Effect of Li Substitution on Bi (Pb)-2223 Superconductors

Saad F. Oboudi, Muna M. Abbas, Nadein Q. Raoof

Abstract—Samples of stoichiometric composition $\text{Bi}_2\text{Li}_x\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_3\text{Cu}_{10+\delta}$ with $x = 0.0, 0.1, 0.2, 0.3, 0.4$ and 0.5 were prepared by a solid state reaction method. The process consists of three steps. Firstly a $\text{Bi}_2\text{Li}_x\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_3\text{Cu}_{10+\delta}$ sample was sintered in the air at 850 °C for 50 hrs; subsequently the sintered sample was regrind and sintered again at 850 °C for another 50 hrs. While in the third step the sample reformed at 830 °C for 40 hrs, and then slowly cooled in furnace with a rate of 2 °C/min. The process enhances growing a superconducting phase unidirectional and suppresses the high phase intrusion which leading to the production of well textured samples. $\text{Li}_x$ was introduced into $\text{Bi}_2\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_3\text{Cu}_{10+\delta}$ powder in various concentrations. Bulk samples were made from the Bi2223/Li powder and heat-treated at various processes. The phase formation and the microstructure were studied for different amounts of Li. It was found that sample with $x = 0.3$ Li showed the highest $T_c$-zero at 130 K. Increasing Li content to 0.5 decreases the critical temperature to 113 K. The samples were characterized by X-ray diffraction, and DC electrical resistivity. The X-ray diffraction studies were done at room temperature and the lattice constants of the material were determined by indexing all the peaks observed.

Keywords: Bi-based superconductors, Li substitution, Phase formation

I. INTRODUCTION

The bismuth-based superconductors have been extensively studied in the past two decades. These materials have fundamental physical properties, higher $T_c$, thermodynamical stability of its different components and good chemical durability; also, they contain no rare earth elements [1-3]. It is now well known that the Bi-based system has layered structure and according to their compositions, it has three different phases Bi-(2201), Bi-(2212), and Bi-(2223), each phase has a different transition temperature to the superconducting state [4 and 5].

Because of the highest critical temperature, the Bi-(2223) phase has attracted greater interest and many workers have spent much effort to obtain the pure 110 K phase of the compound whether it’s in the bulk, thin or thick film form. Early studies showed that Bi-(2223) phase has unstable structure and very difficult to prepare in a single phase. The low $T_c$ phase (2212) has more stable structure than the other phases and during the (2223) phase formation some fraction of the material may be in the low $T_c$ phase [6].

The reaction process of forming Bi-2223 phase experience three stages: (1) Inducing period. (2) Accelerating period. (3) Front merging period. At the first stage of Bi-2223 phase formation, the Bi-2212 phase decreases rapidly, and in second stage the speed of decrease of Bi-2212 phase does not become faster but slightly slower. Therefore we can suppose that Bi-2223 phase cannot be formed by a direct decomposition of Bi-2212 phase, but by the solubilization of Bi-2212 phase. After the Bi-2223 phase formation, the reaction enters the stage of crystal growth [7]. Many research groups succeeded in obtaining pure 110 K phase preparation by using stoichiometric composition of the precursors and long duration of annealing time.

The superconducting properties of BiSrCaCuO superconductor can be controlled by the addition or substitution of the elements with different ionic radius and different bonding characters. For successful results, different receipts can be found in the literature [8]. However, these formulations differ from one system to another as well as the preparation techniques and the preparation conditions. In this work, we study the substitution with Li and the preparation conditions that make the differences between the superconducting properties, especially transition temperatures of the Bi$_2$Li$_x$Pb$_{0.3}$Sr$_2$Ca$_3$Cu$_{10+\delta}$.

II. EXPERIMENTAL PART

Bi$_{2+x}$Li$_x$Pb$_{0.3}$Sr$_2$Ca$_3$Cu$_{10+\delta}$ samples with $0\leq x\leq0.5$ were prepared by the conventional solid state reaction method. Appropriate amounts of high purity powders of Bi$_2$(CO$_3$)$_3$, PbO, Sr(NO$_3$)$_2$, CaO, CuO, and Li$_2$CO$_3$ were used as starting materials. The powders of precursor were mixed together by using agate mortar. The mixture homogenization takes place by adding a sufficient quantity of 2-propanol to form a past during the process of grinding for about 1 hr. The mixture was grounded to a fine powder and then calcined in air by using a tube furnace at 800 °C for 30 hrs with a rate of 2 °C/min. The mixture then pressed into pellets of 1.3 cm in diameter and 0.25 cm thickness, by using hydraulic press type (SPECAC) under pressure of 0.7 GPa. Three steps were used during the sintering process, in the first step the samples were sintered at 850°C for 50hrs, in the second step the samples were sintered at 850°C for 50hrs, while in the third step the samples were sintered at 830°C for 40hrs, then slowly cooled in the furnace with a rate of 2 °C/min. All samples in the present investigation were subjected to gross structural characterization by x-ray diffraction (XRD). The DC electrical resistance was measured with the four probe

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III. RESULTS AND DISCUSSION

The X-ray diffraction patterns of samples Bi$_2$-xLi$_x$Pb$_{0.3}$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$ for (x = 0, 0.1, 0.2, 0.3, 0.4, and 0.5) indicated that the samples consisted of the low-T$_c$ (2212) and high-T$_c$ (2223) phases and contained small amount of impurity phases of Sr$_2$Ca$_2$Cu$_{7}$O$_{\delta}$ as shown in figure 1. The Sr$_2$Ca$_2$Cu$_{7}$O$_{\delta}$ peak was identified in all samples at 20 values of 36.8° except for x=0.2. The occurrence of all those non-superconducting impurity phases will lead to a reduction of the critical temperature T$_c$ of the samples. It can be notice that all the samples studied by XRD measurements were mainly consisting of (2212) and (2223) phases, with the (2223) phase being the dominant one, the appearance of more than two phases could be related to the stacking faults along the c-axis, also it is clear that the relative intensity of the diffraction peaks vary with different samples while peak positions varies slightly with increasing the Li content (which causes a change in the lattice constant of the sample). This result indicate that the substitution by Li may well enhances crystallinity and volume fraction of the 2223 phase and this leads to the increases of the T$_c$ value. Furthermore, sintering the samples at 850 °C cause an increase in the crystallinity, it sharpens the peaks, and increases the peaks intensity. The most intense peak pattern of the samples belongs to the high-T$_c$ phase which also indicates an increase in the volume fraction of the high-T$_c$ phase [9]. The calculated volume fractions of the samples are listed in Table 1. As it can be seen in the table, samples with x = 0.0 and 0.1 contained 67.49% and 65.16% of the 2223 phase, respectively. Increasing Li substitution in the samples to 0.2 resulted in an increase in the 2223 phase to 73.78%, also a decrease of the intensities of the peaks of the 2212 phase were obtained. In samples with x = 0.3, 0.4, and 0.5 the amount of the 2223 phase was 67.83%, 64.34%, and 60.74%, respectively. It was found that the high-T$_c$ (2223) phase has orthorhombic structure with lattice constants a = 5.408 Å, b = 5.473 Å and c = 37.185 Å. The volume fraction and lattice parameters for the phases were calculated by taking into account the peaks corresponding to Bi-2223 phases. Unit cell dimension for the 2223 phase of Bi$_2$-xLi$_x$Pb$_{0.3}$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$ (0≤x≤0.5) samples are given in Table 2. The results obtained in this study were in good agreement with the theoretical results of Bi-2223 system. We observed that the lattice parameters of the samples with Li substitution did not change significantly from the theoretical value.

XRD measurements showed that all the samples were mainly consisting of (2212) and (2223) phases, with the...
(223) phase being the dominant one. We have used all the XRD peaks of Bi-(223) and Bi-(2212) phases for the estimation of the volume fraction of the phases using the following formulas [10]:

\[
\text{Bi-(223)\%} = \frac{\sum I(223)}{\sum I(223) + I(2212)} \times 100
\]

\[
\text{Bi-(2212)\%} = \frac{\sum I(2212)}{\sum I(223) + I(2212)} \times 100
\]

Where: I (223) and I (2212) are the intensities of Bi-2223 and Bi-2212 phases respectively [11]. The calculated volume fraction of the samples is listed in Table 1. As seen in the table the volume fraction of Bi-2223 increases with increasing the Li content to 0.2.

Table 1: The percentage volume fraction of Bi-(223) and Bi-(2212) phases in Bi\(_x\)Li\(_{1-x}\)Pb\(_{0.3}\)Sr\(_2\)Ca\(_2\)Cu\(_3\)O\(_{10+\delta}\) samples

<table>
<thead>
<tr>
<th>X</th>
<th>Volume fraction of phases formed (%)</th>
<th>Bi-223 Phase</th>
<th>Bi-2212 Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>67.49</td>
<td>32.50</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>65.16</td>
<td>34.83</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>73.78</td>
<td>26.21</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>67.83</td>
<td>32.16</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>64.34</td>
<td>35.65</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>60.74</td>
<td>39.25</td>
<td></td>
</tr>
</tbody>
</table>

The percent amount of the 2223 and 2212 phases as a function of x evaluated from the XRD patterns of the Bi\(_{2-x}\)Li\(_{x}\)Pb\(_{0.3}\)Sr\(_2\)Ca\(_2\)Cu\(_3\)O\(_{10+\delta}\) samples are given figure 2.

Figure 2: The volume fraction of Bi-(223) and Bi-(2212) phases.

The parameters a, b, c and V were also calculated from the XRD analysis as shown in Table 2. This Table indicates that the content of Bi-2223 increases and a change in the structural parameters was obtained with increasing Li concentration to 0.2, this change in the lattice parameters affect the volume of the unit cell and then causes an increase in the density. The deformation in the c-axis adjusts the amount of charge transfer from Bi-O layer to Cu-O layer sheet will tend to improve the critical temperature. From the Table random variation in both of a and c lattice constants with the increase of Li content can be observed. This behavior may be explained attributed to the differences in the ionic radii for both of Li and Bi, which results in the c-axis elongation, then heightening of the high-Tc phase which results in the rapid increase of its Tc, as mentioned previously. The change in the c lattice parameter is related to the distribution of holes between bismuth oxides layers and CuO planes. The doped ions may change the spacing between the CuO layers and thus affect the charge transfer to the CuO layers [12]. The variation of the lattice parameter a, b, c, and V, the values of sintering temperature and critical temperature for these samples are listed in Table 2. It can be found that the content of Bi-2223 increases with increasing Li concentration, indicating Li addition in the samples accelerate the reaction rate of Bi2223.

Table 2: The parameters a, b, c and V for all samples.

<table>
<thead>
<tr>
<th>X</th>
<th>a(A)</th>
<th>b(A)</th>
<th>c(A)</th>
<th>V(A (\AA^3))</th>
<th>Tc(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.506301</td>
<td>5.745111</td>
<td>37.02131</td>
<td>1075.5648</td>
<td>113</td>
</tr>
<tr>
<td>0.1</td>
<td>5.428631</td>
<td>5.449396</td>
<td>37.01791</td>
<td>1095.0916</td>
<td>116</td>
</tr>
<tr>
<td>0.2</td>
<td>5.313717</td>
<td>5.757823</td>
<td>37.14384</td>
<td>1136.4322</td>
<td>116</td>
</tr>
<tr>
<td>0.3</td>
<td>5.408422</td>
<td>5.473083</td>
<td>37.18519</td>
<td>1100.7092</td>
<td>130</td>
</tr>
<tr>
<td>0.4</td>
<td>5.446706</td>
<td>5.461773</td>
<td>37.12734</td>
<td>1104.4890</td>
<td>118</td>
</tr>
<tr>
<td>0.5</td>
<td>5.439214</td>
<td>5.456579</td>
<td>37.08603</td>
<td>1100.6948</td>
<td>113</td>
</tr>
</tbody>
</table>

The electrical resistivity versus temperature plots shows that the resistivity decreases linearly with temperature in the normal state. All samples displayed a metallic character above onset temperature, which is defined as the temperature where resistance-temperature plot deviates from linearity [13]. The electrical resistivity versus temperature with various amounts of Li is shown in figure 3. It can be seen from the plots that the onset temperatures Tc (onset) of the samples are in the close vicinity of 110 K. This is consistent with XRD results which showed no change in the peaks position. Furthermore, except for x = 0.3 sample, all the doped samples showed almost similar zero-resistance temperature (Tc-zero).

Figure 3: Temperature dependence of resistivity for Bi\(_{2-x}\)Li\(_x\)Pb\(_{0.3}\)Sr\(_2\)Ca\(_2\)Cu\(_3\)O\(_{10+\delta}\) with 0≤x≤0.5.
The sample with x=0 and the x=0.5 sample showed T_c-zero at 113 K. T_c-zero for the x=0.1 and x=0.2 samples were 116 K. While T_c-zero for the x=0.4 sample was 118 K. A sharp drop of resistivity was observed for the composition of x=(0.0,0.2,0.4, and 0.5). The sharp drop at the transition temperature is due to the transition within the grains and the presence of low-T_c phase Bi-(2212) [14]. Sample with x = 0.3 Li show the highest T_c-zero at 130 K. The increase in the T_c value is mainly due to the strong link and increasing of the contact areas between the grains during the sintering process, such result was also obtained by Mizauno et. al [15]. An increase in the intensities of the Bi2223 peaks and a decrease in the intensities of the Bi2212 peaks in the XRD patterns of the Li added samples may explain the slight increase in the transition temperature for the x = 0.3 sample. Furthermore, increasing Li content to 0.5 decreases the critical temperature to 113 K. The reduction of the critical temperature could be attributed to either crack formation as a result of excessive mechanical deformation, or to amorphous phase formation during the sintering process, and the decrease in T_c gives further evidence that the increasing amounts of Li content in Bi-2223 phase stabilizes and promotes the growth of the Bi-2212 phase at the expense of Bi-2223. This result in good agreement with that obtained by Halim et. al [16].

IV. CONCLUSION

Samples with nominal composition Bi_{2-x}Li_xPb_{0.3}Sr_2Cu_2
Cu_3O_{10+y} with 0≤x≤0.5 were prepared by the solid-state reaction method. The XRD results show the obtaining of Bi_{2-x}Li_xPb_{0.3}Sr_2Cu_2Cu_3O_{10+y} with a majority fraction of Bi-(2223) phase accompanied by Bi-(2212) phase and small amount of impurity phases of Sr,Ca,Cu,O_y. The influence of Li doping on the phase formation and superconducting state properties revealed that the high-Tc (2223) phase in the Bi(Pb)-2223 system by means of Li addition can be obtained. The XRD analysis showed that the samples with x = 0.2 had the highest volume fraction of the Bi(Pb)-(2223) high-T_c phase and was 78%. A remarkable increase in the critical temperature T_c = 130 K was obtained with increasing the Li content to 0.3. On the other hand increasing Li content to 0.4 and 0.5 decreases the critical temperature to 118 and 113 K respectively.

REFERENCES