Bi$_{2-x}$Hg$_x$Sr$_{2-y}$Ba$_y$Ca$_2$Cu$_2$O$_{10}$/Ag Sheath HTSC Wires, (Hg, Ba) Substitution Effect on The Critical Temperature

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Abstract

Bi$_{2-x}$Hg$_x$Sr$_{2-y}$Ba$_y$Ca$_2$Cu$_2$O$_{10}$ High Temperature Superconductor (HTSC) has been prepared as a pellet by solid state reaction with a certain substitution percentages (0 ,0.05 ,0.1) of Hg and Ba substitution instead of Bi and Sr respectively . Then, HTSC wires were fabricated from the prepared superconductor pellets using powder in tube (PIT) method utilizing silver as the tube material. The prepared wires are of three types; with monofilament MOF, 9 multifilament core 9MF and 81 filaments core(81MF). Several cycles of mechanical drawing and rolling process performed to the starting silver tube of 0.4 cm diameter and 5 cm length to minimize the filament diameter. The average filament diameter with 81MFC wire was about 25$\mu$m measured with an optical microscope. $T_c$ critical temperature for superconductivity is measured for the pellets and wires using four point probes techniques. These results show that the substitution Bi by Hg give a rise to the superconductor to improve highly $T_c$ , while substitution Sr with Ba lowers $T_c$. Substitution of 0.05 , 0.1 Hg to the composition Bi$_{2-x}$Hg$_x$Sr$_{2-y}$Ba$_y$Ca$_2$Cu$_2$O$_{10}$ will raise the transition temperature ($T_c$). Also substitution of Sr by Ba decreases the transition temperature ($T_c$), Hg( 0.05 – 0.1 ) substitution still raise $T_c$ after substitution of Ba with (0.05 – 0.1). High – $T_c$ phase (2223) , 2221 phase in B-2223 system and the addition of Ag to silver sheaths and a small amount of impurity phases appear in the result of XRD analysis.

Keywords: Superconductor: wire ,filament: Cryogenic: ,current density:, critical temperature: ,powder in tube .

1- Introduction

Essentially every application of superconductivity to electric power technology, especially with regard to transmission and distribution cables, depends on the successful development of suitable wire or tape in long ...

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lengths. Progress toward this end using the new HTS materials has moved much more rapidly in the 20 years since their discovery than what at first appeared to be likely given the universally poor ductility (one might say nonductility) of ceramic materials. An added factor, the high degree of crystalline, and therefore electronic, anisotropy of the HTS compounds. The two decades since their discovery have seen more than two dozen successful prototype and demonstration projects worldwide involving the new discoveries—ac cables, motors, generators, current limiters, power leads, small superconducting magnetic energy storage units, transformers, reactive power controllers, flywheels, and more[1,2].

In power-law model the electric field \( E \) is proportional to the current \( I \) of power \( n \) in the following way[3]:

\[
E = E_c (I / I_c)^n
\]

where \((E_c)\) is the voltage criterion, \(I_c\) is the corresponding critical current, and the \(n\)-value defines the steepness of the transition curve.

The I-V characteristics of HTS wires can be expressed using the power law [4]

\[
V = k I^n
\]

Where \(V\) is the voltage rise across the voltage tap, \(I\) is the current flowing in the wire, \(n\) is a positive number indicating the index of transition or a measure of the sharpness of transition, and \(k\) is a constant of proportionality.

Within the region where the current \(I\) is less than \(I\) max, the voltage \(V\) increases non-linearly. This is due to the flux creep phenomenon in the superconductor. Afterwards, the voltage \(V\) increases linearly with the current \(I\) because of the homogeneous flux-flow of the wire. The slope corresponds to the full flux-flow resistivity.

Typical electric field and resistivity criteria are 1 \(\mu\)V/cm and \(2 \times 10^{-13}\) \(\Omega\) m, respectively. \(I_c\) is determined as the current corresponding to the point on the I-V curve where the voltage is \(V_c\) measured relative to the baseline voltage [5].

Bi-Sr-Ca-Cu-O System BSCCO conductors represent the basis for all present large-scale applications of HTS. They are called conductors of 1st generation. BSCCO has a well-established manufacturing technology, and commercial conductors are available in long lengths (up to 1 km). Bi – based superconductors have three superconducting phases described by a general formula \(Bi_2Sr_2Ca_{n-1}Cu_nO_{2+\delta}\) \((n = 1, 2, 3)\).

The superconducting BSCCO has an orthorhombic structure[6], they consist of perovskite copper oxide planes sandwiched between double bismuth oxide layers with rock salt coordination, and have been compared to the Aurivillins phase[7,8]. This body – centered orthorhombic Bravais lattice is only an average structure, however as the compounds display incommensurate modulation [9].

Bi-2223 tape conductors with a HTS fill factor of up to 60 % can be produced by simple surface coating of Ag bands. By improved processing (“Pre-Annealing and Intermediate Rolling”PAIR”) tapes with \(J_c\) \((4.2\, K, 10\, T) > 500\, kA/cm^2\) have been fabricated [7] [9] [10].

The aim of the work is to fabricate superconductor \(Bi_{1-x}Hg_xSr_2Ca_2Cu_3O_{8-\delta}/Ag\) Sheath HTSC Wires using powder in tube technology and to find (Hg, Ba) substitution effect on the Critical Temperature.

2- Experimental

The samples were prepared by solid state reaction using appropriate weights of pure materials Bi(NO\(_3\))\(_2\), Sr(NO\(_3\))\(_2\), BaCO\(_3\), CaCO\(_3\) and CuO, and in proportion to their molecular weights. The powders were mixed using agate mortar; 2- propane was used to homogenize the mixture during grinding for 40-60 minutes. The mixtures were dried in an oven at 150 \(^\circ\)C. The mixtures were calcined in programmable tube furnace and the powder was heated to 800 \(^\circ\)C for 24 hours. The calcined powder was then reground and mixed with the appropriate weight of HgO, then pressed into disc-shaped pellets 1.3 cm in diameter and (0.1-0.2) cm thick, under a pressure of 0.370 MPa. The pellets were presintered in \(O_2\) gas flow at(860\(^\circ\)C for 72 hr with 1 \(^\circ\)/min heating rate and then cooled at rate of 60\(^\circ\)/ min to room temperature[11,12].
The presintered pellets were reground, repressed and resintered in O\textsubscript{2} at the same range of temperature for further 24 h. A 10 mA current was supplied to the sample by a current source D.C power supply; the voltage drop was measured by a Keithley model 180 nanovoltmeter with sensitivity of about ± 0.01 nanovolt was used for voltage measurements; The resistivity (\( \rho \)) could be found from the relation\[13\]

\[ \rho = \frac{V}{w t / L} \]

for pellet of 1.3 cm diameter[14] where : I is the current passing through the sample, V is the voltage drop across the electrodes. w is the width of the sample. L is the effective length between the electrodes, t is the thickness of the sample. Critical temperature could be found from the curve of resistivity versus temperature [15]:

To fabricate silver tubes in order to use it in later, these steps were followed: Starting with commercial silver powder of 90% purity we made several steps for purification, firstly washing by water[16].

Technical success with the BSCCO wires has been greatest with the powder-in-tube method. In this method, BSCCO powder is packed in a silver tube and sealed. The tube is then subjected to a series of mechanical deformations, such as drawing, rolling, pressing or swaging, and heat treatments as showing in fig.1.

To fabricate BSCCO/Ag wires, using the powder in tube method [17,18], Pellets that passed the resistivity measurement, as a superconductor and, having well T\textsubscript{c} temperature, were crushed and reground into fine powder by hand in an a gate mortar and a pestle in air for 40 minutes[16].

Superconductor powder is packed in prepared silver tubes enclosed in 0.45 cm outer diameter, 0.37 cm inner diameter and 0.035 cm wall thickness, with 5-10 cm length. One end of the tubes was closed, and other remain open, some tubes were internally inscribed with a thread so that they could be capped at a latter stage. Filling each these tubes was performed by adding approximately 50 mg of powder at a time. To complete filling, repeated the filling for 5-10 times to get rid complete roides or gaseous gap. In this step the ratio powder/Ag approached 70%. The tubes were lightly capped and degassed in alumina boats in air at 800 °C for 3 hours with 3 °C/min, Degassing allowed adsorbed gasses to be driven off prior to sintering in order to reduce defects such as blistering, in order to get the best continuous wire. Before drawing, degassed packed tubes were then capped by plugging the open end of a tube with coil of silver tapes or with an a appropriately threaded cylindrical cap [16].

![Fig.1. Schematic presentation of the OPIT technique [15].](image)

In order to fabricate the wire, attempted to get wires with multifilament. By drawing and rolling the starting packed tubes in three steps. The packed tubes were drawn from 0.45 cm to 0.09 cm diameter wire in 19 step drawing process. Fig.2 shows the drawing bench and rolling machine that were used for drawing operation. An intermediate heat treatment at about 500 °C for 15 minutes in air was carried out after 7\textsuperscript{th} and 16\textsuperscript{th} steps. This annealing operation was above the recrystallization temperature of silver which is 200 °C and served only to the
sheath material. The result at this first step of drawing was producing wire of 0.09 cm outer diameter with more than 600 μm net diameter of single core superconductor.

Fig. 2 (a) Drawing bench (b) Drawing pieces, and (c) Rolling machine.

Wires fabricated in first drawing step of about 30-50 cm length, were cut to short pieces of 4 cm length, 0.09 cm diameter and 9 pieces of these were packed as a beam (bundle) inside other empty silver tube of 0.45 cm outer diameter and 0.37 cm inner diameter; at this point SC/Ag ratio was about 45% by weight. Repeat steps of drawing and rolling as in first step of drawing. The above drawing produced wire of 0.09 cm outer diameter with 9 superconductor filaments, each filament was of about 150-250 μm diameter.

Wires fabricated in second drawing step of about 30-50 cm length, were cut to 9 short pieces of 4 cm length, 0.09 cm diameter, each having 9 filaments of wires packed as a bundle inside another silver tube of 0.45 cm outer diameter and 0.37 cm inner diameter; with about 30% SC /Ag ratio in this step, an outer tube containing 81 fine filaments. Repeat all drawing steps in first and second drawing steps [16].

These steps of drawing produced wire of 0.09 cm diameter with tubes of 9 filaments at each beam which means 81 filament of superconductor wire with 30-50 cm length. Cut many sample from these mono core MOC, 9 multifilament 9MF and 81 multifilament 81MF wires to the desired length for all test Critical temperature XRD, Optical Microscopy, and I-V Characterizations tests.

Samples of wires of three types (1, 9 and 81 filaments), were cut and subjected to one processing treatment. These samples underwent sintering operation on alumina trays in O₂ gas flow for 24 hours at (860 °C for B2223 with 1 °C /min), heating rate and fast cooling rate of 10 °C /min.

The four–point probe D.C is used to measure the resistivity ρ, at temperature range 77-300 K, and to determine the critical temperature T_c. The sample is fixed in the cryostat instrument which is joined to a rotary pump to get a pressure of 10⁻² mbar inside the cryostat, and also joined to a sensor of digital thermometer (type Pt 100 resistance to temperature detection RTD) near the sample position. Fine copper wires attached to the sample by furnace-dried silver paste served as the current and voltage leads [16]. After thermal treatment, critical temperature T_c measurement can be tried or tested. It was carried out under the same cryogenic system with 4cm length of wires, No external field was applied so the measurement was at self-field only (s.f). Resistivity measurement of the standard 4-point direct current DC contact method, using (6) were L=1 cm the distance between the two inner voltage points [16,17].

3 -Results and Discussion

Fig.3 show the DC Resistivity temperature diagrams to obtain T_c of the HTSC Pellet of Bi₂₋ₓ HgxSr₂₋y BaₓCa₂Cu₃O₁₀ compounds and its Hg and Ba substitution with ratio (0,0.05,0.10). Fig.4 Show resistivity – temperatures to obtained the T_c. Results of T_c for pellets and the three types of wires are shown in Table1. These results show that the substitution Bi by Hg give a rise to the superconductor wires to improve highly T_c, but only at these ratio of substitution, while substitution Sr with Ba lowers T_c of the superconductor, G. Hermiz[19] and K.A. Jassim [20] proved that more than 0.1 of Ba lost the superconductivity state of pellets samples.
Fig.3 Temperature dependence of resistivity for Bi$_{2-x}$Hg$_x$Sr$_{2-y}$Ba$_y$Ca$_2$Cu$_3$O$_{10}$ pellet compounds.

Behavior of resistivity with temperature of Bi$_{2-x}$Hg$_x$Sr$_{2-y}$Ba$_y$Ca$_2$Cu$_3$O$_{10}$ samples for the different value of Hg, suggests that the substitution of Hg has effect on the reaction to form the high-temperature phase. A certain amount of Hg (x=0.1, 0.05) is necessary for the occurrence of this reaction. Indeed the amount of Hg suitable for the formation of the high-$T_c$ phase is determined by the competition between these reactions, increases with increasing the addition of Hg as shown in Fig.5 for Bi$_{1.95}$Hg$_{0.05}$Sr$_{2-y}$Ba$_y$Ca$_2$Cu$_3$O$_{10}$. The conduction path in Bi-base and Hg-base are holes in the Cu-O$_2$ layers which is enhanced by the Bi-O and Hg-O layer. The deformation in the c-axis adjusts the amount of charge transfer from Bi layer to Cu layer, this will force the generation of hole pairing in the Cu (3d)-O(2p) band[18].

Substitution Bi by Hg will raise the transition temperature $T_c$, It is found from Fig.4 that the substitution of 0.05, 0.1 Hg to the composition Bi$_{2-x}$Hg$_x$Sr$_{2-y}$Ba$_y$Ca$_2$Cu$_3$O$_{10}$ of different Hg content (x=0.05, 0.1) will raise the transition temperature $T_c$, but more of Hg content (x=0.25) yields semiconductor [19,20] . Also substitution of Sr by Ba decreases the transition temperature $T_c$, Hg( 0.05–0.1 ) substitution still raise $T_c$ after substitution of Ba with (0.05–0.1). This behavior is due to the fluctuation of oxygen excess and the increase in Ba, while it may lead to metastable structure, that decreases $T_c$, thus more $T_c$.

All samples have reflection intensity of the High-$T_c$ phase reflections (peaks labeled H), (006), (115), (0012), (111), (119), (200), (1111), (0212) and (220). And Low –$T_c$ phase reflections (peaks labeled L), (008), (105), (115), (117), (0211), (114) and (0012). The High-$T_c$ phase reflections of the free sample (x=y=0) has lower intensity than samples have Ba. The substitution of Ba in Bi$_{1.9}$Hg$_{0.1}$Sr$_{2-y}$Ba$_y$Ca$_2$Cu$_3$O$_{10}$ compounds increases the High-peaks (H220) at Ba=0.1.

A small amount of Ba substitution is quite effective in decomposing the low-$T_c$ phase (2212) of Bi-Sr-Ca-Cu-O superconductor systems by producing BaBiO$_3$ and BaCuO$_2$ accompanied by high-$T_c$ phase formation as mentioned by Jabur.[18]. It has been reported that the low-$T_c$ phase of double CuO layers strongly prohibits the formation of high-$T_c$ phase [18], and the addition of Ag to silver sheaths and a small amount of impurity phases of (Ca, Sr)$_2$CuO$_3$ and CuO.

The appearance of more than two phases could be related to the stacking faults along the c – axis. The lattice constants evaluated from 20 of major peaks are also listed in Table.2. Thus, the above results suggest that the growth of the high – $T_c$ phase is promoted by Ba – substitution, similar to Hg substitution of the Bi–Sr–Ca–Cu–O system. This may be attributed to the ordered growth under the partial melting point and/or the Ba substitution for Sr.
Table 1: B2223 Compounds wires critical Temperature.

<table>
<thead>
<tr>
<th>Wire type</th>
<th>x</th>
<th>y</th>
<th>(Tc_2) (K)</th>
<th>(Tc_1) (K)</th>
<th>(Tc) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pellet</td>
<td>0.00</td>
<td>0.00</td>
<td>113</td>
<td>107</td>
<td>110</td>
</tr>
<tr>
<td>MoC</td>
<td></td>
<td></td>
<td>110</td>
<td>115</td>
<td>112.5</td>
</tr>
<tr>
<td>9 MF</td>
<td>0.05</td>
<td>0.00</td>
<td>123</td>
<td>127</td>
<td>125</td>
</tr>
<tr>
<td>81 MF</td>
<td>0.05</td>
<td>0.00</td>
<td>123</td>
<td>127</td>
<td>125</td>
</tr>
<tr>
<td>Pellet</td>
<td>0.00</td>
<td>0.05</td>
<td>97</td>
<td>102</td>
<td>99.5</td>
</tr>
<tr>
<td>MoC</td>
<td>0.00</td>
<td>0.05</td>
<td>90</td>
<td>97</td>
<td>93.5</td>
</tr>
<tr>
<td>9 MF</td>
<td>0.00</td>
<td>0.10</td>
<td>94</td>
<td>98</td>
<td>96</td>
</tr>
<tr>
<td>81 MF</td>
<td>0.05</td>
<td>0.05</td>
<td>102</td>
<td>106</td>
<td>104</td>
</tr>
<tr>
<td>Pellet</td>
<td>0.00</td>
<td>0.05</td>
<td>102</td>
<td>106</td>
<td>104</td>
</tr>
<tr>
<td>MoC</td>
<td>0.00</td>
<td>0.05</td>
<td>88</td>
<td>99</td>
<td>93.5</td>
</tr>
<tr>
<td>9 MF</td>
<td>0.00</td>
<td>0.10</td>
<td>94</td>
<td>102</td>
<td>98</td>
</tr>
<tr>
<td>81 MF</td>
<td>0.10</td>
<td>0.10</td>
<td>99</td>
<td>102</td>
<td>100.5</td>
</tr>
<tr>
<td>Pellet</td>
<td>0.05</td>
<td>0.05</td>
<td>90</td>
<td>98</td>
<td>97</td>
</tr>
<tr>
<td>MoC</td>
<td>0.00</td>
<td>0.05</td>
<td>88</td>
<td>99</td>
<td>93.5</td>
</tr>
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<td>0.10</td>
<td>0.10</td>
<td>94</td>
<td>103</td>
<td>98.5</td>
</tr>
<tr>
<td>81 MF</td>
<td>0.10</td>
<td>0.10</td>
<td>94</td>
<td>103</td>
<td>101.5</td>
</tr>
</tbody>
</table>

Table 2 and fig.4 show an increase in the c-axis lattice constant for Ba-substitution samples as comparable with the B2223–free samples, the reason is due to the substitution of Ba for Sr where the ionic radii of \(\text{Ba}^{2+}\) (1.35 Å) is longer than that of \(\text{Sr}^{2+}\) (1.13 Å) which renders c-parameter to be longer or deformed.
Fig. 4  Temperature dependence of resistivity for the sample $\text{Bi}_{2-x}\text{Hg}_{x}\text{Sr}_{2+y}\text{Ba}_{y}\text{Ca}_{2}\text{Cu}_{3}\text{O}_{10}$ for the three types of HTSC wires to obtained $T_c$. 
Indeed the deformation in the c-axis, as a result of substitution or deficiency of some atoms, adjusts the amount of charge transfer from Bi layer to Cu layer, this will be a driving force to the pairing generation of superconductor holes forming bosons [15] which are the current carriers in our superconductor.
From optical microscopy pictures for the transfer cross sections of the three different types of wires MoC, 9 MF and 81 MF the filament diameter is measured; and the HTSC is real area in comparison to total cross section (HTSC + Ag sheath), Fig. 6 shows these, as can see from these figure that 81 MF wire is drawn in three processes in different steps of drawing and rolling; which make it possible to fabricate wires with multifilament of each one with average diameter of 25 μm or less which is near the penetration depth of 500 Å for Bi$_{2-x}$Hg$_x$Sr$_2$-yBa$_x$Ca$_2$Cu$_3$O$_{10}$ [13].

Table 2 Phase intensity and lattice parameter for Bi$_{2-x}$Hg$_x$Sr$_2$-yBa$_x$Ca$_2$Cu$_3$O$_{10}$ compounds wires.

<table>
<thead>
<tr>
<th>X</th>
<th>Y</th>
<th>Phase 2223 %</th>
<th>Other Phases %</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.00</td>
<td>74.8</td>
<td>25.2</td>
<td>5.437</td>
<td>5.510</td>
<td>37.228</td>
</tr>
<tr>
<td>0.05</td>
<td>0.00</td>
<td>78.2</td>
<td>21.8</td>
<td>5.449</td>
<td>5.538</td>
<td>37.129</td>
</tr>
<tr>
<td>0.10</td>
<td>0.00</td>
<td>82.5</td>
<td>17.5</td>
<td>5.383</td>
<td>5.215</td>
<td>37.315</td>
</tr>
<tr>
<td>0.05</td>
<td>0.05</td>
<td>84.6</td>
<td>15.4</td>
<td>5.447</td>
<td>5.626</td>
<td>37.622</td>
</tr>
<tr>
<td>0.10</td>
<td>0.05</td>
<td>82.5</td>
<td>17.5</td>
<td>5.24</td>
<td>5.39</td>
<td>37.8</td>
</tr>
<tr>
<td>0.00</td>
<td>0.10</td>
<td>82.5</td>
<td>17.5</td>
<td>5.494</td>
<td>5.397</td>
<td>37.8</td>
</tr>
<tr>
<td>0.10</td>
<td>0.10</td>
<td>82.2</td>
<td>17.2</td>
<td>5.32</td>
<td>5.45</td>
<td>37.29</td>
</tr>
</tbody>
</table>

Since the median particle size for the two types of HTSC compounds is very fine, then HTSC particles flow easily in the silver tubes through drawing and rolling process and in all types of wires MoC, 9 MF and 81 MF as shown in Fig. 6. Small diameter wires of 81 MF (25 μm) and the sintering process controlled the HTSC grains from misalignment in MoC and 9MF wires to more alignment in 81 MF wire to the very thin platelets or plate like grains [14].

4 -Conclusions

The effect of Ba and Hg content is found to enhance the transition temperature for most samples of Bi$_{2-x}$Hg$_x$Sr$_2$-yBa$_x$Ca$_2$Cu$_3$O$_{10}$ compounds wires. The highest Tc for Bi$_{1.95}$Hg$_{0.05}$Sr$_2$Ca$_2$Cu$_3$O$_8$MoC wire and for pellet, and MoC wire and its pellet for Bi$_{1.95}$Hg$_{0.05}$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ compound. Hg substitution rises Tc while Ba reduces it. The compounds is an orthorhombic structure with an increase in the c-axis lattice constant for the samples doped with Ba as compared with those which have no barium content. It was found that the change of the Ba, and Hg concentrations of all samples produces a change in the volume fraction.
References
[20]- K.A. jassim “Comparison Study of Tc Between the Superconducting Compounds Bi2-x(Hg,Pb)xSr2-y Ba2Ca2Cu3O10-δ and(Hg,Pb)xSr2-y Ba2Ca2Cu2O10+δ” Ph.D. Thesis, Baghdad University ,2005.