The effect of Ag doping on physical and superconducting properties of Bi-2212 superconductors

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Abstract

Samples of Bi$_{2-x}$Ag$_x$Sr$_2$CaCu$_2$O$_y$ (with $x = 0, 0.05, 0.1$ and $0.2$) have been prepared by solid state reaction. The effect of Ag doping has been investigated by electrical resistivity, scanning electron microscopy, XRD, mechanical and dc-magnetization techniques. It has been found that small amounts of Ag, improve the physical and magnetic properties. The best $J_c$ values obtained from dc magnetization measurement (M-H), employing the well known Bean’s critical model, have been obtained for the Bi$_{1.95}$Ag$_{0.05}$Sr$_2$CaCu$_2$O$_y$ samples, reaching about 3000 A/cm$^2$ at 15 K, which is a very high value for bulk materials with randomly oriented grains.

Keywords: Superconductivity; BiSrCaCuO; Magnetic hysteresis loop; Critical current density; Vickers hardness

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1 Introduction

As is well known, the optimization of mechanical and electrical properties of high-temperature superconductors are very important for their application in practical devices. Since the discovery of BSCCO high-temperature superconductors by Maeda et al. [1], it has been found that this family has three different phases. Between them, the Bi-2212 phase has been shown as the most promising due to the easy and quick preparation, together with its relatively high $T_c$. When considering the practical applications of these superconductors, two main characteristics should be fulfilled: high critical magnetic field ($H_c$) and high critical current density ($J_c$). As a consequence, many works have been performed in order to improve $J_c$ and $H_c$ in these materials. Some of them have been based on the doping processes by different elements such as Nb, B, Cd, Sn, Ag, Pb [2-13] or on the synthesis procedures [14].

Usually, ceramic superconductors also possess some intrinsic drawbacks, such as the intergrain weak links and weak flux pinning capability [15]. Some attempts to improve the grains connectivity are based on texturing processes, which have demonstrated an important raise on the transport properties in superconducting [16-18], as well as in other similar systems [19]. Moreover, this raise has been much higher when the texturing processes have been combined with small Ag additions in all cases [3,7,20-23]. In these works, it has been found that Ag improves the links between the grains and the structure of the Bi-based superconductor. Furthermore, it produces an important increase in the critical current density. On the other hand, these systems are usually very
complex due to the high number of cations involved and secondary non-superconductivity phases are produced during their synthesis. Other typical feature of these ceramic superconductors is the important porosity found in the bulk material when produced using the classical methods, implying the decrease of superconductivity properties. Avoiding porosity in the bulk material is not an easy problem to solve as Bi-based materials show incongruent melting and, as a consequence, only solid state sintering processes are adequate to obtain bulk superconducting materials.

In this work, the effect of Ag substitution at Bi-site has been investigated on Ag-doped Bi-2212 samples prepared using the classical solid state reaction method. The structural and microstructural properties are studied and related with the electrical, magnetic and mechanical properties of these samples.

2 Experimental details

Bi$_{2-x}$Ag$_x$Sr$_2$CaCu$_2$O$_y$ (x = 0, 0.05, 0.1 and 0.2) polycrystalline samples were prepared by the standard solid-state reaction method from Bi$_2$O$_3$ (Aldrich, 99%), SrCO$_3$ (Aldrich, 99.9%), CaCO$_3$ (Aldrich, 99.9%), CuO (Aldrich, 99.99%) and Ag$_2$O (Aldrich, 99%) commercial powders. They were weighed in the appropriate proportions mixed and milled in a grinding machine for 2 h. After milling process, the powders were calcined twice at 750 $^\circ$C for 12 h and at 820 $^\circ$C for 24 h under air, with an intermediate manual milling. The calcined samples were reground and pressed into 13 mm diameter pellets with 375 MPa applied pressure.

Finally, the pellets were annealed at 860 $^\circ$C for 140 h in air to produce the Bi-2212 phase with the adequate oxygen content which maximizes T$_c$ values [24].
Samples with $x = 0, 0.05, 0.1$ and $0.2$ will hereafter be named A1, A2, A3, and A4, respectively.

X-ray powder diffraction analyses were used to determine the phases present in the samples. These analyses were performed by using a Rigaku Ultima IV X-Ray Diffractometer with a constant scan rate (2 degree/minute) between $2\theta = 3-60^\circ$. Lattice parameters have been automatically calculated by the PDXL software version 1.6.0.1 with the ICDD version 6.0 database. The surface morphologies of the samples were studied by using a Zeiss/Supra 55 Scanning Electron Microscopy (SEM). Resistivity and magnetic measurements were carried out on samples using Cryogenic Limited PPMS (from 5 to 300 K) which can reach temperatures about to 2 K in a closed-loop He system. In addition, hardness measurements of samples were performed by Micro Hardness Tester (Model HV-1000) at room temperature using different loads.

3 Results and discussions

3.1 XRD characterization

The XRD patterns of $\text{Bi}_{2-x}\text{Ag}_x\text{Sr}_2\text{CaCu}_2\text{O}_y$ samples are shown in Fig. 1. From these data, it is clear that the Bi-2212 high-temperature phase is the major one in all samples. Only minor amounts of the Bi$_2$CaO$_4$ secondary phase can be detected. This is a clear indication that the sintering parameters have been adequate to obtain the superconducting phase. However, with increasing Ag doping for Bi some minor peaks for the metallic Ag are appearing in the A4 sample, indicating that the maximum amount of Ag dissolved in the Bi-2212 crystal structure has been reached. In order to study the influence of Ag on the lattice parameters, they have been automatically determined by the PDXL
software and displayed in Table I. At first sight, it can be easily deduced that the crystal symmetry of all the samples is orthorhombic. On the other hand, the elongation in the c-axis length with the increase in Ag values revealed that the repelling force between charges in Bi-O planes increased. It can be considered that Ag attracts extra charges from Bi-O double planes when it is incorporated into the crystal structure. This can lead to an increase in the positive charge in Bi-O planes, which implies an increase in the repelling force between charges in Bi-O planes.

3.2 SEM analysis

Figure 2 shows fractured surface micrographs for the A1, A2, A3 and A4 samples. As it can be clearly seen in this figure, all samples show randomly oriented plate-like grains which are the general high-T_c ceramic BSCCO structures. Moreover, grain size is higher for the A2 samples, together with a lower porosity, which can, in turn, improve the grain connectivity. This effect can be due to the formation of an eutectic Bi-2212/Ag [25] which can reduce melting point of this system and, as a consequence, improve sintering and grain growth, as reported previously [3,7].

3.3 Electrical measurements

The electrical resistivity versus temperature curves for all the samples, from 5 to 300 K are shown in Fig. 3. All samples show metallic behaviour above T_c (onset) value. Although T_c (onset) and T_c (offset) values with increasing Ag doping slightly change, more important changes on the room temperature resistivity values have been found (see Table I) which decrease for the A2 samples, compared with the A1 ones, and increasing for higher Ag contents, in agreement with the improvement of the grain connectivity already discussed in
the SEM observations. On the other hand, when considering $\Delta T_c$ (transition temperature width) values, they follow the same trends observed for the room temperature except for the A4 samples, which show the lowest $\Delta T_c$.

3.4 Carrier concentration calculations

The hole-carrier concentrations per Cu ion, $P$, have been calculated, for all the samples, using the following relation [26]:

$$P = 0.16 \left[ 1 - \frac{T_c}{T_c^{\text{offset}}} \right]^{1/2}$$

where $T_c^{\text{max}}$ is taken as 85 K for Bi-2212 phase [27,28]. Figure 4 shows it is displayed the variation of the calculated hole-carrier concentration as a function of Ag-content. $T_c^{\text{offset}}$ values for samples are taken from Table I. It is clear that the hole number slightly increases with small Ag additions which implies the enhancement of superconducting properties. The highest hole values are obtained for the A2 samples, which is in good agreement with SEM and resistivity results, where A2 samples shown the biggest grain sizes and the lowest room temperature resistivity values.

3.5 Magnetic properties

The magnetic-hysteresis cycles, between applied fields of $\pm 2$ T, for all the samples, at 15 and 25 K, are presented in Figs. 5 and 6, respectively. As it can be seen in both figures, the highest $\Delta M$ in the hysteresis loops are obtained for the A2 samples. Moreover, the highest magnitude of magnetization in the hysteresis loops is also obtained for these samples, which is a clear indication of their higher magnetic field carrying capacity, compared with the other measured samples.
The increasing Lorentz force during electrical conduction can cause depinning of the vortices, leading to a decrease on J_c values. In addition, the area closed by the magnetization curve of superconductor ceramics can be considered that it is almost equal to the energy required for destroying the pinning of the vortices completely. So, superconducting properties start to degrade when the hysteresis loops in BSCCO ceramics are getting narrower [29-32].

Figure 7 shows the critical current density values at 15 K calculated from M-H loops for all samples up to 2T. The J_c values of the samples were calculated from the hysteresis loops at 15 K, using the Bean’s model [33]:

\[ J_c = 30 \frac{\Delta M}{d} \]

where \( J_c \) is the magnetization current density in ampéres per square centimeter. \( \Delta M = M_+ - M_- \) is measured in electromagnetic units per cubic centimeter, and d is the thickness of sample.

As can be seen from the figure, calculated J_c values of samples show the same behaviour observed for the magnetic measurements as a function of the Ag content. A2 samples possess the highest J_c values due to the features described for the SEM observations, and confirmed by the electrical and magnetical measurements.

3.6 Mechanical properties

The Vickers microhardness values (H_V) were calculated using the traditional definition [34,35]:

\[ H_V = 1854.4 \left( \frac{P}{d^2} \right) \text{(GPa)} \]
where $P$ is the applied load in N and $d$ is the diagonal length of the indentation mark in $\mu$m.

Figure 8 shows the variation of microhardness versus the applied load for all the samples. The variation of microhardness of all samples in the graph show that they have indentation size effect (ISE) which shows lower hardness values at higher applied loads [36-41]. It can be observed that at small applied load values the variation of Vickers microhardness exhibits a fluctuation due to the contact between grains or porosity. These results are in agreement with other results found for the $n=2$ and $n=3$ phases in the BSCCO system [32,42]. In this situation, Meyer’s Law is the most effective way to investigate the ISE or RISE (Reverse Indentation Size Effect) behaviour of microhardness of samples [43]. Meyer number ($n$) and Standard hardness constant can be easily calculated using the following Meyer’s Law relation [41].

$$\log F = n \log d + \log K$$

where $n$ is Meyer number, $F$ is the applied test load, $d$ is indentation diagonal length and $K$ is the standard hardness constant.

Figure 9 represents the plots of $\ln F$ versus $\ln d$ for the samples. The determined $n$ values obtained from the slopes of different lines are displayed in Table II. As can be seen from this Table, the Meyer number for all samples is lower than 2, indicating that all samples have ISE behaviour, in agreement with the microhardness results. It is obvious that Ag doping does not significantly improve the mechanical properties of the bulk material.

On the other hand, Young’s modulus can be defined by the ratio of tensile stress to the strain [44]:

$$\text{Young’s modulus} = \frac{\text{tensile stress}}{\text{tensile strain}}$$
Thus, tensile strain values of samples can be calculated as:

\[
\text{Tensile strain} = \frac{\text{tensile stress}}{\text{Young's modulus}}
\]

where tensile stress is the ratio of the magnitude of the external force (F) to the cross-sectional area (A).

Figure 10 shows stress versus strain curve for all samples. Logarithmic slope for each independent sample displayed in Figs. 10b-e has been plotted for a better visualization of the samples elastic behaviour. \( R^2 \) values displayed in figure 10 shows the accuracy of the fitting with their value close to 1. It is seen from the figure that the elastic properties of all samples are very similar, confirming the hardness data. All these results are summarized in Table III where the calculated load independent Hv, Y and E values, together with tensile stress and strain for all samples are presented. E and Y have been calculated using the relations \( E = 81.9635 \text{ Hv} \) and \( Y \approx \text{Hv}/3 \) \([45,46]\). From these data it is clear that Ag addition does not improve the mechanical behaviour of these samples due to their relatively high porosity \([3,7]\)

4. CONCLUSIONS

In summary, we have investigated the effect of silver addition in Bi\(_2\)\(_x\)Ag\(_x\)Sr\(_2\)CaCu\(_2\)O\(_y\) for \( x = 0, 0.05, 0.1 \) and \( 0.2 \). It has been found the enhancement on the electrical and magnetic properties for small silver additions (\( x=0.05 \)), leading to the increase of \( J_c \) values. On the other hand, no significant changes in the mechanical behaviour have been found, independently of the Ag content, due to the relatively high porosity of these bulk materials.

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The authors are very thankful to Prof. Dr. M. Kemal KÜLEKÇİ and Asist. Prof. Dr. Ugur EŞME from Mersin University for their helping in Microhardness studies. All samples have been prepared in the MEİTAM Central Laboratory in Mersin University in Turkey. Vickers microhardness and SEM measurements have been made in the MEİTAM Central Laboratory in Mersin University, other measurements in this study have been made in the METU Central Laboratory in Middle East Technical University in Ankara in Turkey.

References
Figure captions

**Figure 1.** XRD patterns of the A1, A2, A3, and A4 samples. The symbols indicate the different phases: + Bi-2212; ■ Bi\textsubscript{2}CaO\textsubscript{4}; and ∆ metallic Ag.

**Figure 2.** SEM micrographs obtained on fractured surfaces of a) A1; b) A2; c) A3; and d) A4 samples.

**Figure 3.** Resistivity as a function of temperature curves for the different Ag-content samples.

**Figure 4.** Variation of hole-carrier concentration vs. Ag-content.

**Figure 5.** Magnetization hysteresis curves measured at 15K for all samples.

**Figure 6.** Magnetization hysteresis curves measured at 25K for all samples.

**Figure 7.** Calculated critical current densities for all the samples at 15K, as a function of applied field.

**Figure 8.** Vickers microhardness values versus applied indentation load for all samples.

**Figure 9.** Variation of applied load In \( F \) with diagonal ln \( d \) for the samples.

**Figure 10.** Stress versus strain curve obtained for a) all samples; and for each individual sample, together with their fitting, b) A1; c) A2; d) A3; and e) A4.
Table I. XRD and resistivity measurement results for the samples

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<th>Samples</th>
<th>a(Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
<th>$T_c^{\text{onset}}$ (K)</th>
<th>$T_c^{\text{offset}}$ (K)</th>
<th>$\Delta T_c$ (K)</th>
<th>R(mohm.cm) at 300 K</th>
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<td>5.412</td>
<td>5.392</td>
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**Table II.** Hardness analysis results of all samples for Meyer’s Law

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Table III. The calculated load independent $H_v$, $Y$ and $E$, together with tensile stress and strain for all samples

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<th>$Y$ (GPa)</th>
<th>$E$ (GPa)</th>
<th>Tensile stress (MN/m²)</th>
<th>Tensile strain ($10^{-3}$)</th>
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</table>
Figure 1

Intensity (a.u.)

2 Theta (Deg.)

Sample A4

Sample A3

Sample A2

Sample A1

+ Bi-2212

■ Bi$_2$CaO$_4$

△ Ag

0 10 20 30 40 50 60
Figure 2
Figure 3
Figure 4

Hole-carrier concentration (p) vs. Ag-Content
Figure 6

$T = 25$ K

$M$(emu/gr)

$H$(T)

A1
A2
A3
A4
Figure 8

A1

A2

A3

A4

Hv (GPa)

F(N)
Figure 9
Figure 10

(a) R2 = 0.9348

(b) R2 = 0.9828

(c) R2 = 0.9328

(d) R2 = 0.939

(e) R2 = 0.9727

Stress (MN/m²) vs. Strain

A1, A2, A3, A4

Log. (A1)

Log. (A2)

Log. (A3)

Log. (A4)