Effect of Partial substitution of Ag on the Structural and Electrical Properties of High Temperature HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ Superconductor

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Abstract

The effect of the Ag partial substitution at Hg site in HgO$_x$ layer on the structure, $T_c$ and oxygen content for Hg-1223 have been studied. High temperature superconductor composition Hg$_{1-x}$Ag$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ with $x=0.0, 0.05, 0.1, 0.15, 0.2, 0.25$ and $0.3$ have been prepared using solid state reaction method. Annealing temperature 850°C for (24) hours with a rate of 5°C/min and under a pressure of 7 ton/cm$^2$. XRD analysis showed a tetragonal polycrystalline structure with high ratio of Hg-1223 phase and increase of $c$-axis lattice parameter with increase Ag rate. The surface morphology has been studied by using atomic force microscopes (AFM) in 3D. The results showed that all specimens have good crystalline and homogeneous surface. Also give a best Nano size value is 77.52 nm at $x=0.3$. Four probe technique is used to measured $T_c$. The highest $T_c$ was found to be $T_c=144$ K for $x=0.3$, and oxygen content was observed increase with increase Ag content.

Keywords: HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ Superconductor, Solid state reaction method, Structural Properties.

1. Introduction

Superconductivity is a phenomenon, which was observed by Kamerling Onnes in 1911. When temperature decreases to below a critical value, electric resistance of a superconductor disappeared and the magnetic field is expelled [1]. The first member of HgBa$_2$Ca$_2$Cu$_3$O$_{2n+2}$ series, was HgBa$_2$CuO$_{4+\delta}$ fabricated by Puttilin et. al. in 1993 [2]. In 1993 Schilling et. al. [3,4] concluded that the critical temperature was equal to 133 K for a compound HgBa$_2$Ca$_2$Cu$_3$O$_6$. This has achieved a significant jump in the critical temperature of superconducting compounds at high temperatures. The highest values of $T_c$, which were calculated for HgBa$_2$Ca$_2$Cu$_3$O$_{2n+2}$ series were 97K [5] , 123K [6] 127K [7], and 135K [8], for Hg-1201, Hg-1234 phases, Hg-1212, and Hg-1223 respectively. The $T_c$ value of Hg-1223 raise up to 164 K under high pressures of 30 GPa [9,10]. HBCO superconductor phases most important series of all HTSC cuprates because of the high $T_c$ and the extra oxygen existence appear by this series [11]. There are difficulties in preparation of Hg-based superconductors, because of the toxic mercury steam and the low decomposition temperatures of the compounds containing mercury and the relative instability of these materials. All cuprates are very sentent to carries doping and, it was found that the most efficient way to enhance the stabilization of the Hg-1223 phase is by partial substitution with cations having oxidation states higher than $+2$ i.e. higher than Hg$^{12+}$ (e.g. Tl$^{3+}$, Re$^{4+}$ etc) [12,13,14].

M. M. Abbas [15] reported that substitution of Cu ($0 \leq x \leq 0.5$) at Hg site in HgO$_x$ layer in the Hg-1223 lead to enhanced $T_c$. The $T_c$ HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ was 118K.

While best value of $T_c=153K$ and lattice parameters a=b= 3.841969, c= 15.79734 for sample with $(x=0.3)$.

O. Babych et. al. [16] prepared 15% Pb, 5% Fe and 5% Cd doped mercury HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ using Hg-free precursor Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ which obtained by sol-gel method. They noticed the superconducting plate grains size is (10–20) μm and there are non-superconducting phases of doped Hg-1223 ceramics surface. The Fe doped samples of HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ exhibit decreasing $T_c$, with increase in the critical current in grain to 6800 A/cm$^2$.

M. Abdul-Nebi et. al. [17] studied Hg$_{0.5}$Pb$_{0.5}$Sb$_{2}$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ HTSC ($x=0.0, 0.10$ and 0.15) prepared by solid state reaction method. They founded that the behavior of the composition which has no Sb is semiconductor, whereas the substitution of Sb content in the Hg$_{0.5}$Pb$_{0.5}$Sb$_{2}$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ convert from normal state ($x=0.1$) to superconducting state ($x=0.15$) with ($T_c=126K$).

F. H. S. Eleuterio et. al. [18] analyzed granular

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composition and measure magnetic response of Hg_{0.82}Re_{0.18}Ba_2Ca_3Cu_7O_{7-δ} composition. The AC magnetic susceptibility of a powder sample have \( T_c = 133 \) K with a particle size of 20 \( \mu \)m. The AC magnetic sample susceptibility shows two \( T_c \) at 133 and 98 K after crushed powder and sieved.

K. A. Jassim et al. [19] prepared Hg_{0.6}Tl_{0.4}Ba_2Ca_2(Cu_{1-x}Ag_x)O_{8+δ} samples using solid state reaction for \( x = 0 \), 0.05, 0.1, 0.15, 0.2, 0.25, 0.3. The lattice parameters \( a, b, c \) were calculated by XRD analyses. Figure-I shows the X-ray diffraction patterns for samples which were prepared using solid state reaction. The positions and intensities of the diffraction peaks appear that samples mainly consist of a major \( 1223 \) phase and a small amount of impurity \( (1212 \text{ and } 1213) \) phase and a small amount of a minor \( (1212 \text{ and } 1223) \) phase and a small amount of a minor (1212 and 1234) phase and a small amount of impurity (CaHgO_2) which are agreement with reference [23]. The appearance of more than two phases could be related to the stacking faults along the c-axis. High-\( T_c \) phase (Hg-1223) appeared with increasing Ag content up to \( x = 0.3 \).

2. Experimental methods:

The Hg_{1-x}Ag_{x}Ba_2Ca_3Cu_7O_{8+δ} samples with different Ag \( (x = 0.0, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3) \) were prepared by using solid state reaction method using mixed oxides powder of HgO, AgO, BaO, CaO and CuO with a purity of 99.99%. The starting materials were mixed and ground in a gate mortar. Isopropanol is added during the grinding process to avoid the loss of parts of the powder during the grinding process. Then it is placed inside an electric oven at a temperature of 100 \( ^\circ \)C to remove the isopropanol alcohol. The powder was pressed into disc shaped pellets (1.5 cm) in diameter and (0.3) cm thickness, using hydraulic press under a pressure of (7 ton/cm\(^2\)).The pellets were sintered in air at (850) \(^\circ\)C for (24) hours with a rate of 5\(^\circ\)/min then cooled to room temperature by same rate of heating. Four probe method at temperature range (77-300)\(^\circ\)K was used to measure the resistivity(\( \rho \)) [20].Critical temperature (\( T_c \)) calculated using the relation:

\[
\rho = \frac{(R \times A)}{L} \text{%%%%%%%%(1)}
\]

Where \( R \) is electric resistance, \( A \) is area of specimens and \( L \) is length of specimens. The structure properties of the 1223-phase was checked using X-ray diffraction technique using (Shimadzu XRD-6000) diffractometer with source Cu-K\( \alpha \) (1.5406 \( \text{Å} \)) radiation.

The lattice parameters \( a, b, c \) were calculated by using d-values and (hkI) reflection of the observed XRD using standard card of Hg-1223 (ICDD-045-0615). The oxygen content determined using a chemical method called iodometric titration was described elsewhere [21]. The volume fraction for any phase determined by using the relation:

\[
V_{ph} = \frac{\Sigma I^*}{\Sigma I_{111} + \Sigma I_{112} + \Sigma I_{200}} \times 100\% \text{%%%%%%%%(2)}
\]

Where \( I^* \) is the XRD peak intensity of the phase which were determined, 111, 112, 200 are the peaks intensity of all XRD. The mass density (dm) calculated using the relation [22]:

\[
d_m (\text{g/cm}^3) = \frac{M_{\text{wt}}}{N_A} \times \rho \text{%%%%%%%%(3)}
\]

Where \( N_A \) is Avogadro number (6.022*10^{23} \text{ mol}^{-1}), \( M_{\text{wt}} \) is molecular weight, \( V \) is volume of unit cell which equal \( (a^2 \times c) \) for tetragonal system. Atomic Force Microscopy (AFM) micrographs were recorded by using scanning probe microscope type (SPM- AA3000), Contact mode, supplied by Ångstrom Advanced Inc.

3. Results and discussion:

3.1. X-Ray Diffraction Results: The structures of Hg_{1-x}Ag_{x}Ba_2Ca_3Cu_7O_{8+δ} with \( x = 0.0, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3 \) were well established by X-ray diffraction analyses.
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Figure I
XRD pattern of Hg$_{1-x}$Ag$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$, superconductor compounds with $x$(0.0, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3)

The lattice parameters $a$, $b$, $c$ which presented in the Table-1 shows tetragonal symmetry structure for all our samples. The c-axis lattice constant increase with increase of Ag ratio. These results were almost identical to those reported in reference [24] and a-lattice parameter changes little. This result may be, because of the larger ionic radius of Ag$^{+2}$ (1.26 Å) than that of Hg$^{+2}$ (1.02 Å). This will be a driving force to the pairing generation of superconductor holes forming bosons which are the current carriers in our superconductor.

Table 1
Lattice parameters of Hg$_{1-x}$Ag$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ compounds

<table>
<thead>
<tr>
<th>$x$</th>
<th>$a=b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$v$ (Å$^3$)</th>
<th>$d_m$ (gm/cm$^3$)</th>
<th>$V_{ph}$ (1223)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.8383</td>
<td>15.7817</td>
<td>232.5652</td>
<td>6.2397</td>
<td>70.54</td>
</tr>
<tr>
<td>0.05</td>
<td>3.8385</td>
<td>15.7919</td>
<td>232.6185</td>
<td>6.2052</td>
<td>75.12</td>
</tr>
<tr>
<td>0.1</td>
<td>3.8384</td>
<td>15.7934</td>
<td>232.8632</td>
<td>6.1656</td>
<td>76.65</td>
</tr>
<tr>
<td>0.15</td>
<td>3.8381</td>
<td>15.7954</td>
<td>232.6528</td>
<td>6.1381</td>
<td>76.55</td>
</tr>
<tr>
<td>0.2</td>
<td>3.8388</td>
<td>15.7961</td>
<td>232.8202</td>
<td>6.1007</td>
<td>77.27</td>
</tr>
<tr>
<td>0.25</td>
<td>3.8379</td>
<td>15.7990</td>
<td>232.6580</td>
<td>6.0718</td>
<td>77.47</td>
</tr>
<tr>
<td>0.3</td>
<td>3.8380</td>
<td>15.8011</td>
<td>232.7099</td>
<td>6.0374</td>
<td>78.84</td>
</tr>
</tbody>
</table>

3.2. $T_c$ and Oxygen Content Results: The change of $T_c$ is related with $\delta$. Oxygen content increase with increase Ag concentration as presented in the Table-2. Since the substitution of Ag in Hg site leads to produce chemical pressure in HgO$_2$ layer. generally increase the pressure mean increases the hole which lead to disorders in structure, and this disorder is found reflected the $T_c$ ($\delta$) behavior. At $x$=0.3, the oxygen content ($\delta$) and $T_c$ gets a maximum value. These results were almost identical to those reported in references [15].

Table 2
Oxygen content and critical temperature ($T_c$) for Hg$_{1-x}$Ag$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ compounds

<table>
<thead>
<tr>
<th>$x$</th>
<th>$T_c$(K)</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>120</td>
<td>0.2931</td>
</tr>
<tr>
<td>0.05</td>
<td>126</td>
<td>0.3046</td>
</tr>
<tr>
<td>0.1</td>
<td>128</td>
<td>0.3078</td>
</tr>
<tr>
<td>0.15</td>
<td>133</td>
<td>0.3143</td>
</tr>
<tr>
<td>0.2</td>
<td>138</td>
<td>0.3189</td>
</tr>
<tr>
<td>0.25</td>
<td>140</td>
<td>0.4056</td>
</tr>
<tr>
<td>0.3</td>
<td>144</td>
<td>0.4423</td>
</tr>
</tbody>
</table>

Figure II shows the electrical resistivity as function of temperature for Hg$_{1-x}$Ag$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$, HTSC with (0≤$x$≤0.3). Samples shows a metallic behavior, followed by a superconductivity transition with $T_c$ =120, 126, 128, 133, 138, 140, 144K respectively. This Due to firstly, the Ag partial substitution may lead to change in the carrier density of states indicating unlike magnetic moments, secondly, the positive contribution of the Ag element to the coupling process in the CuO layer which responsible for the superconductivity, leads to an increase in the $c$-lattice parameter, which leads to raise in $T_c$ values.

Figure III shows $T_c$ as a function of Ag content from 0.0 to 0.3. It is found that, with increasing of Ag contents, the $T_c$ will increase.
The $T_c$ vs. Ag concentration for $(0 \leq x \leq 0.3)$.

### 3.3. AFM Results

After the preparation of the samples by solid state interaction method. Using a nanometer agate mortar, the elements were converted to small dimensions and imaged by an atomic force microscope. Figure IV represent 3-D AFM images of $\text{Hg}_{1-x}\text{Ag}_x\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ superconductor compounds for $(0 \leq x \leq 0.3)$. It was noted that there are tortuosity, areas of high and low density with nano scale dimensions different from one site to another location within the sample. The Surface roughness and average diameter of $\text{Hg}_{1-x}\text{Ag}_x\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ compounds for $(0 \leq x \leq 0.3)$ which presented in the Table 3 shows that all specimens have good crystalline and homogeneous surface give a best nano size value is 77.52 nm at $x=0.3$.

<table>
<thead>
<tr>
<th>X</th>
<th>Surface roughness</th>
<th>average diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.522 nm</td>
<td>131.63 nm</td>
</tr>
<tr>
<td>0.05</td>
<td>0.202 nm</td>
<td>112.46 nm</td>
</tr>
<tr>
<td>0.1</td>
<td>0.418 nm</td>
<td>112.06 nm</td>
</tr>
<tr>
<td>0.15</td>
<td>0.84 nm</td>
<td>101.29 nm</td>
</tr>
<tr>
<td>0.2</td>
<td>0.266 nm</td>
<td>96.32 nm</td>
</tr>
<tr>
<td>0.25</td>
<td>0.62 nm</td>
<td>76.93 nm</td>
</tr>
<tr>
<td>0.3</td>
<td>0.668 nm</td>
<td>77.52 nm</td>
</tr>
</tbody>
</table>

Figure IV

3D AFM images of $\text{Hg}_{1-x}\text{Ag}_x\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ superconductor compounds for (a) $x=0$, (b) $x=0.05$, (c) $x=0.1$, (d) $x=0.15$, (e) $x=0.2$, (f) $x=0.25$, (g) $x=0.3$. 

Table 3

Surface roughness and average diameter for $\text{Hg}_{1-x}\text{Ag}_x\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ compounds
Conclusions
In the present paper, we have investigated Hg$_{1-x}$Ag$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+δ}$ superconductor compounds for (0≤x≤0.3) which prepared by solid state reaction method. XRD pattern analyses have showed tetragonal structure with high ratio of Hg-1223 superconductor phase, and, increase of the c-axis lattice constant for the samples doped with Ag as compared with this has no Ag content. The best value for x is that the best substitution ratio for Ag in the compound Hg$_{1-x}$Ag$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+δ}$, is at x = 0.3 where a high percentage of phase Hg-1223 appears. The T$_c$ of un-doped Hg-1223 was (120K). The substitution of Ag in Hg for the compounds Hg$_{1-x}$Ag$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+δ}$, has exhibited a maximum value of T$_c$ (144 K) at x=0.3 in addition, oxygen content δ have been found increases with increasing Ag concentration since the substitution produced of local pressure, hole carrier concentration, variation electronic state and its distribution. AFM results showed that the values of the surface roughness and average diameter that samples have good crystalline and homogenous surface and give a best Nano size value is 77.52 nm at x=0.3

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