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STUDY OF STRUCTURAL, MORPHOLOGICAL AND ELECTRICAL PROPERTIES IN THE $(Bi_{1.6}Pb_{0.4})(Sr_{1.8}Ba_{0.2})Ca_2(Cu_{1-x}Gd_x)_3O_y$ SUPERCONDUCTORS

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ABSTRACT. X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and electrical resistivity measurements are performed to investigate some physical properties of $(Bi_{1.6}Pb_{0.4})(Sr_{1.8}Ba_{0.2})Ca_2(Cu_{1-x}Gd_x)_3O_y$ superconducting samples fabricated at sintering temperatures of 840 ^{0}C and 845 ^{0}C and the uniaxial pressures of 196MPa and 392MPa respectively. The samples were prepared by standard solid-state reaction methods. XRD measurements show that the samples obtained at 840 °C contain two phases. With the increase of the sintering temperature at 845 ^{0}C, a decrease in the diffraction peaks of the phase 2212 is observed, and with the increase of the pressure at 392MPa this phase falls below 10%. SEM analysis show that the superconductors have a uniform surface, but the size of the granules changes so that the sample sintered at 845 °C and the uniaxial pressure of 392 MPa has the best crystallinity.

Keywords: *BiPb 2223 doped superconductors, XRD, SEM, electrical properties*

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1. INTRODUCTION

Since the discovery of the high-temperature ceramic superconductors; numerous researches have been carried out to characterize properties of the materials [1–14]. It is well-known that a CuO-based superconductor, in general, behaves like a Mott–Hubbard insulator at low carrier concentrations, like a superconductor with semiconducting normal state resistivity behavior at intermediate carrier concentrations and like a superconductor with a typical metallic normal state resistivity behavior at sufficiently high carrier concentrations. Gadolinium substitution in BSCCO (2212) system for various doping levels [15] showed that the density of states at the Fermi level was reduced with increasing gadolinium ion contents at calcium sites.

In this work, investigations were carried out to determine the structural and transport properties for Gd doped BSCCO samples fabricated at sintering temperatures of 840 ^{0}C and 845^{0}C and the uniaxial pressures used were 196MPa and 392MPa. In addition, X-ray diffraction (XRD) and scanning electron microscopy (SEM) measurements were performed to investigate the phase analysis and surface morphology of the samples considered.

2. EXPERIMENTAL

Policrystalline bulk samples with nominal composition $(Bi_{1.6}Pb_{0.4})(Sr_{1.8}Ba_{0.2})Ca_2(Cu_{1-x}Gd_x)_3O_y$ were prepared by the conventional solid-state reaction of appropriate amounts of the metal oxides and carbonates of 99.99% purity [16–18]. Two sets of samples were fabricated at sintering temperatures of 840 ^{0}C and 845^{0}C and samples were pressed in the form of pills with a diameter of 7 mm using a hydraulic press. The uniaxial pressures used were 196MPa and 392MPa. The calcination was carried out at 800 °C for 30 hours. Table 1 gives the composition and sintering temperatures for the two systems. The temperature dependence of electrical resistivity was

measured using standard four probe method. The sample was cooled down in the absence of magnetic field; excitation current was applied to the sample plane perpendicular to the pressing direction (in the (ab) plane).

Table 1. Composition and fabrication conditions for BSCCO compounds

Sample	**Sintering temperature**	**Uniaxial pressure**
$\mathbf{(Bi_{1.6}Pb_{0.4})(Sr_{1.8}Ba_{0.2})Ca_2(Cu_{1-x}Gd_x)_3O_y}$	840 ^{0}C	196MPa
$\mathbf{(Bi_{1.6}Pb_{0.4})(Sr_{1.8}Ba_{0.2})Ca_2(Cu_{1-x}Gd_x)_3O_y}$		392MPa
$\mathbf{(Bi_{1.6}Pb_{0.4})(Sr_{1.8}Ba_{0.2})Ca_2(Cu_{1-x}Gd_x)_3O_y}$	845 ^{0}C	196MPa
$\mathbf{(Bi_{1.6}Pb_{0.4})(Sr_{1.8}Ba_{0.2})Ca_2(Cu_{1-x}Gd_x)_3O_y}$		392MPa

3. RESULTS AND DISCUSSION

The samples of $(Bi_{1.6}Pb_{0.4})(Sr_{1.8}Ba_{0.2})Ca_2(Cu_{1-x}Gd_x)_3O_y$ were placed on the X-ray diffractometer support. The X-rays interact with electrons in atoms, causing elastic or inelastic collisions. X-Ray elastic spreading contains data on the electron distribution in the material, the method used to determine the crystalline structure. Determination of the size of crystallites was performed using the Debye-Scherer relationship for diameter:

$$\boldsymbol{D = \frac{0.9\lambda}{B cos\theta}}$$

where B represents the width of the half-maximum for different peaks in the diffractogram. The assessed values for crystallite size are shown in Table 3.

By measuring angles and intensities of X-ray diffraction, a 3D image of the electrons in the crystal will be obtained. From the density of the electrons measured, the position of the atoms in the crystal is obtained, as well as information about their order / disorder.

Powder X-ray diffraction measurements aim to study the influence of sintering temperature and axial pressure on the structure and composition of the phase of the samples. The sintering temperature was 840 °C, 845 °C and axial pressures of 196MPa and 392MPa (Figure 1).

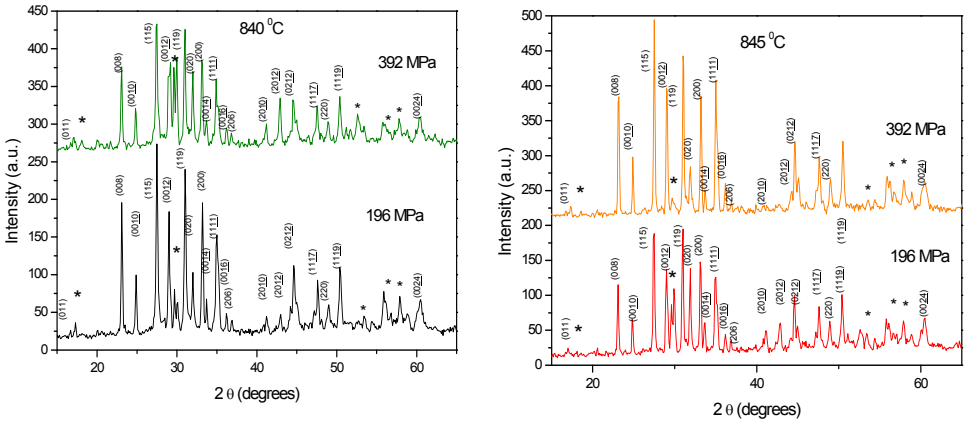


Figure 1. XRD diffractograms for sample sintered at la 840°C and 845°C

Also from the XRD analysis we calculate the presence of Bi: 2212 phase, with a relatively small percentage for both axial pressures, which can be seen from Table 2.

Table 2. Phase percentage calculated from XRD measurements.

		2223 %	2212 %
196MPa	840° C	80.8	19.2
	845° C	85.7	14.3
392 MPa	840° C	84.2	15.8
	845° C	90.4	9.6

Phase percentages were calculated using the formulas:

$$\mathrm{Bi:2223}(\%) = \frac{\sum I[\mathrm{Bi:2223}]}{q} \times 100$$

$$\mathrm{Bi:2212}(\%) = \frac{\sum I[\mathrm{Bi:2212}]}{q} \times 100$$

,

were q= $\Sigma I[Bi{:}\,2223] + \Sigma I[Bi{:}\,2212]$ and I is the intensity of the present phases.

The analysis of the crystalline structure of the $(Bi_{1.6}Pb_{0.4})$ $(Sr_{1.8}Ba_{0.2})$ Ca_2 $(Cu_{1-x}Gd_x)_3O_y$ compound was performed using a high resolution Brucker D8 diffractometer with a Bragg-Brentano configuration, copper anode with λ = 0.15406 nm; θ-2θ range was 10 - 90, 0.1 step and time of 5s / step.

3.1 Variation of sintering temperature and uniaxial pressure

Starting from previous studies [19] showing that by increasing the sintering temperature samples with good intergranular coupling were obtained, we varied the sintering temperature in the range around 845 ^{0}C, for which the samples had high critical current densities. To study the effect of thermal treatments and uniaxial pressures on critical current density we varied in two different ways. When we varied the temperature between 840 ^{0}C and 845 ^{0}C, we kept the pressure of sample constant, and when we kept the constant sintering temperature we varied the pressure of sample between 196 and 392 MPa. The first temperature of the heat treatment applied to the samples - calcination was 840 ^{o}C for 9 days and the second to 845 ^{o}C, which is shown in Figure 2.

To have the desired effect the application of the uniaxial pressure is indicated is indicated to have high values. For this reason, we applied 196 and 392 MPa which leads to a good compaction of the sample and the atomic diffusion becomes approximately uniform.

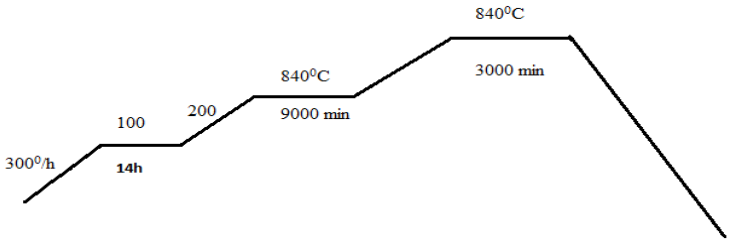


Figure 2. Schematic representation of heat treatment

The temperature dependence of the electrical resistivity was measured using the standard four-probe method. The sample was cooled in the absence of the magnetic field; an excitation current was applied to the sample in the plane, perpendicular to the direction of pressing (in plane (ab)). The voltage in the sample was measured as the temperature dropped to 60K.

Figure 3 shows the dependence of the temperature resistivity for the two Bi: 2223 samples at 196MPa or 392MPa respectively. Resistance behavior is a predictable transition from normal to superconducting conditions below 110K. The critical temperature of the samples was obtained from the temperature-dependent resistor I-derived derivative.

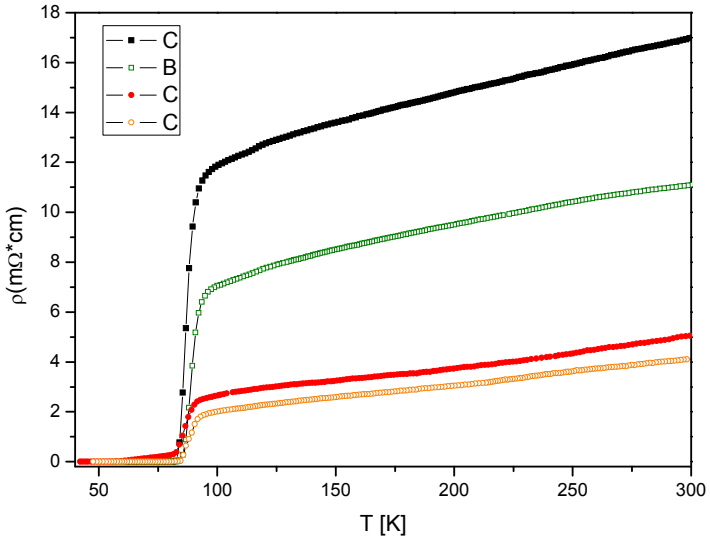


Figure 3. Resistivity dependence vs. temperature

The curves show a "metallic" behavior in the temperature region corresponding to the normal state indicating that the electric current flow occurs in the plane ab.

Table 3. Parameters obtained from data of x-ray diffraction and electrical measurements

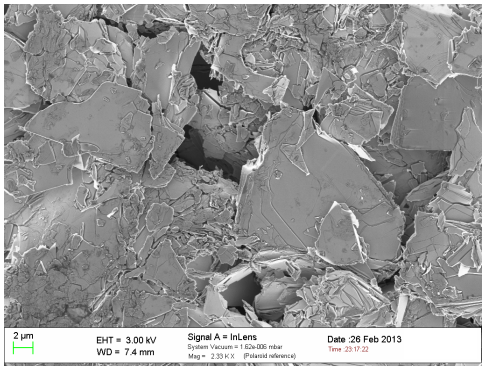
Sample	Tc (K)	ρ at 300 k (mΩ* cm)	Epsilon * 10^{-3}	(D) (nm)
196 Mpa, 840 ^{0}C	95.2	16.91	9.06	22.9
392 Mpa, 840^{0}C	98.1	11.09	7.83	31.5
845 196 Mpa,^{0}C	96.7	5.05	4.94	38.6
845 392 Mpa,^{0}C	99.2	4.13	3.29	101.4

Study of electrical resistance depending on temperature shows that by increasing the pressure of the uniaxial tensile strength decreases (Table 3) due to betterment of electrical contacts between granules and their orientation perpendicular to the direction of applying the pressure and temperature of growth.

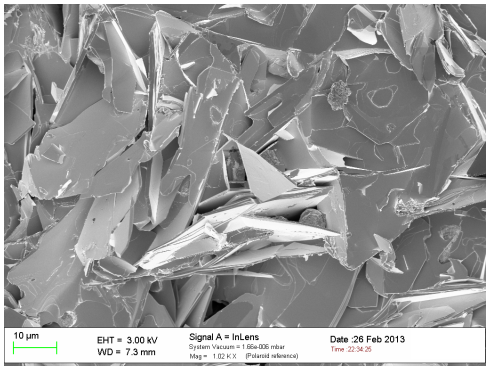
3.2 SEM measurements

Following the SEM analysis, it is observed that the superconductors have a uniform surface, but the size of the granules is changed, so that their size increases by decreasing the degree of crystallization. It can also be seen a change in the shape of the crystallites, as the distance decreases. Temperature has an important role because its growth leads to an increase in the size of the crystallites, which leads to an improvement of the superconducting conductivity, according to the results obtained in the literature, Figure 4.

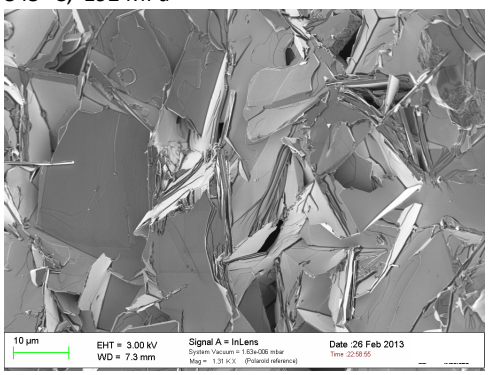
840 ^{0}C, 192 MPa



840 ^{0}C, 392 MPa



845 ^{0}C, 192 MPa



845 ^{0}C, 392 MPa

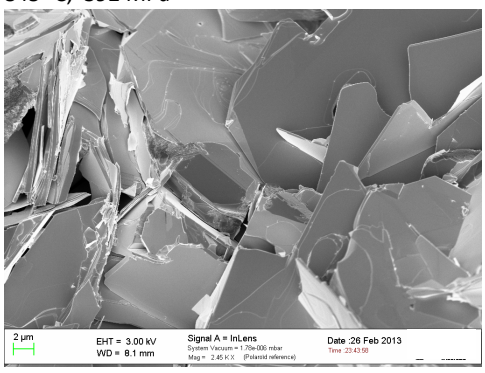


Figure 4. SEM images for the sample sintered at 840 ^{o}C and 845 ^{o}C using uniaxial pressure of 196 Mpa and 392 Mpa

The stoichiometry of the obtained samples (Figure 5) was assessed from the EDX measurements using the ZAF approximation.

Using this correction the atomic percentage of the elements was normalized by the percentage of Cu = 3 and the stoichiometry obtained for all samples was Bi: Pb: Sr: Ba: Ca: Cu: Gd = 1.65: 0.35: 1.85: 0.25: 1.57: 2.88: 0.12.

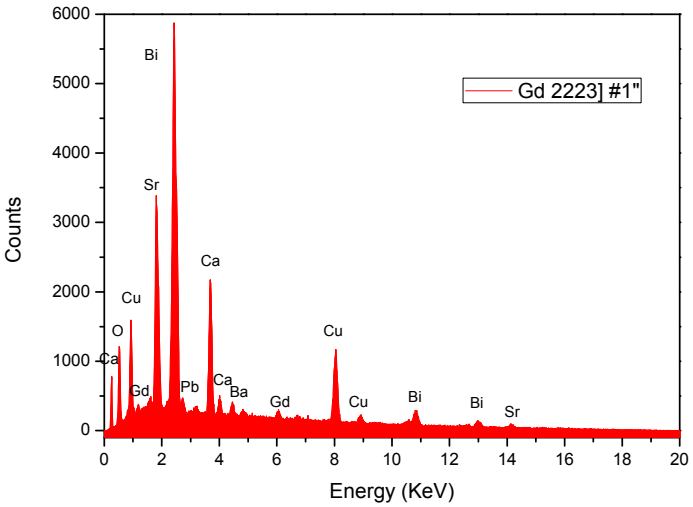


Figure 5. The stoichiometry obtained from EDX

4. CONCLUSION

Following experimental investigations to synthesize and characterize the structural and electrical properties of the compound $\mathbf{(Bi_{1.6}Pb_{0.4})(Sr_{1.8}Ba_{0.2})Ca_2(Cu_{1-x}Gd_x)_3O_y}$ when we modified the sintering temperature from 840 ^{0}C to 845 ^{0}C and we applied a uniaxial pressure of 196MPa and 392MPa respectively, we reached the following conclusions: the samples obtained at 840 °C contain two phases: Bi: 2223 - the major phase and Bi: 2212-minority phase. With the increase of the sintering temperature at 845 ^{0}C, a decrease in the diffraction peaks of the phase 2212 is observed, and with the increase of the pressure at 392MPa this phase falls below 10%. By increasing the uniaxial pressure the electrical resistance decreases due to the improvement of the contacts between the granules and their orientation perpendicular to the direction of application of the pressure. Following the SEM analysis, it is observed that the superconductors have a uniform surface, but the size of the granules changes so that the sample sintered at 845 °C and the uniaxial pressure of 392 MPa has the best crystallinity.

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