Superconducting properties of Bi$_{2-x}$Sb$_x$Pb$_{0.3}$Sr$_{1.9}$Ba$_{0.1}$Ca$_2$Cu$_3$O$_{10+y}$ compounds

M.M. Abbas, L.K. Abbas, H.S. Bahedh,

Department of Physics, College of Science, University of Baghdad, Baghdad, Iraq

Received: 3 October 2015; Accepted: 28 November 2015

ABSTRACT

Studies of the doping process, brings the possibility to a better understanding the complexity of superconductivity mechanisms in BiSrCaCuO system. In order to evaluate the Sb doping effect on the superconducting behavior of this system, solid state reaction method was used to prepare Bi$_{2-x}$Sb$_x$Pb$_{0.3}$Sr$_{1.9}$Ba$_{0.1}$Ca$_2$Cu$_3$O$_{10+y}$ compounds were 0.0 ≤ x ≤ 0.5. The prepared samples were characterized structurally by X-ray diffraction (XRD) and morphologically by scanning electron microscopy. The X-ray diffraction analysis showed that all samples have two phases: high-T$_C$ phase (2223- phase) and low-T$_C$ phase (2212- phase). Four point probe method was used to study the electrical properties of the samples. The highest T$_C$ value 122 K was found at concentration 0.3 for maximum oxygen content.

Keywords: High T$_C$ superconductors, doping, Bi$_{2-x}$Sb$_x$Pb$_{0.3}$Sr$_{1.9}$Ba$_{0.1}$Ca$_2$Cu$_3$O$_{10+y}$

INTRODUCTION

Superconductivity is a phenomena observed in certain materials. These materials lose their resistance to electrical conduction and expulse magnetic fields when cooled below a characteristic critical temperature. It is a macroscopic quantum phenomenon.

The more we know about the mechanisms involved in the appearance of this phenomenon, the more critical current density we can achieve by optimizing the superconductor under application.

Several attempts were carried out to discover high temperature superconductivity, many of them have been found in cuprate materials. The cuprate superconductors have a number of features in common. It has emerged that there compounds possess a number of unusual normal state and superconducting properties due to a complicated interplay of electronic spin and lattice degrees of freedom (different types of inhomogeneities in the atomic-scale electronic ]1, 2]).

All cuprates are very sensitive carries doping and are only superconducting for a particular range of doping levels, often requiring non-stoichiometric compositions. Among the cuprate materials, Bi-2223 phase is regarded as one of the most technological significant high T$_C$ phases in the BiSrCaCuO system. Its special physical properties attracted the attention of many physicists, material scientists and electrical engineers. The highlighting feature of this type of superconductors that is more attractive for application.

It has been established that addition or substitution of elements of varying ionic radii can play a crucial role in modifying the formation and stability of the 2223 phase. This variation is thought to be related to the density of charge carriers in the CuO planes [3, 4 and 5].

The effect of Sb doping on the T$_C$ along with or without Pb of BPSCCO ceramics has not been understood yet or clarified in Bi-2223 compounds. Some articles claim that doping by Sb increases critical temperature and enhances the amount of Bi-2223 phase [6, 7, 8 and 9]. On other hand , the results collected by others do not show such enhancement and they found different T$_C$ depression behaviors[10, 11, 12, 13, 14, 15 and 16].

Azhant et al[17] showed that the value of zero resistance temperature, T$_C$ decreased as the content of Sb increased except for sample x = 0.2 that shows the improvement of T$_C$=100K. Samples with Sb content of x ≤ 0.3 were dominated with 2223 phase
while other samples ($x > 0.3$) were dominated with Bi-2212 phase.

Heat treatment of Bi-2223 is a long process, which must be carefully regulated, or the material can break down into the second BiSrCaCuO phase, Bi-2212 and second phase precipitates [18]. Shenand Abass et al. [5 and 19] observed that synthesis Bi-2223 within short sintering time by multiple pressing and sintering process which lead to larger growth of grain size and thus yield stronger coupling at the grain boundaries. It did improve the superconductivity properties and growth the high-$T_c$ phase.

An intriguing property of such materials is that although the substitution lies at optimal doping, the $T_c$ anomaly low. The main reason is that the properties of these materials are very sensitive to the fabrication process.

Xu et al. [20] studied the superconductivity and microstructure of Bi$_{1.92}$Pb$_{0.48}$Sb$_{0.1}$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$ and Bi$_{1.8}$Pb$_{0.3}$Sb$_{0.1}$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$ samples. They found that different superconducting behavior was due to different sintering conditions.

Although a lot of progress has been made as far as technologically important aspects of Bi-2223 compounds are concerned, still many basic characteristics of these compounds are not well understood.

On other hand, Ba belongs to the same alkaline earth metal group as Sr and Ca, having different ionic radii. This suggested that there is possibility to promote $T_c$ by Ba compensation and the related structure. Therefore, some researchers found that appropriate amount of substituted Sr by Ba in Bi-2223 had the effect of raising $T_c$ to a higher temperature region, a single transition phase and improved superconducting properties [21 and 22].

Thus we found it is interesting to study the effect of the partial substitution Bi by Sb, on structural perfection and electrical properties of Bi$_{2-x}$Sb$_x$Pb$_{0.3}$Sr$_{1.9}$Ba$_{0.1}$Ca$_2$Cu$_3$O$_{10+\delta}$ compounds.

**Experimental**

First of all the molar ratios of high purity powders of Bi$_2$O$_3$, Sb$_2$O$_3$, PbO, Sr(NO$_3$)$_2$, CaO and CuO were taken accurately. Then the powders were well mixed using agate mortar. The mixture was ground to a fine powder and then calcined in air at 800 °C for 24 hr with repeated intermediate re-grinding. The powder pressed into disc-shaped pellets with 13mm in diameter and (25-28) mm thickness using a manually hydraulic press type (Specac) under pressure of 0.5 GPA.

The samples were sintered at 840 °C for 140 hr with multiple grounding, pressing and sintering process.

The structure of the prepared samples was obtained by using X-ray diffractometer type Philips with the Cu-Kα radiation. A computer program was used to calculate the lattice parameters, based on Cohen’s last square method.

The resistivity measurements were performed by the standard four-probe method.

The oxygen content in the oxide samples was determined by using the sample iodometric titration technique.

The nature of the grains was performed by scanning electron microscopy (SEM) from FEL. Inspect S50, Netherlands. The elemental analysis of specimen has been verified through Energy dispersive X-ray analyzer (EDX) attached to the SEM.

**Results and Discussion**

EDX technique was utilized to confirm the chemical composition for the Bi$_{2-x}$Sb$_x$Pb$_{0.3}$Sr$_{1.9}$Ba$_{0.1}$Ca$_2$Cu$_3$O$_{10+\delta}$ ($x=0$, 0.2 and 0.3) samples. The EDX spectrum shows the elemental distribution in the samples. Figs. (1-3) demonstrated that there is no unwanted element in the samples which implies that there is no contamination during the synthesis process.

**Fig.1:** The EDX image for Bi$_{2-x}$Pb$_{0.3}$Sr$_{1.9}$Ba$_{0.1}$Ca$_2$Cu$_3$O$_{10+\delta}$ superconductor.
In addition, the EDX spectra of those samples shows that there is no change in the position of the Bi, Pb, Ca and Sr elements peaks after the partial replacement of Bi$^{3+}$ and Sr$^{2+}$ by Sb$^{3+}$ and Ba$^{2+}$ respectively. These results indicate that these ions are well substituted in the (Bi, Pb)-2223 phase. An overlapping of some peaks which correspond to Bi and Pb at the same value of energy was observed which means that Pb ions have partially replaced Bi ions in the system. Same overlapping noticed for Sb and Ca ions.

The crystal structure of Bi$_{2-x}$Sb$_x$Pb$_{0.3}$Sr$_{1.9}$Ba$_{0.1}$Ca$_2$Cu$_3$O$_{10+\delta}$ samples sintered at different temperature with different nominal composition $x=0, 0.1, 0.2, 0.3$ and 0.4 studied by XRD and represented in Fig.(4).

The analysis of the samples showed polycrystalline and correspond to orthorhombic structure. Most of the peaks belong to the 2223 phase with a few low-intensity peaks belonging to the 2212.

Tanaka et al. [23] attributed this phase to the appearance of the high-T$_C$ phase.

There is a consistence variation in the intensity and the position of the peaks with increasing Sb content indicating the change in phase composition and the lattice parameters of the samples. Also there was merging of peaks observed for some samples.

However, change of crystalline arraignment degree yielded lower Bragg intensities. This could be due to multi grinding and sintering causing the destruction of the integrin junction, where the treatment led to recrystallization processes causing interruption of integrin contacts.

A small amount of Ba addition is quite effective in decomposing the low-T$_C$ phase by producing BaBiO$_3$ and BaCuO$_2$ at 2$\theta$ =29 $^\circ$ and 29.3 $^\circ$ accompanied by high –T$_C$ phase formation as referred by Kawai et al. [24]. The destruction of the low T$_C$ –phase by Ba at the early stage may enhance the nucleation and the formation of high T$_C$ phase.

The relative volume fractions of the Bi-2223 and Bi-2212 phases were estimated from the peak intensities of the same particular reflections, using the following formulas [25]:

$$\text{Bi} - (2223)\% = \frac{\sum I(2223)}{\sum I(2223) + I(2212) + I(\text{impurities})} \times 100 \text{------(1)}$$

$$\text{Bi} - (2212)\% = \frac{\sum I(2212)}{\sum I(2223) + I(2212) + I(\text{impurities})} \times 100 \text{------(2)}$$

where: I(2223) and I(2212) are the intensities of Bi-2223 and Bi-2212 phases respectively. The calculated relative portion of all samples is listed in Table 1.

A higher volume fraction of the 2223 phase observed at 0.2 for Sb concentration. According to the model suggested by Grivel and Fliikiger [26], the (Bi,Pb)-2223 phase forms through a distinct nucleation and growth process in the pre-existing (Bi,Pb)-2212 grains. Thus, the faster conversion rate of this composition might be a reason for the slightly larger volume fraction of the (Bi,Pb)-2223 phase present in the concentration 0.2.

The lattice constants evaluated from 2$\theta$ of major high –T$_C$ phase peaks are listed in Table (2). UponSb substitution a parabolic curve for lattice...
parameter c is observed as shown in Fig. 5, the substitutions up to 0.2 caused increasing the c parameter, whereas beyond it unsystematic variation noticed. This characteristic could be due to several factors such as: The increase in lattice parameter c revealed that cations of the, Ca\(^{2+}\) in addition to Bi\(^{3+}\) may partly be substituted by Sb\(^{3+}\) ions; similar behavior has been noticed by Yilmazlar et al.[27], while the shortened could be to the increment of oxygen in BSCCO system [17].

The deformation in the c-axis adjusts the amount of charge transfers from Bi-O layer to Cu-O layer, which will be a driving force to the pairing generation of superconductor holes forming bosons. This behavior may, because of the ordered arrangements of the oxygen vacancies and the cation substitution at the same time, led to change the spacing between the CuO layers and thus affect the charge transfer to the CuO layers [28].

![Figure 5: Volume fraction and c parameter Bi\(_{2-x}\)Sb\(_x\)Pb\(_{0.3}\)Sr\(_{1.9}\)Ba\(_{0.1}\)Ca\(_2\)Cu\(_3\)O\(_{10+δ}\) superconductors with different concentrations.](image)

Table 1: Volume fraction of phases% for Bi\(_{2-x}\)Sb\(_x\)Pb\(_{0.3}\)Sr\(_{1.9}\)Ba\(_{0.1}\)Ca\(_2\)Cu\(_3\)O\(_{10+δ}\) superconductors with different concentrations.

<table>
<thead>
<tr>
<th>x</th>
<th>Volume fraction of phases %</th>
<th>Bi-2223</th>
<th>Bi-2212</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>67.96875</td>
<td>23.04688</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>63.40467</td>
<td>31.26721</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>82.06977</td>
<td>11.7803</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>68.80245</td>
<td>26.40815</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>67.97252</td>
<td>28.0076</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: The lattice parameters, c/a, volume cell \(δ\) and \(T_c\) for Bi\(_{2-x}\)Sb\(_x\)Pb\(_{0.3}\)Sr\(_{1.9}\)Ba\(_{0.1}\)Ca\(_2\)Cu\(_3\)O\(_{10+δ}\) superconductors with different concentrations.

<table>
<thead>
<tr>
<th>(T_c) (K)</th>
<th>c/a</th>
<th>(V(\text{Å})^3)</th>
<th>c(Å)</th>
<th>b(Å)</th>
<th>a(Å)</th>
<th>(δ)</th>
<th>x</th>
</tr>
</thead>
<tbody>
<tr>
<td>106.5</td>
<td>0.691</td>
<td>6.857556</td>
<td>1070.951</td>
<td>37.125</td>
<td>5.328515</td>
<td>5.413736</td>
<td>0.0</td>
</tr>
<tr>
<td>107.5</td>
<td>0.0814</td>
<td>6.856991</td>
<td>1071.104</td>
<td>37.12759</td>
<td>5.328094</td>
<td>5.41456</td>
<td>0.1</td>
</tr>
<tr>
<td>109</td>
<td>0.771</td>
<td>6.849504</td>
<td>1078.441</td>
<td>37.0704</td>
<td>5.375278</td>
<td>5.412129</td>
<td>0.2</td>
</tr>
<tr>
<td>122</td>
<td>0.8105</td>
<td>6.700674</td>
<td>1054.161</td>
<td>36.6084</td>
<td>5.270522</td>
<td>5.463456</td>
<td>0.3</td>
</tr>
<tr>
<td>108.8</td>
<td>0.015</td>
<td>6.836691</td>
<td>1091.278</td>
<td>37.11673</td>
<td>5.41554</td>
<td>5.429049</td>
<td>0.4</td>
</tr>
</tbody>
</table>

The effect of Sb substitution on the electrical resistivity of the Bi\(_{2-x}\)Sb\(_x\)Pb\(_{0.3}\)Sr\(_{1.9}\)Ba\(_{0.1}\)Ca\(_2\)Cu\(_3\)O\(_{10+δ}\) compounds with x = 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5 have been studied.

All samples are superconductors except the composition with x = 0.5 which is exhibited like semiconductor resistivity, as shown in Fig. 6.
Sample without Sb have two steps superconducting transitions, indicating existence of small amounts of the secondary phase and or fluctuation of the oxygen content. The presence of the second transition is intimately linked to the effect of chemical pressure on the electronic structure due to the the inclusions of Pb and Ba in this sample. The critical temperature determined to be 106.5 K.

While for the composition with 0.1 \( \leq x \leq 0.4 \) there was one step in the resistivity transition with almost sharp drop (small tail) was noticed. The critical temperature \( T_C \) of the samples were 107.5, 109, 122 and 108.8 K for \( x= 0.1, 0.2, 0.3 \) and 0.4 respectively.

Samples demonstrate the one step transition (nearly sharp), indicates the formation of nearly 2223-single phase.

However, Bi\(_{1.8}\)Sb\(_{0.2}\)Pb\(_{0.3}\)Sr\(_{1.9}\)Ba\(_{0.1}\)Ca\(_2\)Cu\(_3\)O\(_{10+\delta}\) sample exhibit an anomalous upturn (an infliction) in the resistivity curve at low temperature followed by an abrupt decrease at the expected superconducting \( T_C \). The exact origins of this behavior are enigmatic, although the rise in resistivity at low temperature is reminiscent of a charge density wave transition.

In many strongly correlated electronic systems, superconductivity seems to be related to the vicinity of an electronic or magnetic instability with a characteristic phase diagram. Electronic instability is a charge density wave charge density waves CDWs (in large compounds) are found in low-dimensional materials with highly anisotropic electronic structures. Superconductivity and CDW share the electron-phonon interaction in terms of microscopical mechanism.[29, 30 and 31]

Implicit in all of the above clarification, the behavior of this sample is thought to be a consequence of competitions between the superconductivity and CDW where they coexist.

Unfortunately this does not explain why the effect is restricted to certain samples and not others. Although substituting Sb\(^{3+}\) for Bi\(^{3+}\) does not disturb the electroneutrality of the lattice but one should note that the partial replacement of Bi by Pb and Sb atoms permits synthesis of stable superconducting properties of the combination and an increase in \( T_C \), similar results found by[32].

On the other hand addition of Pb to the compounds may relax the modulation by influencing the charge balance, oxygen content \( \delta \) and structural of the relevant layers[33]. Another advantages of substituting Pb\(^{2+}\) in Bi\(^{3+}\) sites is to relieve the internal stress[34].

The significant point which can be deduced from the results above is the substitution (Sb, Pb) on Bi sites in combination with Ba stipulates the improvement of links on intergranular interfaces of high temperature 2223-phases.

Highest \( T_C \) was determined at 0.3 which confirm that the sample is in optimal doping regime while decrease of \( T_C \) beyond this concentration seems to be due to the shift of this sample towards the overdoped region.

The results indicate the improvement of the samples, suggesting that appropriate amount of the doping acts as the effective pinning centers of the fluxes in the samples. Sb\(^{3+}\) and Ba\(^{2+}\) can fill the intergrain spaces, and thereby reinforce the coupling between granules.

However, the enhancement of the samples behavior could be attributed also to increasing the contact between the grains and the growth of 2223 - high \( T_C \) phase during the sintering process time. Moreover, multi –step technique improve the superconductivity that is necessary for growth of the high-\( T_C \) phase[5].

The oxidation for ceramic superconductor materials refers to heat treatment and sintering conditions which can occur within the nucleation, growth and reaction process. The oxidation Bi-2223 is very sensitive to oxygen; it has been found that the oxygen content increased by multi-step technique[35].

It is observed from Fig.7 higher value of \( \delta \) at Sb concentration 0.3, and then reduced for further increasing of substitution. This apparently due to Bi replacement by Sb ion or tendency for some Sb\(^{3+}\) to substitute on Ca\(^{2+}\) site as noted from EDX for \( x=0.3 \). Furthermore, increasing of \( \delta \) could be related for existence of Pb where it was emphasized for Pb-
doped 2223 superconductor, most experimental results indicated that $T_C$ would increase with increasing oxygen content Zhou et al. [36]. While, the reduction of oxygen content with increasing Sb concentration to 0.4 may be argued to be out of plane substitution of Pb, where it shows a longer wavelength of structural modulation [37].

It can be easily inferred from Fig. 7 and Table 2 that both the $\delta$ and $T_C$ increased, with increasing $x$ to 0.3 and then reduced for further increasing of substitution, giving the evidence of the series role of oxygen in the superconducting mechanism. Similar behavior was indicated by other researchers [5 and 36].

Indeed, increasing the amount of oxygen atoms can be considered to alter the local structure of the BiO layer. So the excess oxygen attracts electrons from the CuO plane, thereby, increasing the hole concentration in the CuO2 layers in the perovskite layers, the creation of holes will shorten the Cu-O2 bond length and this leads to an improvement of the $T_C$ [4 and 38].

Thereafter increasing Sb concentration beyond 0.3, caused decrease both $\delta$ and $T_C$ as well as the phonon interaction due to the charge ordering phenomenon, probably induced by Sb, Pb and Ba as a pair breaker. This may be a accompanied by changes in oxygen content or oxygen order effects which is decreases the number of holes in the lattice from the optimum value [39]. Results suggest that as the hole concentration of the compound increases above a critical value, the superconductor is suppressed.

![Fig. 7: The oxygen content and $T_C$ with different concentrations for Bi$_{2-x}$Sb$_x$Pb$_{0.3}$Sr$_{1.9}$Ba$_{0.1}$Ca$_2$Cu$_3$O$_{10+\delta}$ superconductors with different concentration.](image)

Interestingly, ordering of super electrons coupling is enhanced in the materials due to even a tiny inhomogeneity. The perfect perovskite structure of the studied system has, built in deformation, comes from: firstly, the difference in the sizes of the atoms in the body centered part of the perovskite lattice structure and secondly, from the vacant sites of the oxygen [40].

The surface morphology of Bi$_{2-x}$Sb$_x$Pb$_{0.3}$Sr$_{1.9}$Ba$_{0.1}$Ca$_2$Cu$_3$O$_{10+\delta}$ with $x$=0.0-0.4 was studied by SEM and shown in Fig. (8.a-e). A notable change of the grain size, shape and distribution of grains was observed indicating the influences of Sb substitution on the morphology of the samples.

Fig. (8.a and b) shows large size plate and stacks of thin flake like grains for undoped and 0.1 Sb concentration specimens. Each of these stacks composed of thousands of layers, apparently each grain (group of layers) grows in random directions. A drastic change in the grain morphology grain size, shape and grain orientation gradually changed and reduce with increasing the amount of Sb substitution.

It can be seen that from the Fig.(8.c and d) for ($x$=0.2, and $x$=0.3) samples, large grains seems to have decomposed into small grains with formation of small plate like.

Increasing Sb concentration up to 0.4 changes the morphology of the surface as shown in Fig. (8.e). Distribution of smaller grains in the main matrix was noticed. In addition, it was found that some precipitation of particles on the surface for Sb concentration 0.2-0.4 as shown in Fig. (4-28,c-e), it could belong to Sb (appear as whit areas). In our opinion, existence of Sb in the grain boundaries leads to coalescence. This means that the growth of the superconducting phase on the account of its surrounding phase. This supports our explanation for the higher $T_C$. Together with the XRD results, we deduce that the substitution with Sb affect the structure of samples in different manners.
All the XRD, SEM and resistivity studies implied that higher amount of Sb promotes the formation of 2223 phase to achieve higher $T_C$ values. This may be due to the capability of Sb to facilitate oxygenation of the samples and could be responsible for nucleating more of the 2223 grains with the desired stoichiometry.

From the results above, it is obvious that the optimum sample have the nominal composition $\text{Bi}_{1.7}\text{Sb}_{0.3}\text{Pb}_{0.3}\text{Sr}_{1.9}\text{Ca}_{2}\text{Cu}_3\text{O}_{10+\delta}$, where higher $T_C$ is accompanied by higher $\delta$.

**Conclusion**

The significant point which can be deduced from the results above is the substitution (Sb and Pb) on Bi sites in combination with Ba stipulates the improvement of links on intergranular interfaces of high temperature 2223-phases. In our view, the improvement of the samples, suggesting that a small amount of the doping acts as the effective pinning centers of the fluxes in the samples and improves the electric connection between superconducting grains. However, substitution of Sb in Bi sites enhanced the superconducting properties. Highest transition temperature has been determined 122 K for the composition with Sb concentration 0.3.

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