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EFFECT OF GRAPHENE OXIDE AND REDUSED GRAPHENE OXIDE ON ELECTRICAL PROPERTIES OF YBCO AND YBCO/Ag COMPOSITES

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ABSTRACT

Series of bulk composites based on YBCO superconductors, silver and graphene oxide/reduced graphene oxide are synthesized. The aim of this study is to determine the effect of GO and RGO on the superconducting properties of YBCO composites. Series of YBCO and YBCO/Ag phases are synthesized by the ceramic method. GO and RGO are obtained by the modified Hammer's method. Series of YBCO, YBCO/Ag composites with GO or RGO are studied. The temperatures of the superconducting transition of the obtained composites are determined and the effect of GO/RGO is investigated.

Keywords: graphene oxide, reduced graphene oxide, superconducting ceramic, composites, YBCO, superconducting transition, electrical properties.

INTRODUCTION

Since the discovery of YBCO superconductivity, lots of attempts have been made to enhance this property [1]. Some additives have been used to change the properties of YBCO superconductor [2 - 5].

Graphene oxide is a promising material with various applications in next generation technologies (electronics, optoelectronics and technologies connected with energy transformation and storage) [6 - 12]. With its thermal, electrical and mechanical characteristics graphene oxide is studied as an additive introduced to improve the material properties [13 - 15]. It is reported that MgB_2 doping with GO results in an increase of the critical current density and the critical magnetic field observed [14, 15]. Graphene oxide contains a range of reactive oxygen functional groups, rendering it a good candidate for use in energy-related materials. It has excellent electrical, mechanical, and thermal properties. GO is composed of carbon, hydrogen, and oxygen, resulting in an increase of the overall mass of the flake graphite [16].

Graphene oxide is electrically insulating to its disrupted sp2 bonding networks. The electrical conductivity can be recovered by restoring the p-network, so the reduction of the graphene oxide is required. The resulting product of this reduction is called reduced graphene oxide (RGO), chemically-reduced graphene oxide (CReGO) or graphene. The reduced graphene oxide and pristine graphene are similar. This refers also to their electrical, thermal and mechanical properties. That is why the reduction process (achieved through chemical, thermal, or electrochemical reduction pathways) is very important reaction and often used by scientists who investigate graphene and its applications [16].

The aim of the present work is to synthesize series of bulk composites based on YBCO superconductors, silver and graphene oxide (GO)/reduced graphene oxide (RGO) and to study the effect of GO and RGO on the superconducting properties of the ceramics obtained.

EXPERIMENTAL

YBCO/YBCO + 5 $\%_{mass}$ Ag superconducting ceramic and GO/RGO were separately synthesized. A series of composites on their base was obtained by varying GO/RGO (1 $\%_{mass}$, 3 $\%_{mass}$ and 5 $\%_{mass}$).

Stoichiometric amounts of oxides and carbonates (Y_2O_3, $BaCO_3$, CuO, $AgNO_3$) were mixed, grinded and fired in air at 930°C within 16 h for the synthesis of YBCO and YBCO/Ag ceramics.

GO was obtained from a graphite powder by the modified Hummer's method. A planetary mill (Fritsch – Pulverisette) with a rotation speed of 500 rpm was used for 1 h for grinding the powder. 200 ml of H_2SO_4 and 50 ml of H_3PO_4 were used for the oxidation of 10 g of a graphite powder. This mixture was stirred in an ice bath and 30 g of $KMnO_4$ and 460 ml of distilled water were slowly added. The obtained suspension was left to stand for 18 h. A solution of 50 ml of 30 % hydrogen peroxide in 700 ml of distilled water was added drop wise within an hour under constant stirring. The suspension was washed with 1M HCl and several times with deionized water and the graphite oxide obtained was dried for 12 h at 70°C. The exfoliation of graphite oxide to GO sheets was performed by sonication of the graphite oxide suspension for 2h using Bandelin Sonorex (35 KHz, 240W) ultrasonic processor. GO was used for some of the YBCO/Ag composites studied aiming to compare the effect of GO and RGO on the composites superconducting properties.

The next step was to obtain RGO. It was prepared by chemical reduction of GO with sodium borohydride. 0.2 g of GO, 2.0 g of NaOH and 2 g of sodium borohydride were added to 100 ml of deionized water. The mixtures were stirred at a room temperature for 24 h. The resulting RGO materials were washed several times with deionized water and dried for 12 h at 70°C.

Two series of superconducting composites were synthesized mixing powders of YBCO or YBCO + 5 $\%_{mass}$ Ag ceramic with GO (1, 3 and 5 $\%_{mass}$) or RGO (1, 3 and 5 $\%_{mass}$). All compositions were mixed and homogenized for 2h using Bandelin Sonorex ultrasonic processor.

The obtained samples were characterized by powder XRD using Bruker D8 Advance powder diffractometer with Cu Kα radiation and a LynxEye detector. The data collection was performed in the range of 10°2θ to 90°2θ with a step of 0.03°2θ and counting time of 57 s/a step. The sample was rotating at 15 rpm. Diffracplus EVA and ICDD-PDF2 (2014) database was used for the phase composition identification.

SEM and EDX analyses of GO, RGO, YBCO, YBCO/Ag and YBCO/graphene composites were performed on a microscope: SEM / FIB LYRA I XMU by TESCAN (Electronic source: tungsten heater; Resolution - 3.5 nm at 30 kV; Acceleration voltage - 200 V to 30 kV; EDX detector: BRUKER's Quantax 200; Spectroscopic resolution at Mn-Kα and 1 kcps of 126 eV). The obtained composite powders were tableted at 7 t pressure using a hydraulic press and then fired in air for 6 h at 930^{o}C. This was done aiming to study their physical properties.

An ac contactless inductive method [17, 18] was used for investigation of the critical temperature Tc of YBCO samples. The magnetic screening ac response of the superconducting sample under ac (1 kHz) magnetic field was measured. The sample was placed between two small flat coils (drive and receive coils). A sinusoidal magnetic field was applied to the drive coil and the module of the basic component of the voltage induced in the receiving coil (the response signal) was measured in the temperature range of 77K - 110K. The magnetic field in a superconducting state (at $T < T_C$) was screened by the super currents in the sample. The signal in the receiving coil was small. The sample lost its superconducting properties with an increase of the temperature to $T \sim T_C$ and became practically transparent in respect to the magnetic field. This caused a sharp increase of the response signal in the receiving coil demonstrating the critical temperature of the sample.

RESULTS AND DISCUSSION

The phase formation in the YBCO superconducting composites obtained with Ag and GO/RGO is investigated by XRD, SEM, EDX analyses and a color mapping elements distribution.

Fig. 2 shows XRD patterns of YBCO/5 % Ag composites containing GO and RGO. The presence of the superconducting orthorhombic $YBa_2Cu_3O_{7-\delta}$, phase, $Y_2Ba_1Cu_1O_{6-\delta}$ phase and Ag in composites is verified.

The SEM analyses of YBCO + 5 % Ag composites with GO/RGO are presented in Figs. 3 - 6. The silver particles are located along the YBCO crystallites' edges.

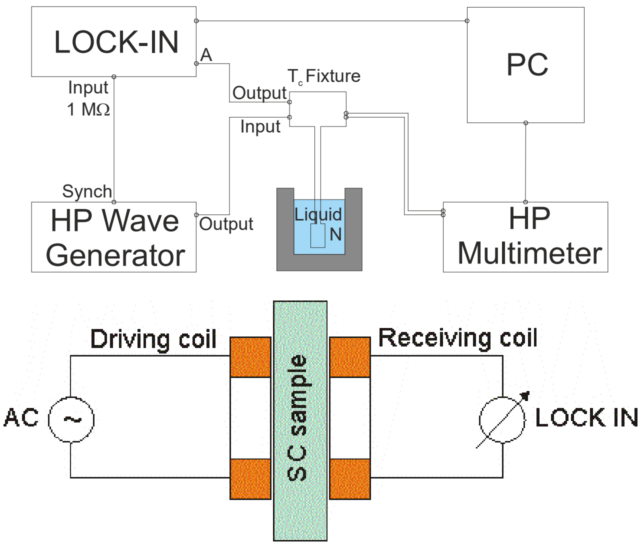

Fig. 1. Scheme of ac contactless inductive method for measurement of T_c.

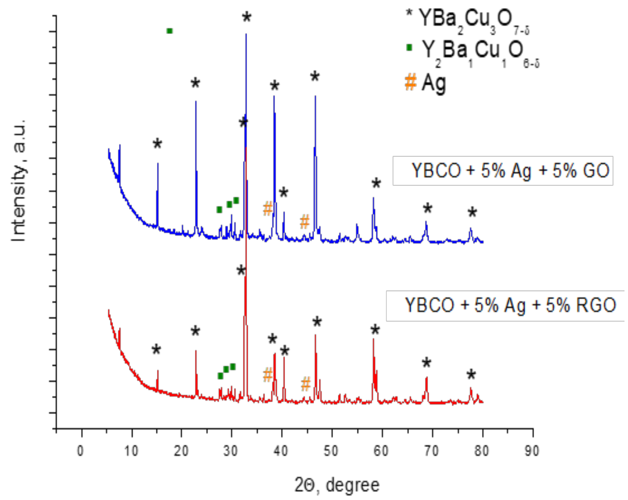

Fig. 2. XRD patterns of YBCO/Ag composites with GO and RGO.

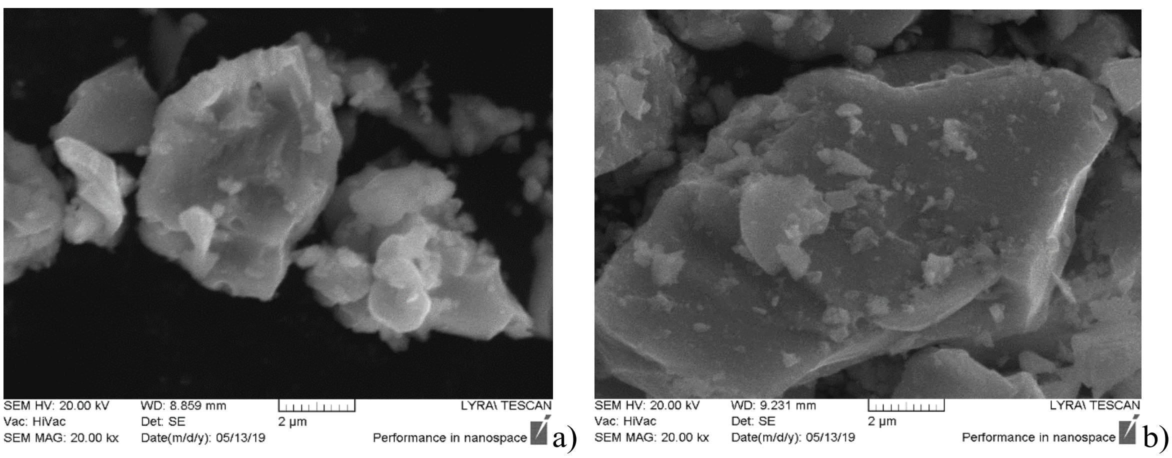

Fig. 3. SEM images of a) YBCO; b) YBCO + 5 % Ag.

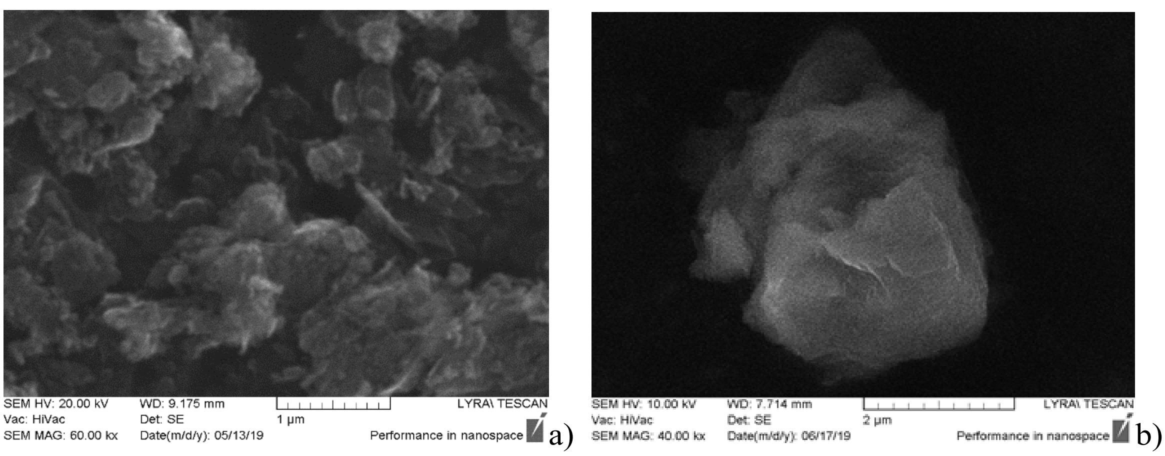

Fig. 4. SEM images of a) RGO and b) GO.

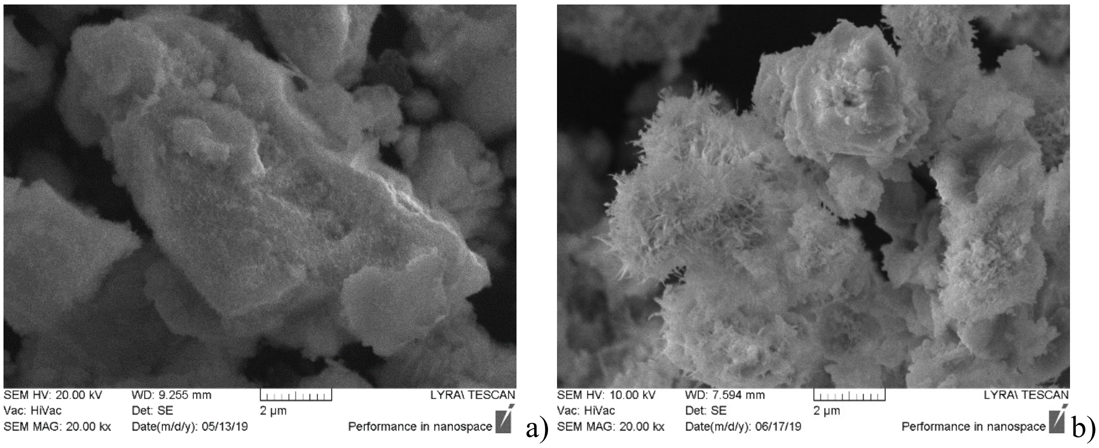

Fig. 5. SEM images of a) YBCO + 1 % RGO; b) YBCO + 1 % GO.

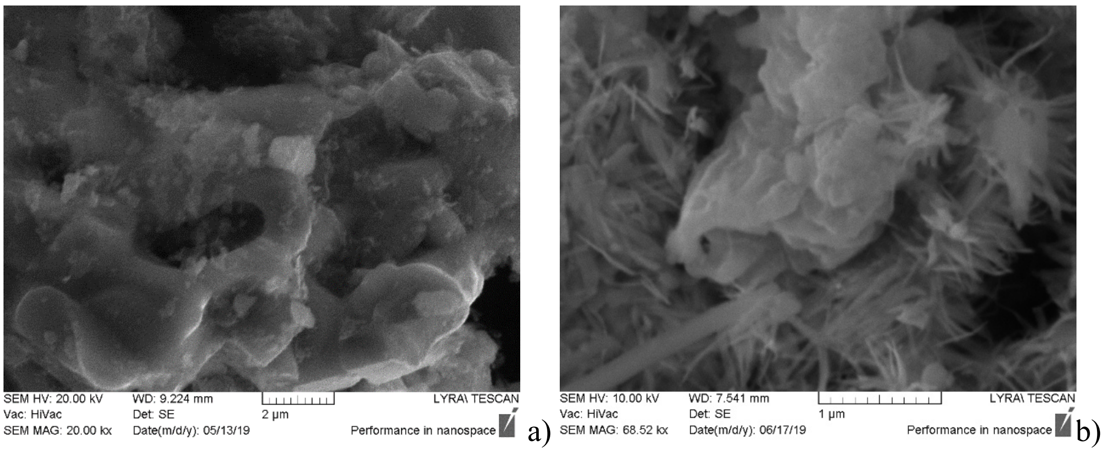

Fig. 6. SEM images of a) YBCO + 5 % RGO; b) YBCO + 5 % GO.

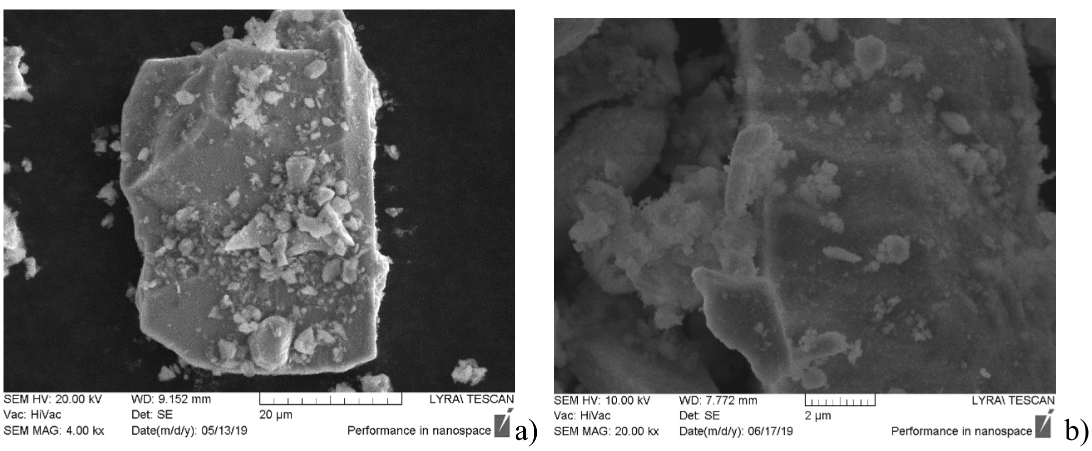

Fig. 7. SEM images of a) YBCO + 5 % Ag + 1 % RGO; b) YBCO + 5% Ag + 1% GO.

Graphene flakes are observed in case of huge magnifications of the SEM images of the composites containing GO/RGO (Figs. 5 - 8).

The EDX analyses of all composites show the distribution of Y, Ba, Cu and O elements, which corresponds to the stoichiometric ratio of the superconducting phase $YBa_2Cu_3O_{7-\delta}$ (Figs. 9 - 12).

The EDX analyses of all composites containing

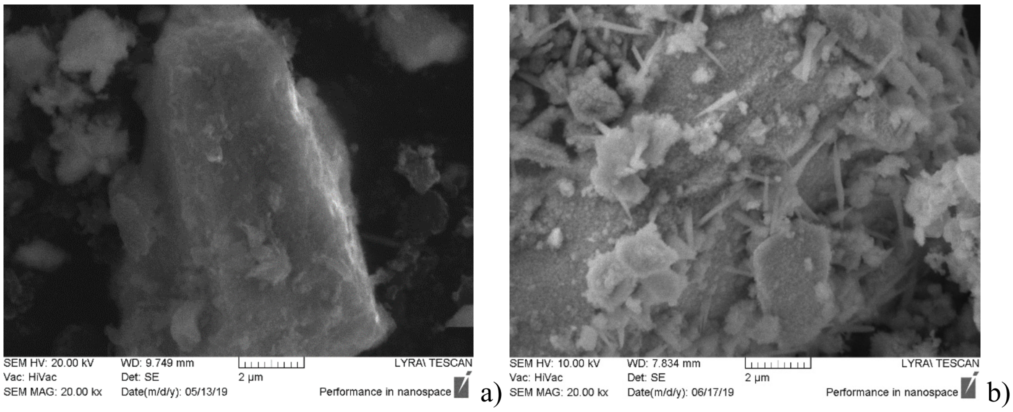

Fig. 8. SEM images of a) YBCO +5 % Ag + 5 % RGO; b) YBCO +5 % Ag + 5 % GO.

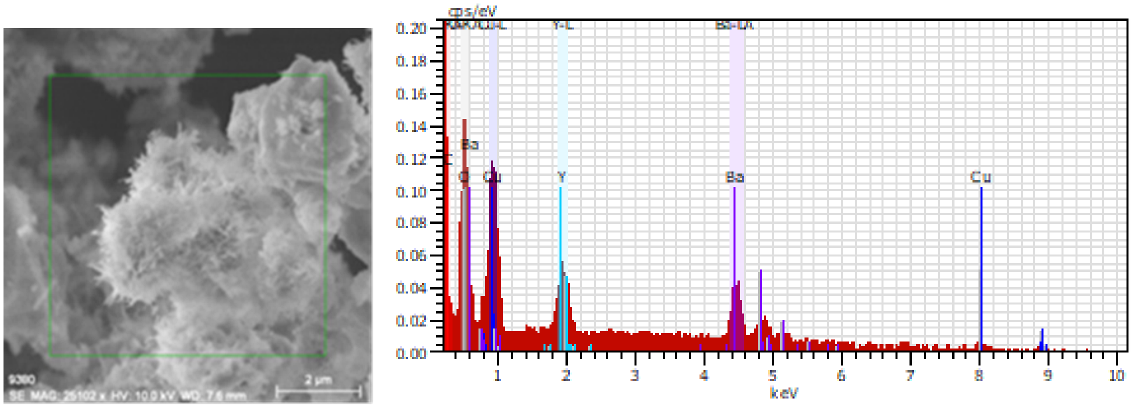

Fig. 9. EDX analyses and color mapping of elements distribution of YBCO + 1 % GO.

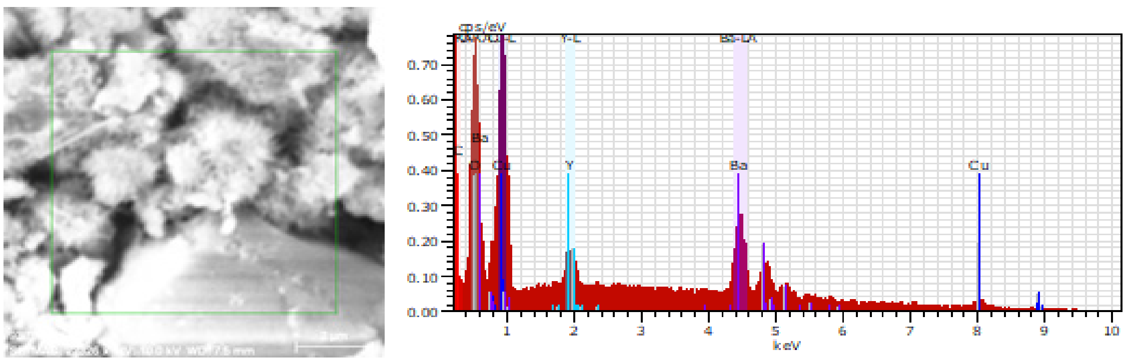

Fig. 10. EDX analyses of YBCO + 5 % GO.

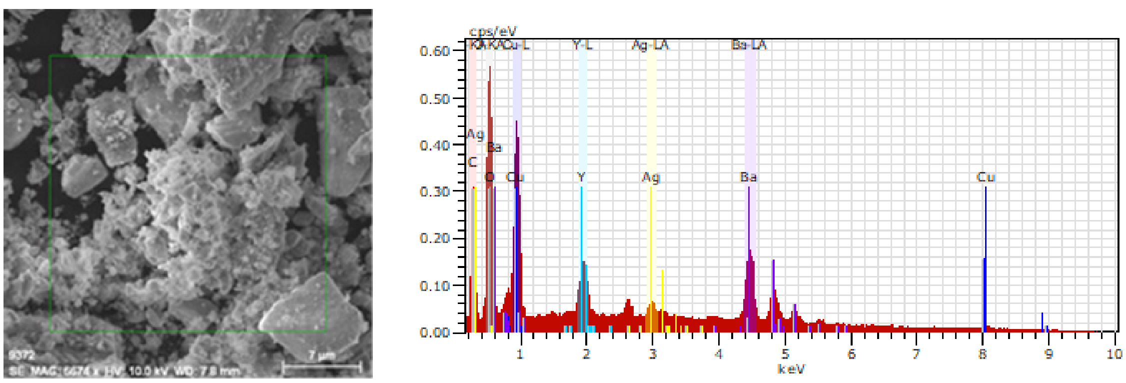

Fig. 11. EDX analyses and color mapping of elements distribution of YBCO + 5 % Ag + 1% GO.

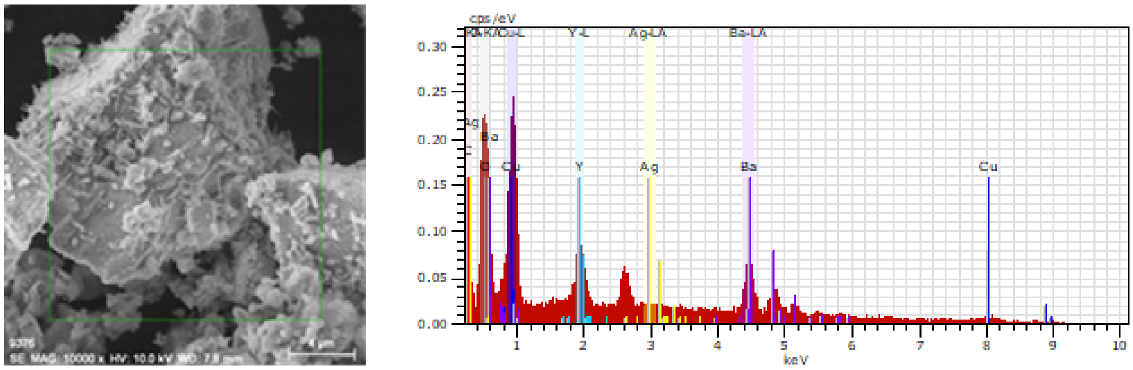

Fig. 12. EDX analyses and color mapping of elements distribution of YBCO +5% Ag + 5%GO.

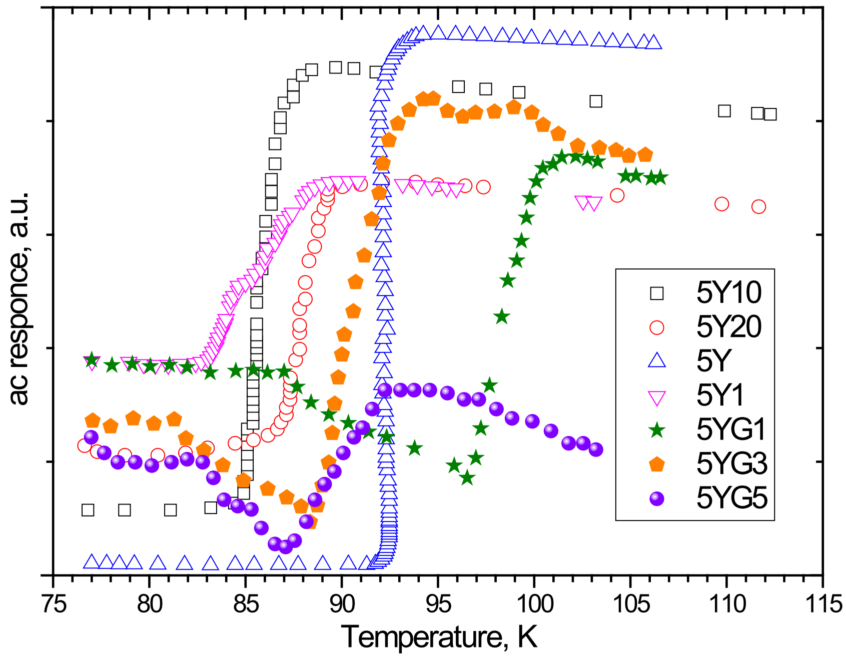

Fig. 13. A magnetic behavior of YBCO/ Ag/(GO or RGO) composites (Table 1).

GO demonstrate the presence of carbon in an amount corresponding to the compositions of the respective composites.

All phases obtained are superconductive. Their critical temperature values are measured (Table 1).

All samples, except Y and 5Y, are characterized by a low Meissner effect and a low critical current density. As the samples are polycrystalline, this could be due to the fact that the grains in the samples are not well connected.

The magnetic behavior of some compositions is followed (Fig. 13). Samples 5Y, 5Y10 and 5Y20 have a typical superconductor behavior of a critical temperature of 93 K, 89 K and 90 K, respectively. These samples transition from a superconducting to a normal state is relatively sharp. The transition of 5Y1 sample consists of 2 components. This could be due to the presence of two different superconducting phases attributed for example to inter- and intra-granular super currents. This sample is characterized by two temperatures – that of the end of the first transition and that of the superconducting state inset, 84.5 K and 89 K, respectively. It is interesting to note that the last 3 samples – 5YG1, 5YG3 and 5YG5 show an atypical behavior. The ac response signal starts to decrease with the temperature increase and reaches a local minimum at some temperature T_{min}. Afterwards the signal increases and reaches its

Table 1. Critical temperatures of obtained superconducting samples.

Designation	Composition	T_c, K	T_{min}, K	T_{max}, K
Y	YBCO	91.8		
5Y	YBCO + 5 mass.% Ag	93		
5Y1	YBCO + 5 mass.% Ag+ 1 mass.% RGO	89		
5Y3	YBCO + 5 mass.% Ag+ 3 mass.% RGO	90.6		
5Y5	YBCO + 5 mass.% Ag+ 5 mass.% RGO	89.3		
5Y10	YBCO + 5 mass.% Ag+ 10 mass.% RGO	89		
5Y20	YBCO + 5 mass.% Ag+ 20 mass.% RGO	90		
5YG1	YBCO + 5 mass.% Ag+ 1 mass.% GO	> 93	90.5	96
5YG3	YBCO + 5 mass.% Ag+ 3 mass.% GO	> 93	88.5	94
5YG5	YBCO + 5 mass.% Ag+ 5 mass.% GO	> 92	87	92.5

maximal value at T_{max}. This anomaly could be due to some magnetic behavior which is in competition with the superconducting behavior.

An additional investigation is required to identify the origin of the anomaly effect observed.

CONCLUSIONS

Series of YBCO and YBCO/Ag composites containing GO or RGO are synthesized. The effect of GO and RGO on the superconducting properties of YBCO ceramics is investigated. The electrical measurements carried out show that all composites obtained are superconductors. Their critical temperature values are measured. All YBCO/5 % Ag composites containing 1 %, 3 % and 5 % of GO have higher critical temperatures when compared to those of YBCO/RGO composites.

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