Partial substitution of Zn Effects on the Structural and Electrical Properties of High Temperature Hg$_{0.95}$Ag$_{0.05}$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ Superconductors

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Abstract. The effect of the Ag partial substitution at Hg site in HgO$_2$ layer and Zn partial substitution at Ca site in CaO layer on the structure, $T_c$, electrical properties, and oxygen content for Hg-1223 have been studied. Bulk polycrystalline Hg$_{1-x}$Ag$_x$Ba$_2$Ca$_2$Zn$_y$Cu$_3$O$_{8+\delta}$ compound samples with $x=0.05$ and $y=0.0, 0.05, 0.1, 0.15, 0.2, 0.25$, and $0.3$, are synthesized by a solid state reaction process. Structural properties are studied by using X-ray powder pattern, the high temperature phase superconductor (Hg-1223) of the tetragonal structure didn't change with the partial substitution of Zn and Ag ions, lattice parameters $c$, $c/a$ are established to vary with Ag and Zn substitution. The surface morphology has been studied by using atomic force microscopes (AFM), showed that all specimens have good crystalline and homogeneous surface. Also give a best nano size value is 75.72 nm at $x=0.05$ and $y=0.3$. Four probe technique is used to measure $T_c$. The $T_c$ were found to be increases from 129 K to 147 K and oxygen content were found to be increases with increasing Zn. In addition, dielectric properties (dielectric constant, dielectric loss factor, and the alternating electrical conductivity) are characterized directly by relating with Ag and Zn concentration.

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 Kammerlingh 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$_2$Can$_{1-n}$Cu$_n$O$_{2n+2+\delta}$ series, was HgBa$_2$CuO$_{4+\delta}$, fabricated by Putilin 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 Hg Ba Ca Cu O. 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$_2$Can$_{1-n}$Cu$_n$O$_{2n+2+\delta}$ series were 97K [5], 123K [6] 127K [7], and 133K [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]. HBCCO 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 sentient 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+2 (e.g. Tl+3, Re+4 etc) [12,13,14]. All the superconducting phases of the HgBa$_2$Can$_{1-n}$Cu$_n$O$_{2n+2+\delta}$ system crystallize with a tetragonal cell having the symmetry of space group P4/mmm. The a-parameter is ~ 3.5 Å and the c-parameters of the various phases follow the formula $c \sim 9.5 + $
Electrical properties of HgBaCaCuO8+δ HTSC compounds to make the stal structures are based on the = 0 I = 2 D lid state reaction method using mixed oxides powder of 2 s under a pressure of (7 ton/cm = 23 or dielectric measurements at the room temperature with frequency range (50 Hz = 2 ε = ε = ε = ε = ε eat, superconducting copper-oxide layers or planes, and the insulating block layers which can act as electronically active charge-reservoirs for hole or electron donation to the copper-oxygen layers. The copper-oxide layers can be thought of as being derived from the perovskite structure-type by deintercalation of oxygen from between the copper-oxide planes, while the insulating block is derived from the rock-salt structure. The aim of this paper was investigated the effect of partial substitution of Ag in Hg site and Zn nano scale in Ca site, on the oxygen content, structural, and electrical properties of HgBa2CaCuO8+δ HTSC compounds to make the characteristic more better.

2. Experimental
The Hg1-xAgxBa2Ca22-xZn0.5Cu3O8+δ samples with different Zn (y=0.0, 0.05, 0.1, 0.15, 0.2, 0.25, and 0.3) and Ag (x=0.05) were prepared by using a solid state reaction method using mixed oxides powder of HgO, AgO, ZnO, 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 °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/cm2) .The pellets were sintered in air at (850) C ° for (24) hours with a rate of (5C°/min) then cooled to room temperature by same rate of heating. Four probe technique is applied for electric resistivity measurements of the prepared samples in a temperature from 300 down to 77 K, and to calculate the critical temperature (Tc) by using the relation:

\[ \rho = \frac{(R-\rho)}{L} \]  

(1)

Where R is electric resistance, A is area 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-Kα (1.5406 Å) radiation. The lattice parameters a, b and c were calculated by using d-values and (hkl) 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 [17]. The volume fraction for any phase determined by using the relation:

\[ V_{ph} = \frac{\sum r}{\sum (r+\sum 11+\sum 12+\sum 1m)} \times 100 \text{%} \]  

(2)

Where I is the XRD peak intensity of the phase which was determined, I1, I2,…In are the peaks intensity of all XRD. The mass density(determined by using the relation:

\[ d_m \left( \frac{gm}{cm^3} \right) = \frac{M_{tot}}{N_A \times V} \]  

(3)

Where N_A is Avogadro number (6.022*10^23 mol^-1), M_{tot} is molecular weight, V is volume of unit cell which equal (a^2*cm), LCR meter (Hewlett-Packard, USA)- HP-R2C unit 4274A in the range (100 kHz–10 MHz) and the Agilent 4275B LCR meter of (Agilent Technologies Japan, Ltd.) are employed for dielectric measurements at the room temperature with frequency range (50 Hz – 1 MHz). Silver electrode is applied to both surfaces of the specimen. The capacitance (C) was recorded, then dielectric constant (εr), dielectric loss factor (ε′′), and the alternating electrical conductivity (σ_{ac}) have been calculated by using the following expressions [18]:

\[ \varepsilon_r = \frac{C}{A \cdot t} \]  

(4)

\[ \varepsilon'' = \varepsilon_r \cdot D \]  

(5)

\[ \sigma_{ac} = 2\pi f \varepsilon_r \]  

(6)

Where t is the thickness of the pellet (0.3cm), ε is the permittivity of space (8.85*10^-12 F/m), A is the effective cross area of the applied electrode, and D is dissipation factor.
3. Results and Discussion

![Graphs showing results and discussion](image-url)
Figure 1. XRD pattern of Hg1-xAgxBa2Ca2-yZnxCu3O8+δ, superconductor compounds with x=(0.0, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3)

Figure(1), shows series XRD patterns for Hg1-xAgxBa2Ca2-yZnxCu3O8+δ compound with Ag=0.05 and different Zn (y=0.0, 0.05, 0.1, 0.15, 0.2, 0.25, and 0.3).

The figure observes high transition temperature phase (Hg1223 phase) with a small amount of the second phase Hg1212 (low phase) and Hg1234 for all compounds that have been composed during syntheses of samples which are agreement with reference [19]. Furthermore, it is significant to notice that a small amount of impurity such as (CaHgO2) is present. The appearance of more than two phases could be related to the stacking faults along the c-axis. It can be clearly seen from table-1 that with increasing Zn content, the lattice parameters (a) for all samples are close to each other (a ≈ 3.83 Å), while c parameter and ratio (c/a) is significantly increasing. This increases indicate to partial replacement of Ca atoms by Zn, and Hg atoms by Ag since the ionic radii of Ag+2 (1.26 Å0) is larger than that of Hg+2 (1.02 Å0) which render c-parameter to be longer or get deformed. This will be a driving force to the pairing generation of superconductor holes forming bosons which are the current carriers in our superconductor, and the volume of lattice become bigger that explains the reason behind the decrease of \( T_c \).

Table 1. Lattice parameters of Hg1-xAgxBa2Ca2-yZnxCu3O8+δ, superconductor compounds with x=0.05 and y=(0.0, 0.05, 0.1, 0.15, 0.2, 0.25, and 0.3).

| y   | a=b(Å)   | c(Å)   | c/a ratio | V(Å³)  | \( \rho \) (gm/cm³) | V-ph (1223) |
|-----|----------|--------|-----------|--------|----------------------|-------------|
| 0.05| 3.8393   | 15.7966| 4.1144    | 232.845| 6.2082               | 73.92       |
| 0.1 | 3.8364   | 15.7974| 4.1177    | 232.505| 6.2263               | 75.49       |
| 0.15| 3.8353   | 15.8254| 4.1262    | 232.784| 6.2279               | 79.37       |
| 0.2 | 3.8348   | 15.8362| 4.1296    | 232.882| 6.2343               | 80.92       |
| 0.25| 3.8341   | 15.8511| 4.1342    | 233.016| 6.2397               | 82.11       |
| 0.3 | 3.8338   | 15.8715| 4.1398    | 233.279| 6.2417               | 82.55       |

3.1. \( T_c \) and Oxygen Content Results:

The change of \( T_c \) is related with \( \delta \). Oxygen content increase with increase Zn concentration as presented in the Table-2. Since the substitution of Ag in Hg site leads to produce chemical pressure in HgO\( \delta \) 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 [20].
Table 2. Oxygen content and critical temperature ($T_c$) of $\text{Hg}_{1-x}\text{Ag}_x\text{Ba}_2\text{Ca}_2\text{Zn}_y\text{Cu}_3\text{O}_{8+\delta}$, superconductor compounds with $x=0.05$ and $y=(0.0, 0.05, 0.1, 0.15, 0.2, 0.25, \text{and} 0.3)$.

| $x=0.05$ | $y$ | $T_c$ (K) | $\delta$ |
|----------|-----|-----------|-----------|
|          | 0.05| 129       | 0.3419    |
|          | 0.1 | 136       | 0.3684    |
|          | 0.15| 137       | 0.4050    |
|          | 0.2 | 140       | 0.5238    |
|          | 0.25| 144       | 0.5376    |
|          | 0.3 | 147       | 0.5521    |

'Figure(2)' show the electrical resistivity as function of temperature for $\text{Hg}_{1-x}\text{Ag}_x\text{Ba}_2\text{Ca}_2\text{Zn}_y\text{Cu}_3\text{O}_{8+\delta}$, superconductor compounds with $x=0.05$ and $y=(0.0, 0.05, 0.1, 0.15, 0.2, 0.25, \text{and} 0.3)$ HTSC. Samples shows a metallic behavior, followed by a superconductivity transition with $T_c=129$, 136, 137, 140, 144, and 147K respectively. This Due to firstly, the Ag and Zn 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 2. The electrical resistivity vs. temperature behavior of of $\text{Hg}_{1-x}\text{Ag}_x\text{Ba}_2\text{Ca}_2\text{Zn}_y\text{Cu}_3\text{O}_{8+\delta}$, superconductor compounds with $x=0.05$ and $y=(0.0, 0.05, 0.1, 0.15, 0.2, 0.25, \text{and} 0.3)$.

'Figure(3)' show $T_c$ 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.

Figure 3. The critical temperature vs. Zn concentration of $\text{Hg}_{1-x}\text{Ag}_x\text{Ba}_2\text{Ca}_2\text{Zn}_y\text{Cu}_3\text{O}_{8+\delta}$, superconductor compounds with $x=0.05$ and $y=(0.0, 0.05, 0.1, 0.15, 0.2, 0.25, \text{and} 0.3)$. 
3.2. Dielectric Results:

The variations in the real part ($\varepsilon'_r$), the dielectric loss factor ($\varepsilon''_r$), and the alternating electrical conductivity ($\sigma_{acs}$) of Hg$_{1-x}$Ag$_x$Ba$_2$Ca$_{2-y}$Zn$_y$Cu$_3$O$_{8+\delta}$, superconductor compounds with $x=0.05$ and $y=(0.0, 0.05, 0.1, 0.15, 0.2, 0.25,$ and $0.3$) at room temperature, as a function of frequency within the frequency (50Hz-1MHz) are shown in figure-4, figure-5, and figure-6. The dielectric constant ($\varepsilon'_r$) and dielectric loss factor ($\varepsilon''_r$) decreasing with increasing frequency from (50Hz) to (1MHz) at room temperature with the effect of Zn doping. This is due to the ionic radii of Zn which is substituted with Ca smaller than it. The real part of the dielectric constant ($\varepsilon'_r$) awards the magnitude of the part of energy which is stored within the material when the electrical field is applied to the material. Inter grains are the most likely places at which this energy can be stored, and the dielectric loss factor ($\varepsilon''_r$) express the absorption and the attenuation of energy. The value of the alternating electrical conductivity ($\sigma_{acs}$) increases with the increase of frequency. At low frequencies, the number of electrons which transmit is few, because the amount of kinetic energy in which the electrons must have to cross the crystal is few, that means the alternating electrical conductivity ($\sigma_{acs}$) is few and the dielectric loss factor increase. At high frequencies the amount of kinetic energy in which the electrons must have to cross the crystalline increases, so the number of electrons transmitted is more, so ($\sigma_{acs}$) increasing and the dielectric loss factor decrease. These results were almost identical to those reported in references [21].

**Figure 4.** The dielectric constant($\varepsilon'_r$) as function of frequency of Hg$_{1-x}$Ag$_x$Ba$_2$Ca$_{2-y}$Zn$_y$Cu$_3$O$_{8+\delta}$, superconductor compounds with $x=0.05$ and $y=(0.0, 0.05, 0.1, 0.15, 0.2, 0.25,$ and $0.3$).

**Figure 5.** The dielectric loss factor ($\varepsilon''_r$) as function of frequency of Hg$_{1-x}$Ag$_x$Ba$_2$Ca$_{2-y}$Zn$_y$Cu$_3$O$_{8+\delta}$, superconductor compounds with $x=0.05$ and $y=(0.0, 0.05, 0.1, 0.15, 0.2, 0.25,$ and $0.3$).
Figure 6. The alternating electrical conductivity ($\sigma_{ac}$) as function of frequency for Hg$_{1-x}$Ag$_x$Ba$_2$Ca$_2$Y$_{2+y}$Zn$_y$Cu$_3$O$_{8+\delta}$ superconductor compounds with $x=0.05$ and $y=(0.0, 0.05, 0.1, 0.15, 0.2, 0.25, and 0.3)$.

### 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 7 represent 3D AFM images of Hg$_{1-x}$Ag$_x$Ba$_2$Ca$_2$Y$_{2+y}$Zn$_y$Cu$_3$O$_{8+\delta}$ superconductor compounds with $x=0.05$ and $y=(0.05, 0.1, 0.15, 0.2, 0.25, and 0.3)$. 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 Hg$_{1-x}$Ag$_x$Ba$_2$Ca$_2$Y$_{2+y}$Zn$_y$Cu$_3$O$_{8+\delta}$ superconductor compounds with $x=0.05$ and $y=(0.05, 0.1, 0.15, 0.2, 0.25, and 0.3)$ which presented in the Table 3 shows that all specimens have good crystalline and homogeneous surface give a best Nano size value is 75.72 nm at $y=0.3$ and $x=0.05$.

### Table 3. Surface roughness and average diameter for Hg$_{1-x}$Ag$_x$Ba$_2$Ca$_2$Y$_{2+y}$Zn$_y$Cu$_3$O$_{8+\delta}$, compounds.

| $x$   | Surface roughness | Average diameter |
|-------|-------------------|------------------|
| 0.05  | 0.433 nm          | 182.94 nm        |
| 0.1   | 0.205 nm          | 166.56 nm        |
| 0.15  | 0.717 nm          | 121.51 nm        |
| 0.2   | 0.769 nm          | 95.76 nm         |
| 0.25  | 0.387 nm          | 89.80 nm         |
| 0.3   | 0.136 nm          | 75.72 nm         |

x=0.05 , y=0.05
4. Conclusions
In the present paper, it was investigated Hg$_{1-x}$Ag$_x$Ba$_2$Ca$_2$$_y$Zn$_y$Cu$_3$O$_{8+\delta}$, superconductor compound with Ag $x=0.05$ and different Zn $y=(0.0, 0.05, 0.1, 0.15, 0.2, 0.25, \text{ and } 0.3)$ which prepared by using a solid state reaction method. XRD pattern analyses have showed tetragonal structure with high ratio of Hg-1223 superconductor phase, and , the c-axis lattice constant increase, as the zinc incorporation is increased, the content of high phase and the critical transition temperatures ,are increase . The best value for $y$ is that the best substitution ratio for Zn in the compound Hg1-
xAgxBa2Ca2-yZnyCu3O8+δ, is at x = 0.05 and y=0.3 where a high percentage of phase Hg-1223 appears. The substitution of Zn in Ca for the compounds Hg0.95Ag0.05Ba2Ca2-yZnyCu3O8+δ, has exhibited a maximum value of oxygen content δ (0.5521) and Tc (147 K) at y=0.3, since the substitution produced of local pressure, hole carrier concentration, variation electronic state and its distribution. AFM results showed that the samples have good crystalline and homogeneous surface and gives the best nano size value is 75.72 nm at y=0.3. In addition, the dielectric properties are directly decreasing with increasing the frequency from (50Hz) to (1MHz) with Zn content.

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