Cumhuriyet Sci. J., 45(2) (2024) 407-413
DOI: https://doi.org/10.17776/csj.1429356

Cumhuriyet Science Journal

| csj.cumhuriyet.edu.tr | Founded: 2002 ISSN: 2587-2680 e-ISSN: 2587-246X Publisher: Sivas Cumhuriyet University

Investigation of BSCCO Superconductors with Ga Substitution by Solid State Method

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Research Article

History
Received: 31/01/2024
Accepted: 03/04/2024

ABSTRACT

Samples of $(Bi_{2-x}Ga_x)Sr_2CaCu_2O_2$ superconductors with varying Ga substitution levels (x=0, 0.06, 0.12, 0.20) were synthesized using the solid-state reaction method. The effects of partial substitution of bismuth and gallium elements on the BSCCO structure were investigated in terms of their electrical, magnetic, structural, and mechanical properties. X-ray diffraction (XRD) was used to determine the crystalline phases, and samples A and B exhibited sharp peaks, indicating well-crystallized material with no Ga_2O_3 phase. SEM images were used to obtain microscopic views of all samples, and the elemental compositions of each element were determined from EDX spectra. The critical temperature was calculated from R-t measurements, and Sample A exhibited the highest Tc at 96K. Magnetic properties were investigated for all samples, including magnetic hysteresis behavior and magnetic moment. The critical current density (J_c) values were calculated using the Bean model by utilizing magnetic hysteresis.

Keywords: BSCCO, Critical current density, Solid-state method, Superconductivity.

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Introduction

Superconductivity is a physical property where electric current passes without resistance. Dutch physicist Heike Kamerlingh Onnes discovered superconductivity with his studies in 1911 [1]. Onnes observed that some metals became less resistive at low temperatures. He then cooled the materials to low temperatures using liquid helium in glass tubes and discovered the superconductivity feature on mercury at 4.2 Kelvin (-268.95 °C) [2] [3]. With this discovery, the foundations of superconductivity were laid and later, it was discovered that many materials were superconducting and studies in the field of superconductivity accelerated. Superconductivity is of great importance for many applications such as magnetic resonance imaging (MRI) systems operating in cryogenic environments, particle accelerators, magnetic levitation [4].

With the study, it was discovered that polyatomic connections can be connected to each other and that semiconductors can also exhibit superconductivity. In 1987, BiSrCaCuO (BSCCO), which has a high critical temperature value presented as Tc value, can reach up to 110 K and is also Cu-O based, showing high-temperature superconductivity properties similar to HgBaCaCuO and TlBaCaCuO [5]. With this invention, studies in this field have intensified considerably by reducing the transition temperature of these materials by cooling them with liquid nitrogen. Among these methods, many theses and articles have been published in many studies and reviews on BSCCO superconducting materials, especially Bismuth (Bi) based. The reason for this is that Bismuth (Bi) based superconducting materials have a very comprehensive field of study due to their suitability for partial replacement applications and doping with the parts of different phases such as Bi-2201, Bi-2212, Bi-2223 [6].

Superconducting materials, also known as BSCCOs, are the subject of intense research due to their remarkable physical and electrical properties, including high-temperature superconductivity. These materials conduct electricity without resistance but are sensitive to magnetic fields [6] [7]. Bi-2212 superconductors, in particular, exhibit high-temperature superconductivity after thermal processing and optimization of their crystal structures [8]. This article presents a thorough review of the structure, synthesis, properties, and potential applications of Bi-2212 BSCCO superconductors. The study is a significant step towards a better comprehension of superconducting materials and their future industrial applications [6].

The primary structural formula, $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$, represents three phases of bismuth-based superconductors, with the number of CuO_2 layers denoted by 'n' [6]. For the first phase (n=1), Bi-2201 exhibits a T_c of 20K, while for the second phase (n=2), Bi-2212 has a Tc of 80K, and for the third phase (n=3), Bi-2223 has a T_c of 110K. The subunit cells of the Bi-2201, Bi-2212, and Bi-2223 phases vary in the number of CuO_2 layers depending on the value of n [9] [10]. It is suggested that an increase in the number of layers is associated with higher Tc values. Therefore, modifications in superconductors typically target the Cu region, as superconductivity is linked to the CuO_2 layer[11].Furthermore, it is believed that the CuO_2 layers, which contain magnetic Cu^{2+} ions in all HTC superconductors, enhance superconductivity. Recent studies on doping rare earth elements in bismuth-based superconductors have shown that cationic impurities affect the critical temperature (T_c) of the system. Despite significant changes in carrier density due to cation doping, the primary crystal structure of the system remains unchanged [12].

Samples of superconducting $(Bi_{2-x}Ga_x)Sr_2CaCu_2O_2$ were synthesised in this study by substituting the Bi-Ga part with ratios of x=0, 0.06, 0.12, and 0.20. The aim of this work was to increase the critical current density through a double calcination and sintering process. The materials were prepared using the solid-state reaction method with high-purity elements in stoichiometric ratios. The quality of the synthesised materials and their crystalline structural properties were analysed using X-ray powder diffraction. Surface and grain analysis were conducted using scanning electron microscopy (SEM). The critical temperatures were determined using the four-point resistance method, and the magnetic properties were characterised using a vibrating sample magnetometer (VSM).

MATERIALS AND METHODS

$(Bi_{2-x}Ga_x)Sr_2CaCu_2O_2$ samples with x values of 0, 0.06, 0.12, and 0.20 were prepared using chemical powders with 99% purity of Bi2O3, SrCO3, CaO, CuO, Ga2O3, and $CaCO_3$ in appropriate stoichiometric ratios. Each sample weighed 3 g and was prepared by weighing and mixing the powders in a mortar for 1.5-2 hours to ensure homogeneity. The samples underwent a 12-hour heat treatment for the first calcination. After the initial calcination, the samples were mixed for approximately two hours to ensure homogeneity before undergoing a second calcination. Subsequently, the samples were placed in an oven at 750°C for 12 hours, followed by one hour of grinding. The thoroughly ground samples were then pressed into pellets at a pressure of 4000kg/cm^2 and placed in a crucible inside a cylindrical high-temperature furnace for the sintering phase. The samples were heated from room temperature to 845°C over a period of 100 minutes and held at this temperature in the furnace for 60 hours. Subsequently, they were cooled to 750°C over a period of 100 minutes and held at this temperature for an additional 12 hours. Finally, the samples were cooled from 750°C to room temperature over a period of 100 minutes and were ready for measurement. To avoid confusion, the samples were labelled as A, B, C and D.

RESULTS AND DISCUSSION

X-ray diffraction (XRD) measurements were made to explain the crystal phases of the samples we produced. The patterns for all samples are displayed in Figure 1. samples A and B exhibit sharp peaks, indicating well-crystallized material and the absence of Ga_2O_3 phase. However, Sample D shows additional peaks, indicating the presence of Ga_2O_3 and suggesting that the solubility limit of gallium in the structure has been exceeded. Sample C is similar, suggesting that gallium may be substituting into the structure. The peak intensity across samples indicates good crystallinity of the Bi-2212 phase. However, the variation in peak intensity and broadening, particularly in C and D, may suggest structural changes or strain. The analysis suggests that gallium doping affects the structure of the BSCCO phase and that there is a threshold beyond which gallium forms a separate phase.

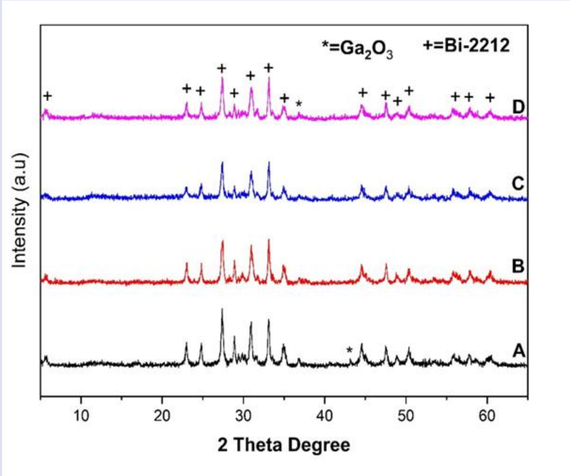


Figure 1. X-ray diffraction patterns of the $(Bi_{2-x}Ga_x)Sr_2CaCu_2O_2$ superconducting samples. (+) Bi-2212 phase, and (∗) Ga_2O_3 secondary phases.

SEM images offer microscopic views of the surface morphology of a sample. Figure 2 a, Figure 2c, Figure 2 e and Figure 2 g, displays the polished grain morphologies of samples A, B, C and D.,respectively. The grain morphology exhibits clear and distinct changes with increasing Ga content. The characteristic flaky grains of (Bi,Pb)-2212 are visible in all samples. At higher Ga contents, the microstructures display secondary phases with round or square edges dispersed within the main matrix. As substitution increases, the homogeneity deteriorates, resulting in the appearance of needle-like structures and particle shrinkage.

This indicates disordered bonding and weakened transmission. Elemental percentages remain consistent across all samples, as observed by EDX analysis and shown also in Figure 2 b, Figure 2 d, Figure 2 f and Figure 2 h, respectively, with corresponding EDX spectra below each SEM image. EDX is employed for elemental analysis and chemical characterisation. The sample is analysed by interacting X-rays with it and identifying the elements based on their unique electromagnetic emission spectra. The spectra show peaks that represent the elements, with the peak position indicating the element and the intensity related to its concentration. The EDX spectra indicate the presence of several elements in each sample, including oxygen (O), carbon (C), silicon (Si), copper (Cu), and aluminium (Al). The results confirm that the materials are composed primarily of the intended substances. However, it is said that the hole concentration in the CuO2 layer, which is one of the variables that changes the Tc value, also affects it. In this case, we can calculate the number of holes, expressed as p, with equation 1 called the Presland method [13].

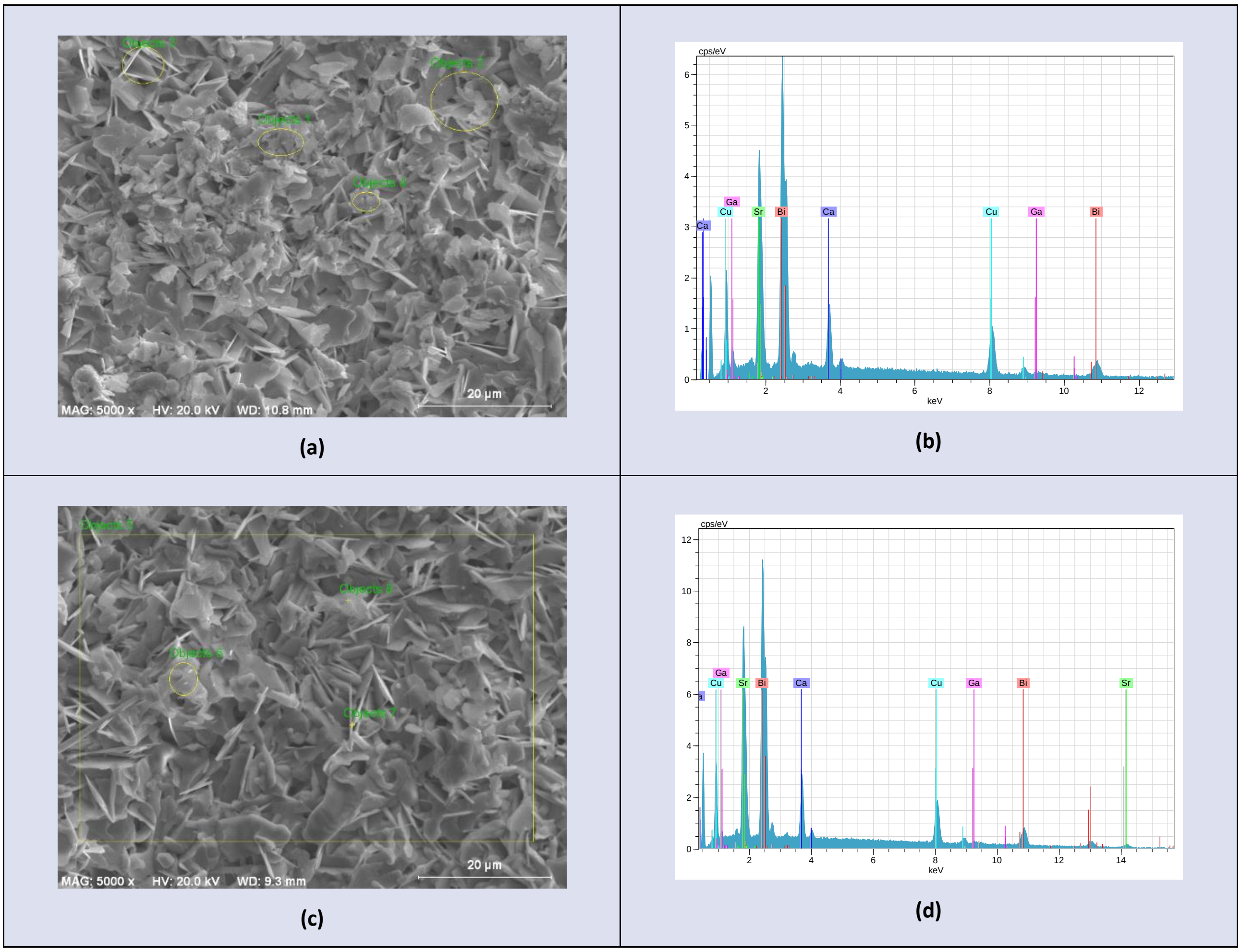
$$\frac{T_C}{T_C^{max}} = 1 - 82{,}6(p - 0{,}16)^2 \qquad (1)$$

The hole concentration, , T_C^{onset} , T_C^{offset}values and other parameters we calculated for $(Bi_{2-x}Ga_x)Sr_2CaCu_2O_2$ superconductor samples are given in table 1. We can say that as the number of holes decreases in the Bi-2212 system, which is formed with the increase in the displacement of the Bi-Ga part, the superconductivity properties of the system decrease [14].

As can be seen from these limited studies in the literature, no definite interpretation can be made about the dimensions of the contact pin. Therefore, in this study, the detector was modeled in three different ways using the PHITS Monte Carlo simulation program. It is first modeled without including the contact pin, then with the 3.5 mm contact pin, and finally with the 4.5 mm contact, which is the inner hole diameter of the detector. Also, there is one study in the literature on how this contact pin will have an effect on the detector response and the full energy peak efficiency [18]. In this paper, the effect of the copper contact pin on the detector efficiency was examined in the point source geometry in the energy range of 59.5 keV-1408 keV and it was determined that it changed of up to 1.9% in the efficiency of the detector. The current study investigates the effect of a copper contact pin on the full energy peak efficiency by calculating efficiency values for higher gamma ray energies up to 2614.5 keV in both cylindrical and point source geometry in the high-energy region where the effect is dominant.

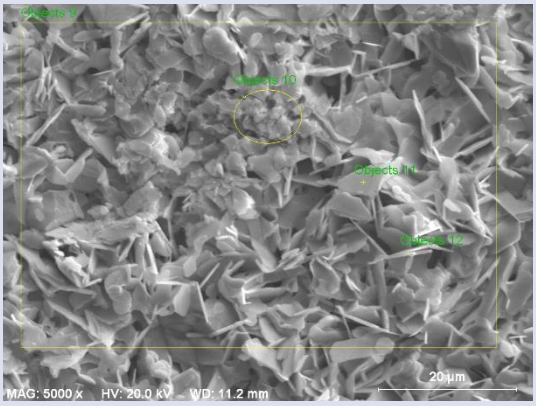
Table 1. Nominal compositions and structural parameters of $(Bi_{2-x}Ga_x)Sr_2CaCu_2O_2$ (x = 0.0, 0.06, 0.12 and 0.20) compounds.

Samples	Ga dopant, x	Lattice parameters a = b (Å)	Lattice parameters c (Å)	T_C^{onset} (K)	T_C^{offset} (K)	ΔT_c (K)	hole concentration (p)
A	x=0			70	55	15	0.259
B	x=0.06			70	55	15	0.259
C	x=0.12			68.75	40	28.5	0.249
D	x=0.20			61.75	43.12	18.63	0.257



(a) (b)

(c) (d)



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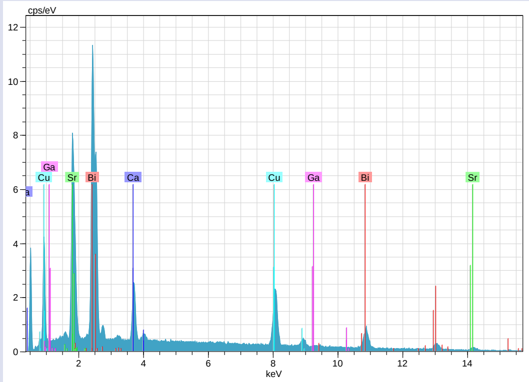

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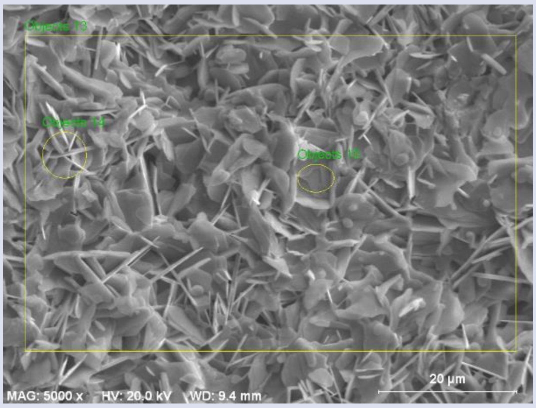

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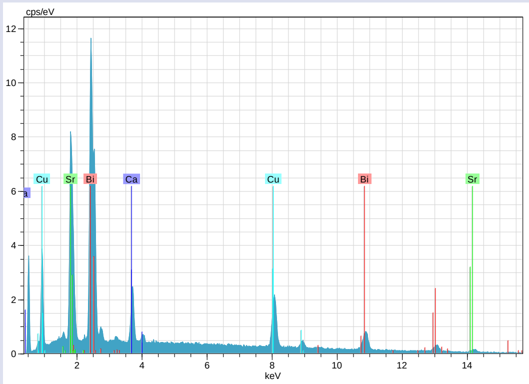

(h)

Figure 2. SEM and EDX analysis of all samples (a,c,e and g Sem Images and b,f,d and h EDX analysis).

Figure 3 shows Resistivity measurement vs. temperature for all the samples. The Tc values are similar for all samples, and samples A and B have the same transition temperature, indicating that the x=0.06 substitution does not affect the structure. A single phase transition is observed for all samples, and the resistance decreases with increasing temperature up to a certain point, where a sharp transition occurs. Furthermore, all samples demonstrate metallic behaviour at room temperature, that is, above the transition temperature, and exhibit superconductivity upon cooling. The transition temperature is the point at which a material undergoes a phase change, typically from a non-superconducting to a superconducting state. T_{conset} and $T_{coffset}$ remain the same for samples A and B, but increase for samples C and D as the partial substitution of Bi-Ga increases. The superconducting transition temperature, represented by ΔT, changes correspondingly, with an increase in ΔT indicating a deterioration in the superconducting properties. Electrical resistivity measurements indicate that partial substitution of Bi-Ga degrades the superconducting properties in some aspects. This is a prominent property. The decline in superconductivity can be attributed to the emergence of less doped phases between superconducting particles, the formation of gaps between particles, or the appearance of secondary phases that do not exhibit superconducting properties.

Figure 4 shows M–H hysteresis loops of samples. Magnetic hysteresis curves were measured at a temperature of 10K and over ±10 kOe fields. To expel any trapped magnetic flux, all samples were heated above the superconducting transition temperature before the measurement. The results of the magnetic hysteresis measurements indicate that the M-H curves are nearly symmetrical. As the amount of Bi-Ga partial substitution increases, both the area within the hysteresis curve and the maximum magnetization value increase. The magnetization of the samples resulting from the generated current causes thermal fluctuations that affect the Cooper pair density, leading to a decrease in the area within the M-H curve. When a magnetic field (H) above the critical Hc1 range is applied, flux lines penetrate the sample, narrowing the hysteresis curve. The penetration of the magnetic field into the structure results in the release of a Lenz force, which generates resistance and reduces the critical current density.

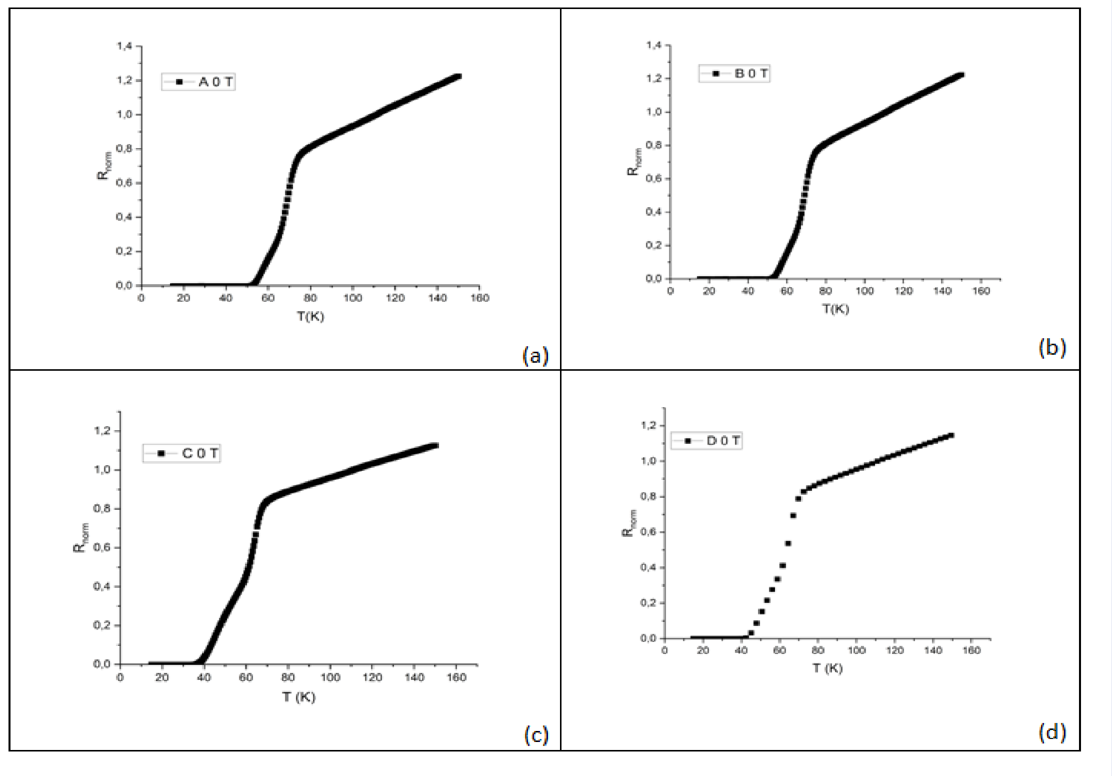

Figure 3. Resistivity measurement vs. temperature for all the samples.

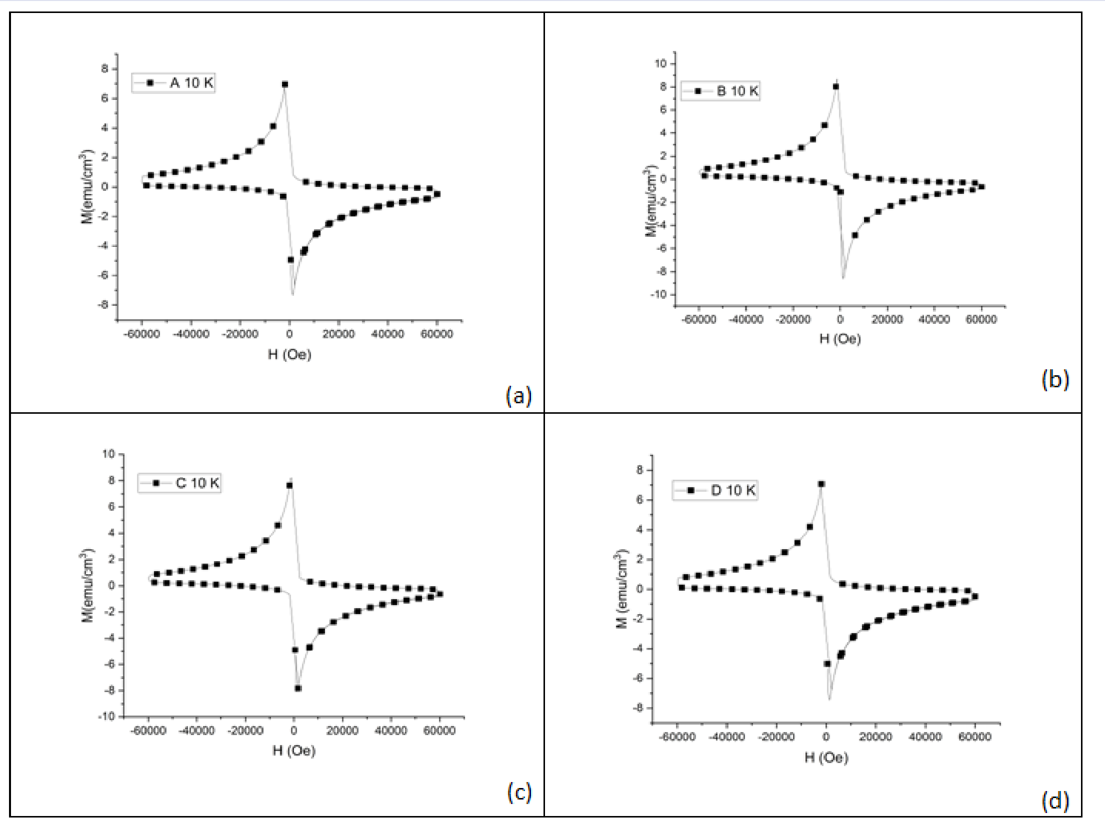

Figure 4. M–H hysteresis loops of samples at T = 10 K and applied external fields of ±10 k

The critical current density (Jc) can be calculated from the M-H curve using the Bean model (Bean 1962) as shown in equation 2. [15]

$$J_c = 20\frac{|\Delta M|}{a(1-\frac{a}{3b})} \qquad (2)$$

Figure 5 displays the calculated critical current densities for samples A, B, C, and D as a function of the applied magnetic field at a constant temperature of 10K. The figure illustrates the variation of Jc with respect to the field, where Jc is obtained from the non-zero H portion of the hysteresis curve. The critical current density increases with increasing magnetic field up to a certain value (H) and then decreases at higher magnetic field strengths. At constant temperature, the critical current density theoretically decreases with increasing magnetic field. Increasing the magnetic field to a certain value of H enhances the interparticle interactions and thus the critical current density due to weak interactions between particles in polycrystalline crystals. This is observed as a small region of increase in the curve, and the magnetic field value decreases at higher temperatures, resulting in an increase. Figure 5 shows a decrease in Jc value for sample D at zero magnetic field, while an increase in Jc value is observed for the other samples as the substitution amount increases which is typical for type-II superconductors.

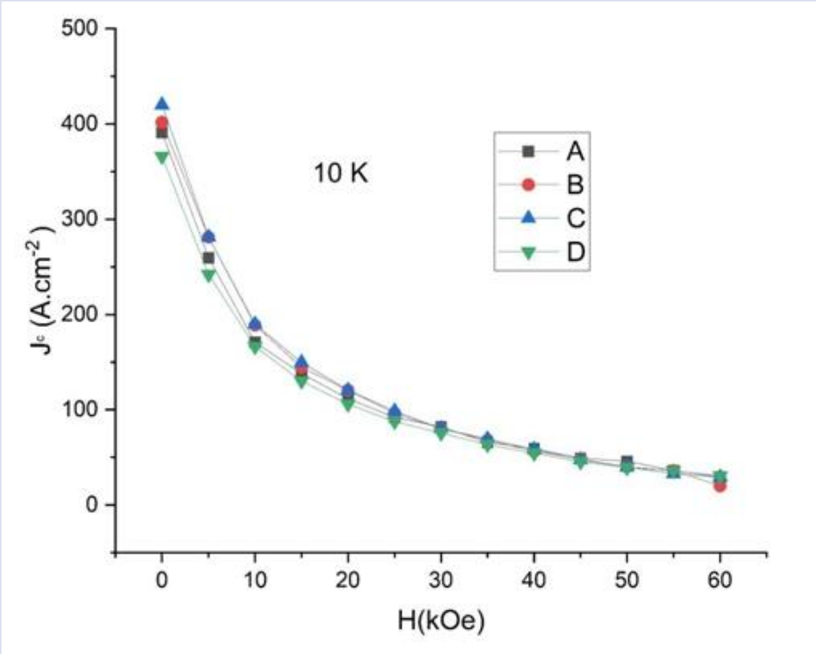

Figure 5. Calculated J_c results of samples at T = 10 K from their hysteresis loop.

Figure 6 shows the results as a function of the applied magnetic field. The magnetisation's temperature dependence was measured for all samples under an external magnetic field of 50Oe in the range of 0-100K. The results obtained from partially substituting Ga-Bi indicate that the samples' superconducting properties are lost when the applied magnetic field exceeds the initial T_{conset} value. The magnetic moment usually increases as the temperature decreases, indicating stronger magnetic ordering at lower temperatures. The curves show a significant change in slope at specific temperatures, which may correspond to magnetic or structural phase transitions. The different samples exhibit varying behaviors, which could be due to differences in composition, structure, or magnetic properties.

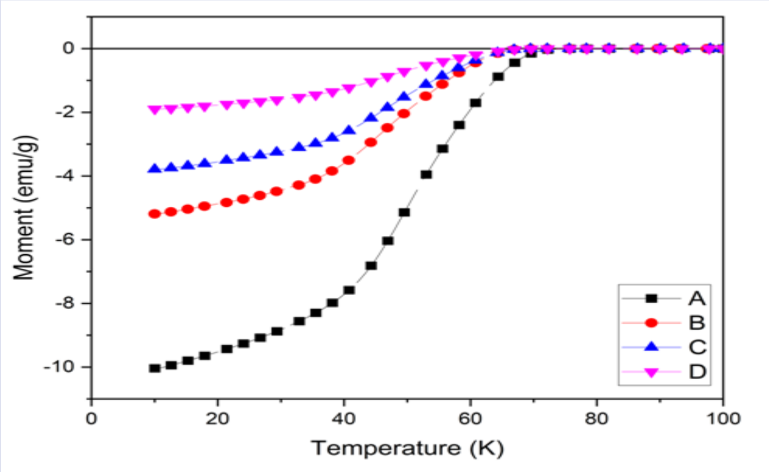

Figure 6. The magnetic moment (moment in emu/g) as a function of temperature (K) for the same samples A, B, C, and D..

CONCLUSION

The $(Bi_{2-x}Ga_x)Sr_2CaCu_2O_2$ system samples (x=0, 0.06, 0.12, 0.20) were synthesized using the solid-state reaction method. The effects of Bi-Ga partial substitution on BSCCO superconductivity were investigated through resistance measurements, EDX, SEM, magnetisation hysteresis measurements, and XRD measurements. The results show that the superconducting transition temperatures, where the resistance becomes zero, decrease as the Bi-Ga partial substitution increases. In contrast, the range of the superconducting transition, ΔT, increases. The electrical resistance measurements indicate that the superconducting properties are degraded by partial substitution. The results of the electrical resistivity measurements are consistent with those of the XRD and SEM analyses.

Acknowledgments

This work was supported by Hakkari University Scientific Research Projects Coordination Office, by the project numbered FM22LTP3.

Conflicts of interest

There are no conflicts of interest in this work.

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