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Effect of Nano-Sized Europium Substitution on Strontium Sites on Diamagnetic Properties in BiPb-2223 Superconductor System

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In the current study, different amounts of nano-sized Eu (80 nm) (x = 0.0, 0.20 and 0.25) were substituted to strontium sites in the $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_{2.75}Na_{0.25}O_y$ system. Ceramic samples produced by the solid state reaction method were analyzed by performing X-ray diffraction measurements (XRD), scanning electron microscope measurements (SEM) and M-H measurements. In the results of X-ray diffraction measurement, it was determined that the main phase structure was Bi-2223 superconductivity phase, although some impurity phases were formed in all samples. In the findings obtained from scanning electron microscopy measurements, it was observed that all samples consisted of flaky plate-like grain structures containing the presence of Bi-2223 phase structure. With the formation of minor impurity phases in the morphological structure, differences in grain behavior have occurred in some regions. M-H measurements were performed to characterize the magnetic properties of the samples. In M-H measurements, diamagnetic behavior, which is characteristic of the Bi-2223 superconductor phase, was observed in sample, nano sized Eu-free.

1. Introduction

Due to their zero resistance and strong diamagnetic properties, superconductors have opened new horizons for their use in various applications such as electrical conduction elements, magnetic circuits and superconducting magnets [1-3]. Since the discovery of high-temperature superconducting materials, various strategies have been developed by researchers to improve the existing properties of these materials for use in various fields of technology [4,5]. Among the high-temperature superconducting families, Bi-Sr-Ca-Cu-O (BSCCO), Y-Ba-Cu-O (YBCO) and iron-based superconducting systems are among the popular families that are being developed by researchers. Bi-based high temperature superconductor structure with the general formula $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+x}$ is preferred by many research groups due to its high transition temperature (Tc) and relatively high critical magnetic field [6,7]. Various problems such as weak bonds between grains, brittle behavior due to ceramic nature, mechanical stabilization, highly anisotropic structure, and random orientation of grains are parameters that negatively affect the superconductivity performances of bismuth-based high-temperature superconductors [8,9]. In addition, due to the vortex mechanism of Type II superconductors, magnetic flux lines penetrate the structure in a quantized manner, weakening their superconductivity properties. In order to maintain superconducting properties, it is necessary to limit flux movements by creating flux pinning mechanisms under the magnetic field. [10,11]. To promote the widespread use of bi-based superconductors in magnetic applications in technology, it is necessary to increase the flux stabilization forces (Fp) by artificially incorporating effective flux stabilization centers into the system [12]. In BSCCO superconducting materials, flux pinning centers can be formed by doping or adding elements of different ionic radii and creating crystal defects in the structure. [13,14]. In addition, nano-sized elements can settle between grains and act as

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flux pinning centers, improving the current density performance of materials under high magnetic fields [15].

The number of valence electrons of the element substituted in ceramic superconducting materials is an extremely important parameter [16]. As is well known, alkali metals, which have one electron in their outer shell, have a highly reactive structure and can easily lose the electron in their last orbit in order to reach a stable energy structure [17,18]. In this case, when alkaline elements with a reactive structure are added into the BSCCO superconductor, it can change the hole concentration in Cu-O layers. For this reason, due to the benefits of sodium substitution to copper oxide sites in the literature, sodium was substituted to the starting composition at a fixed rate in the present study [19]. In the present study, the effect on diamagnetic properties of nano-sized Eu substituting on strontium sites in ceramic superconductors in the initial composition of $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_{2.75}Na_{0.25}O_y$ (x = 0.0, 0.20 and 0.25) properties was investigated. On ceramic samples produced by the solid state reaction method, X-ray diffraction (XRD) for phase analysis, scanning electron microscopy (SEM) for morphological structure analysis and M-H measurements for diamagnetic properties were performed.

2. Results and Discussion

X-ray diffraction measurements of BiPb-2223 superconductor samples substituted with nano-sized Eu at different rates are in Figure 1, 2 and 3, respectively. As is well known, since it is very difficult to synthesize the Bi-2223 high temperature superconducting phase in the single phase structure, minor impurity phases that can act as flux pinning centers may occur.

In X-ray diffraction patterns, the Bi-2223 superconductivity phase is symbolized by +, while the Bi-2212 superconductivity phase, $Ca_4Bi_6O_{13}$ phase and CaPb03 phase are symbolized by ●, ■ and ⋆ respectively. Despite the formation of some secondary phases, the Bi-2223 superconducting phase is the main phase in all samples.

The broadening and sharpness of peaks in X-ray diffraction patterns can provide very important information about the behavior of grains in morphological structure as well as indicating optimum phase definitions [20,21]. In the X-ray results, the position and sharpness of the peaks of the Bi-2223 phase were formed optimally in all samples. This indicates that a good crystallization process has occurred in the Sample A. In addition, with the introduction of nano-sized Eu into the system, different types of phases were formed and differences in the intensities of the peaks occurred. Moreover, in the nano sized Eu substituted Samples, a decrease in the intensities of the characteristic peaks of the Bi-2223 phase is observed. In nano sized Eu substituted samples, the increase in the density of the impurity phase led to a decrease in the homogeneity in the crystal structure. The decrease in homogeneity due to the increase in the density of impurity phases caused the peak intensities to decrease, indicating a deterioration in the crystal structure. As is well known, while the low amount of non-superconducting phases does not significantly affect the superconductivity critical temperature (Tc), it can improve the critical current density performances by improving the flux pinning centers. However, an increase in the ratio of impurity phases significantly affects superconductivity performance.

With the increase of Eu contribution, the intensities of the peaks belonging to the Bi-2223 phase decreased significantly. In phase analysis results, decreases in peak intensities and increases in the density of impurity phases may lead to weakening of the diamagnetic properties of ceramic superconductors.

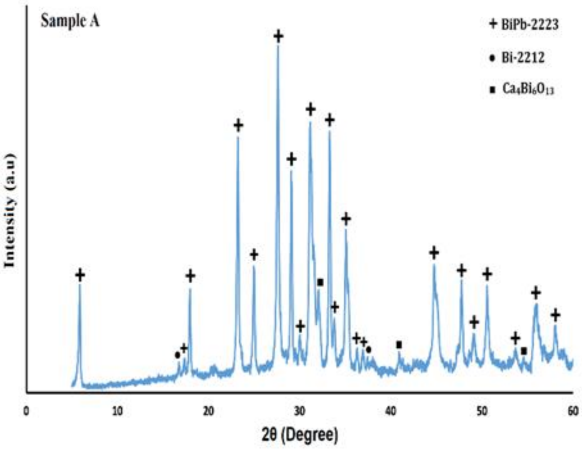


Figure 1. X-ray diffraction patterns of Sample A.

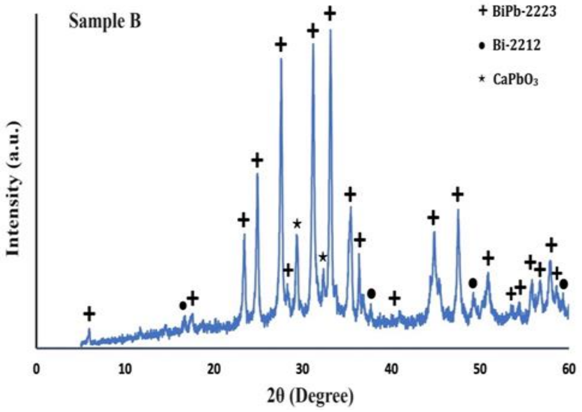


Figure 2. X-ray diffraction patterns of Sample B.

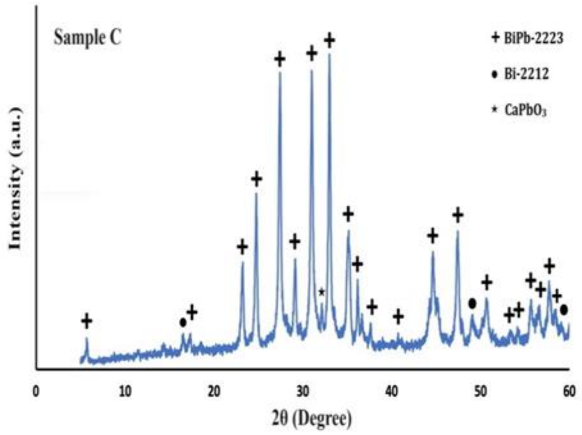


Figure 3. X-ray diffraction patterns of Sample C.

Figure 4 shows the morphological structures of the samples obtained by SEM measurement. As is well known, flaky plate-like grain structure is characteristic of the Bi-2223 superconducting phase, while plate-like grain structures is characteristic of the Bi-2212 superconducting phase [22,23]. In the morphological structure of ceramic superconducting samples, flaky plate-like grain and plate-like grain structures are formed together. As observed in the X-ray diffraction results, the formation of the Bi-2212 superconducting phase at the minor level and the formation of the Bi-2223 superconducting phase at the main level resulted in two types of grain behavior in morphological structure.

A random oriented granular structure is observed in the examples, which is the nature of the solid-state reaction method. As is well known, when alkaline elements are substituted into the BSCCO ceramic, they can expand the grain sizes by reducing the phase formation temperatures [16,17]. Especially in sample A, the positive effect of sodium, a substitution to copper oxide sites on the grains, is observed. Moreover, flaky plate-like grain structures that are strongly bonded to each other were formed in Sample A. In sample B and Sample C, which contain nano-sized Eu at a ratio of x = 0.20 and 0.25, flaky plate-like grain structures and plate-like grain structures, indicating the existence of Bi-2223 high temperature superconducting phase and Bi-2212 superconducting phase, were formed together. In addition, irregular distribution of grains, increases in grain boundaries and void structures between grains also occurred in the morphological structure of Eu-doped samples. In ceramic superconducting materials, deteriorations in the morphological and granular structure can negatively affect the magnetic properties.

Quantitative analysis of the ratios of the elements that make up the content of ceramic superconducting materials was made by EDS measurements. The results obtained from EDS analyzes are shown in Figure 5, 6 and 7, respectively. In the findings obtained by EDS measurement, while all ceramic samples consisted of elements used in the material preparation process (Bi-Pb-Sr-Eu-Ca-Cu-Na-O), no results were obtained for the europium element in Sample A. Moreover, EDS results show that there are no undesirable elements. These results show that the substitution of nano-sized Europium element to strontium sites was successfully carried out during the material preparation process.

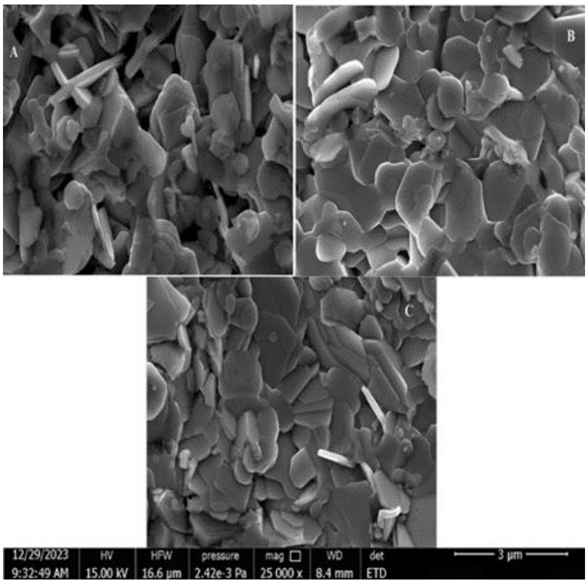
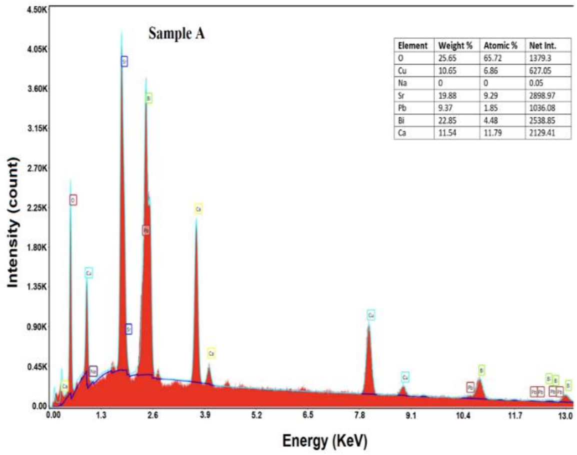
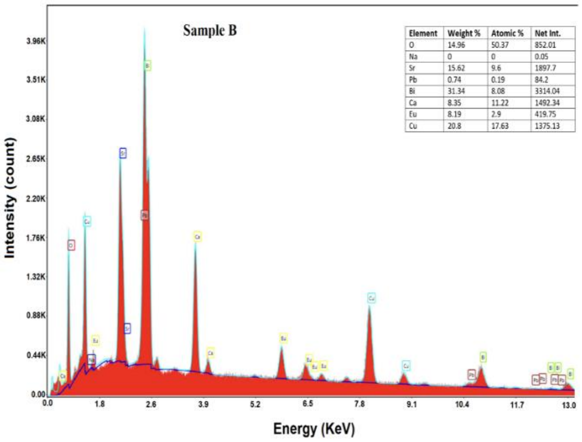


Figure 4. SEM results of the (a) Sample A, (b) Sample B and (c) Sample C



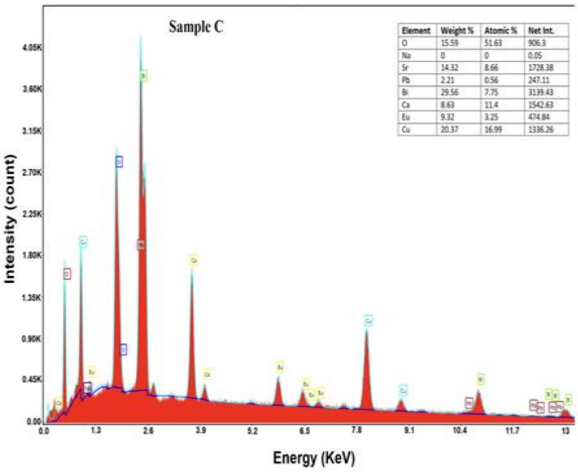
Element	Weight %	Atomic %	Net Int.
O	25.65	65.72	1379.3
Cu	10.65	6.86	627.05
Na	0	0	0.05
Sr	19.88	9.29	2898.97
Pb	9.37	1.85	1036.08
Bi	22.85	4.48	2538.85
Ca	11.54	11.79	2129.41

Figure 5. EDS measurement results of Sample A.



Element	Weight %	Atomic %	Net Int.
O	14.96	50.37	852.01
Na	0	0	0.05
Sr	15.62	9.6	1897.7
Pb	0.74	0.19	84.2
Bi	31.34	8.08	3314.04
Ca	8.35	11.22	1492.34
Eu	8.19	2.9	419.75
Cu	20.8	17.63	1375.13

Figure 6. EDS measurement results of Sample B.



Element	Weight %	Atomic %	Net Int.
O	15.59	51.63	906.3
Na	0	0	0.05
Sr	14.32	8.66	1728.38
Pb	2.21	0.56	247.11
Bi	29.56	7.75	3139.43
Ca	8.63	11.4	1542.63
Eu	9.32	3.25	474.84
Cu	20.37	16.99	1336.26

Figure 7. EDS measurement results of Sample C.

M-H measurements of ceramic samples performed under a magnetic field of ± 20000 Oe at 15 K and 25 K temperatures are shown in Figures 8 and 9, respectively.

Closed loop hysteresis behavior resulting from M-H measurements in ceramic superconducting samples is a characteristic feature. M-H measurement results show that hysteresis behavior can be observed in all samples, indicating that the main phase structure is the Bi-2223 superconducting phase. On the other hand, the hysteresis field corresponds to the magnetic energy required to eliminate the superconductivity feature, and the width of this field and the geometry (symmetry) of the field depend on parameters such as the quality of intergranular connections, impurity phases and orientation states of the grains [24,25].

In the *M-H* results performed at both temperatures, closed-loop hysteresis behavior with better geometry was observed in Sample A which is

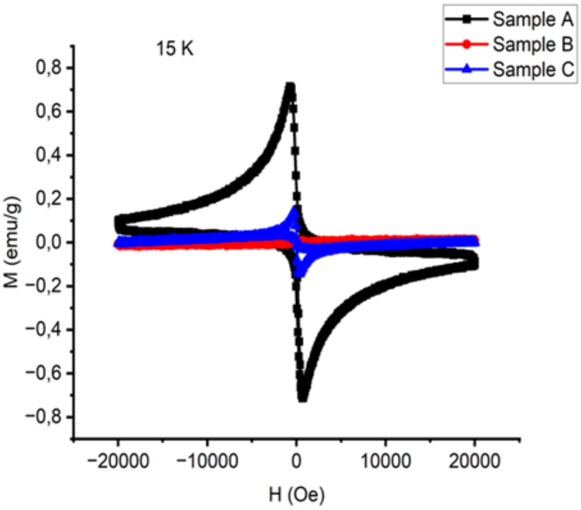


Figure 8. *M-H* graph of Sample A, B and C performed under ± 20000 Oe magnetic field at 15 K temperature.

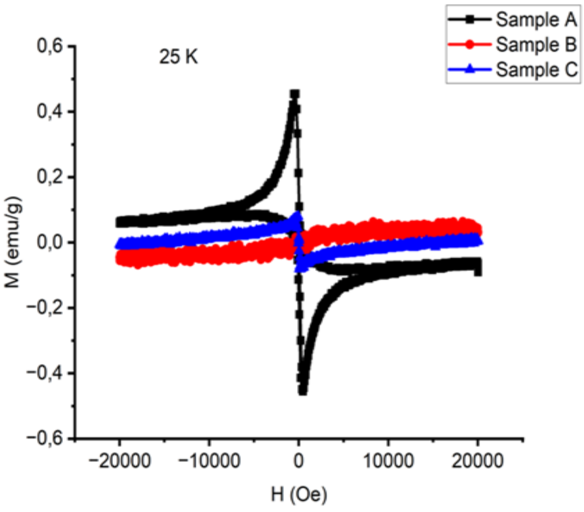


Figure 9. *M-H* graph of Sample A, B and C performed under ± 20000 Oe magnetic field at 25 K temperature.

the nano-sized Eu-free. In Sample B, closed loop hysteresis behavior could not be observed due to the increase in the ratio of impurity phases and distortions in the morphological structure. Although the diamagnetic signal started to form in sample C, parameters such as the high percentage of impurity phases and the decrease in homogeneity in the morphological structure led to a decrease in the hysteresis loop area and deterioration of its geometry.

3. Conclusion

In the present study, different amounts of nano-sized Eu (x = 0.0, 0.2 and 0.25) were substituted to the strontium sites in the $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_{2.75}Na_{0.25}O_y$ system. The samples produced by the solid-state reaction method were characterized by X-ray diffraction measurements (XRD), scanning electron microscopy (SEM) and magnetization (M-H) measurements. In the findings obtained with XRD measurements, it was determined that the main phase structure in all samples was the Bi-2223 superconducting phase. However, with the increase in nano-sized Eu substitution, the ratio of impurity phases gradually increased. In the SEM measurement results, the formation of flaky plate-like grain and plate-like grain structures is observed in all samples. A more homogeneous grain structure was formed in the sample that did not contain nano-sized Eu substitution, compared to other samples. In the EDS results, it was observed that the elements were distributed within the structure in the desired proportions in all samples. As a result of magnetization, optimum phase formation and homogeneous grain structure and the best diamagnetic properties were observed in the nano-sized Eu-free sample. According to the findings obtained as a result of the analysis, diamagnetic properties deteriorate with the increase of impurity phases and the decrease of the homogeneous structure in the morphological structure with the substitution of nano-sized Eu such as rates of 0.2 and 0.25.

Method

Ceramic superconductor samples in the initial composition of $Bi_{1.7}Pb_{0.3}Sr_{2-x}Eu_xCa_2Cu_{2.75}Na_{0.25}O_y$ (x = 0.0, 0.20 and 0.25) contain high purity Bi_2O_3 (Thermo, 99%), $SrCO_3$ (Thermo, 99%), $CaCO_3$ (Thermo, 99 %), CuO (Thermo, 99 %), $NaCO_3$ (Thermo, 99 %) and Eu (TekKim, 98.5+%) (80 nm) precursor powders were produced using the conventional solid state reaction method. First, high-purity precursor powders were weighed into appropriate proportions and ground using an agate mortar. After the grinding stage, the precursor powders mixed homogeneously were pressed into pellets with a diameter of 1.5 cm by applying a pressure of 375 MPa in a hydraulic press machine. After the pressing stage, the first heat treatment, calcination, was applied to the pelletized samples at 750 °C for 12 hours. The calcined pellets were ground in an agate mortar, pressed under 375 MPa pressure, and calcined again at 820 °C for 12 h to initiate the formation of high-purity Bi-2223 phases. These processes, which included grinding, pressing and calcination steps, were repeated two more times. In order to increase the density of high-purity Bi-2223 superconducting phases and minimize crystal defects, ceramic samples must be annealed. To apply the annealing process to the pelletized samples, they were ground, pressed and annealed at 860 °C for 160 hours.

In order to detail the characterization studies after the synthesis process, ceramic samples according to the nano-sized Eu substituting ratio were labeled as Sample A (x = 0.00), Sample B (x = 0.20) and Sample C (x = 0.25).

Resistivity and magnetic measurements were carried out on the samples using Cryogenic Limited PPMS (from 5 to 300 K) which can reach the cryogenic temperatures about to 2 K in a closed-loop He system. X-ray powder diffraction analyses to determine the phases present in the samples were performed by using a Rigaku Ultima IV X-Ray Diffractometer with a constant scan rate (2^o/min) in the range $2\theta = 3^o–60^o$. The surface morphologies of the samples were studied by using a Zeiss/ Supra 55 scanning electron microscopy (SEM).

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All samples were prepared in the NanoMaterials/Magnetic Materials Research Laboratory at Adana Alparslan Türkeş Science and Technology University in Türkiye. All measurements were carried out at Çukurova University central laboratories in Türkiye.

Authors' contributions:

All authors contributed to the design and concept of the study. All authors contributed to the preparation of materials, characterization studies, creation of the first draft of the manuscript, and the final version of the article. All authors read and approved the final version of the manuscript.

Data Availability Statement

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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