {}^7F_4$ transitions can be due to not only Eu^{3+} concentration but also structure of the host matrix.

5. CONCLUSION

In this study, the luminescence spectra, and real parts of dielectric function for (Eu_1Bi_0)-212 and ($Eu_{0.3}Bi_{0.7}$)-212 materials have been investigated for the first time. As is known, the dielectric function describes the response of the materials to the electromagnetic radiation mediated through the interaction of photons and the electrons and it depends upon the electronic band structure of the material. Also, the real part of the dielectric constant determines some optical property of a material [23]. In this context the luminescence spectra of the (Eu_1Bi_0)-212 and ($Eu_{0.3}Bi_{0.7}$)-212 materials give the comparison of the concentration of the europium element in the materials investigated. The higher luminescence intensity occurs due to the higher mole concentration of the europium. As is known, the mole concentration of the europium affects the dielectric properties of the materials. Hence, europium as dopants ions makes the materials a promising candidate for some electronic devices needing color red on their displays [24]. NRP for (Eu_1Bi_0)-212 sample was observed at temperature with 373 K and higher temperatures and below than the cross over frequency with 14 Hz for the first time. Moreover (Eu_1Bi_0)-212 and ($Eu_{0.3}Bi_{0.7}$)-212 materials which displays dielectric properties depending on temperatures operating and Eu-concentration, may be utilized for some chemical sensors, light emitting devices or solar energy conversion.

Conflicts of interest

There are no conflicts of interest in this work.

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