Comparison of the methods of solid state reaction and sol-gel in the preparation of $\text{HgBa}_2\text{Ca}_2\text{Cu}_{2.8}\text{Zn}_{0.2}\text{O}_{8+\delta}$ superconducting compound

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Abstract: This paper investigated the influence of the preparation method change on the superconductivity properties and crystal structure of $\text{HgBi}_2\text{Ca}_2\text{Cu}_{2.8}\text{Zn}_{0.2}\text{O}_{8+\delta}$. The crystal structure was examined by XRD for all prepared samples, it was found that consist of a major 1223 high-Tc phase. However, the electrical resistivity as a function of temperature was used to calculate critical temperature $T_c$, $T_c$ (offset) = 121K,126K and Tc(onset)=124K ,131K for (SSR),(SG) respectively. While the samples dielectric properties which includes (Dielectric constant (real & imaginary),Loss tangent and Alternating electrical conductivity),were studies as a function of the frequency and range (50 Hz-1MHz) at room temperature.

Keywords $\text{HgBa}_2\text{Ca}_2\text{Cu}_x\text{O}_{8+\delta}$, superconductivity, critical temperature, XRD

1. Introduction

In 1911, Onnes, while studying electrical resistance changes with the temperature of solid mercury (Hg) and at very low temperatures using liquid helium, observed that mercury loses its electrical resistance when its temperature is less than 4.2 K), the liquid helium boiling point, which led to the realization of a new phenomenon in the solids called superconductivity electrical. [1]

The state of superconductivity is characterized by important factors: critical temperature ($T_c$), critical current density ($J_c$), and critical magnetic field ($H_c$), all of which depend heavily on other workers. The state of superconductivity Requires that the previous three factors be under a certain critical value and any difference or increase in the value of any factor of its critical value, the superconductivity is eliminated and the matter returns to normal. [2]

Considered HBCCO is the highest member of HTSC family. Common formula of HBCCO system is $\text{Hg}_1\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+x}$ (n is Cu-O layers) with critical temperature alternating from $T_c=94K$ for (when $n=1$), $T_c =127$ K for (when $n=2$) and $T_c = 136$ (when $n=3$) [3]."all the super phases of the $\text{Hg}_1\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+x}$ (n=1,2,3,4,……8) have system crystallizes with a tetragonal structure cell and perovskite layers". [4]

2. Experimental

By using a sensitive balance to appropriate weights of pure powders of the compound under study, synthesis the specimens with chemical formula $\text{Hg}_2\text{Bi}_2\text{Ca}_{2.8}\text{Zn}_{0.2}\text{O}_{8+\delta}$ by
solid state reaction (SSR) method, as starting materials, according to the general chemical formulas:

\[ \text{HgO}+2\text{BaO}+2\text{CaO}+3\text{CuO}+\text{ZnO} \rightarrow \text{HgBi}_2\text{Ca}_2\text{Cu}_{2.8}\text{Zn}_{0.2}\text{O}_{8+\delta} \]

and by sol-gel (SG) method according to the chemical formulas:

\[ \text{Hg(NO}_3\text{)}_2.2(\text{H}_2\text{O})+2\text{Ba(NO}_3\text{)}_2+2\text{Ca(NO}_3\text{)}_2+3-x\text{Cu(NO}_3\text{)}_2.2(\text{H}_2\text{O})+x\text{Zn(NO}_3\text{)}_2.6(\text{H}_2\text{O}) \rightarrow \text{HgBa}_2\text{Ca}_2\text{Cu}_{2.8}\text{Zn}_{0.2}\text{O}_{8+\delta} +8(\text{H}_2\text{O})+16(\text{NO}_2) \]

After the weight of each reactant, the powders were mixed together by using agate mortar to homogenization the mixture and to form slurry during the process of grinding for about 40-60 minute. The powder was pressed into disc-shaped pellets 1.5 cm in diameter and 0.25 cm in thickness, using hydraulic press under a pressure of (7 ton/cm²) for 60 sec. The pellets were pre-sintered at (860)ºC (in SSR method) and (800)ºC (in SG method) for 24h by using electric furnace at heating rate 5 ºC/min and cooling to the room temperature at the same rate of heating, by same rate Structure of crystal such as phase of crystalline the polycrystalline amorphous grain size and parameter of lattice of all specimens prepared were examined by XRD technique system (SHIMADZU) Japan XRD 600 by records the intensity in the range of Bragg’s angle θ from (2θ=0) Cu Kα radiation source of (wavelength λ=15405 Å , current 20 mA, voltage 40 kV). [5]

Also the tests include the dielectric constants (ε’ and ε’’), (tan δ) and (σ ac) as a function of frequency applied field in the ranging from (50-1000000) Hz , at R.T. [6] The dielectric constant is an essential property of dielectric materials hence its determination is very important.

3. Result and Discussions

The X-ray diffraction pattern of HgBi₂Ca₂Cu₂.8Zn₀.₂O₈₊δ samples are shown in Fig(1,2). We can show that all the specimens have polycrystalline nature with tetragonal phase formation. The peaks are noted due to diffraction from various planes shows mixed phases.[7]

It is clear from the figure(1,2) that there is a significant rise in the peaks of the high phase (H-peak) 1223 and a significant decrease in the peaks of the low-phase (1212) (L-peak) in the mode of sol-gel than in the mode of solid state reaction and this is evidence that the structure obtained by the sol-gel method is more uniformly crystalline than the structure obtained from solid state reaction.

Figure (1): X-ray diffraction pattern preparation by solid state reaction method
For the composition of the HgBi₂Ca₂Cu₂.8Zn₀.2O₈δ specimens it was found that content a high phase and low phase and some impurity phases. In order to calculate the volume fraction of the phase the following formula will be used [7,8]

\[ V_{ph} = \frac{\sum V_i}{\sum V_i + \sum \frac{100}{V_i}} \times 100\% \]

the mass densities \( d_m \) were calculated by using following equation:

\[ d_m = \frac{M_{wt}}{N_A V} \]

Where: \( d_m \) is density calculated from XRD in units mg/cm\(^3\), \( M_{wt} \) is molecular weight, \( N_A \) is Avogadro number \( 6.022 \times 10^{23} \) mol\(^{-1} \), \( V \) is volume of unit cell which equal \( a^2 \cdot c \) for tetragonal system molecular weight.

The resistivity measurement is given as a function of temperature by using the four point probe technique at temperature range 300K\(^\circ\) The value of \( \rho \) is found by using the relation[7,9]

\[ \rho = \frac{\rho_{wt}}{I} \]

Where: \( I \) is the current, \( V \) is the voltage, \( t \) is the thickness ,\( w \) is the width and \( L \) is the length.

| Table(1) Values of the parameters a,b,c with different substitution |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| method          | \( a(A^\circ) \) | \( b(A^\circ) \) | \( c(A^\circ) \) | \( c/a \)        | \( V(A^\circ)^3 \) | \( d_m(\frac{g}{cm^3}) \) | \( V_{ph(high)} \) | \( V_{ph(Low)} \) |
| S.S.R.          | 3.692           | 3.697           | 15.479          | 4.1925          | 211.27          | 6.8675          | %81.8           | %18.2           |
| S.G.            | 3.532           | 3.537           | 15.612          | 4.4201          | 195.03          | 7.4394          | %88.5           | %5.11           |

The results obtained showed the critical temperatures prepared in different ways. It was found that the highest critical temperature is for the prepared form by the sol-gel method, which reached 126 K\(^\circ\) followed by the critical temperature of the prepared compound in the solid state reaction method at 121 K\(^\circ\), the results are showed in Table(2). This is due to the fact that the value of the phase ratio of the high temperature of the compound prepared by the sol-gel method is the largest if compared to that of the prepared compound in the solid state reaction method, this is compatible with what you get in the X-ray test.
Table (2) Values of the critical temperatures (Tc) with the Oxygen content values (δ)

| method | $T_c$ (offset) (K°) | $T_c$ (onset) (K°) | $T_c$ (mid) (K°) | Oxygen content (δ) |
|--------|--------------------|--------------------|-----------------|-------------------|
| SSR    | 121                | 124                | 122.5           | 0.4991            |
| SG     | 126                | 131                | 128.5           | 0.5737            |

It was also found that the best ratio of oxygen in the compound is when preparing the sample in a method of sol-gel, where this percentage increases in this method and decreases by other methods. These ratios gave the highest value to the critical temperature (Tc) because the oxygen ratio in the compound has a basic role in increasing the value of the critical temperature. Fig (3) shows the electrical resistivity versus temperature for HgBi$_2$Ca$_2$Cu$_2$Zn$_{0.2}$O$_{8+δ}$ Compound, where the Tc is determined from figure. [7,10]

Figure (3): The relationship between the resistance and the critical temperature of the prepared compound by: a-Solid State reaction(SSR), b-Sol-Gel(Sg)
Dielectric constant for of the composition of HgBi$_2$Ca$_2$Cu$_{2.8}$Zn$_{0.2}$O$_{8+\delta}$ as a function of frequencies at (R.T). Figure(4) shows that the values of the true insulation constant have high values in the method of solid state reaction compared to the sol-gel method. These high values can be due to defects in the formation or because of the high ratios of multiple phases, which is consistent with the analysis of XRD results. Polarization at low frequencies because all polarization mechanisms are working and thus increase the constant real insulation.

Figure (4) Change the true insulation constant as a function of the frequency

Figure(5) The behavior of the imaginary part of the insulation constant is a function of the frequency of the samples of the prepared compounds, and it is noted that the frequency of the frequency increase in the values of the imaginary isolation constant of the sample prepared by solid state reaction method compared to the sol-gel method, which may be attributed to the presence and multiplicity of these phases, Absorbed or dispersed energy, and therefore a diminution in the value of the imaginary insulation constant. [11] The amount of variation in granular boundaries and their distribution within the crystalline structure of the sample significantly affects the value of the imaginary insulation constant.

Figure (5) Change the imaginary insulation constant as a function of the frequency
Figure (6) shows the difference in the values of $\tan \delta$ and the other isolating factors may be due to the heterogeneity of the distribution of the phases within the sample due to the possibility of different distribution of heat on the sample inside the furnace during the process of sintering of the sample as well as between samples [11].

Figure (7) shows the correlation between frequency and frequency of the samples of the compound is shown. The correlation is increased with increasing frequency. This increase can be attributed to the presence of point defects. Surface leakage on the surface of the sample due to moisture and impurities. This leads to increased alternating conductivity until it reaches the state in which the maximum energy is absorbed from the field in which the amplified field frequency is equal to the normal frequency of the material and the maximum value of the electrical conductivity. The difference in the conductivity behavior of a single model in the frequency profile can be explained on the basis of the different methods of sample preparation and its multiple phases, which causes asymmetry in the behavior of the alternating conductivity relative to the directions of the cell axes where the conductivity may be towards axis (c) differs from its behavior towards the level (a,b) [10].
4. Conclusions
In the present work we have successfully synthesized HgBi$_2$C$_2$Cu$_2$Zn$_{0.2}$O$_{8+\delta}$ high Tc superconducting compounds sample have been synthesized through the two methods SSR , Sg doing. The XRD data collected from various samples show that all the samples are polycrystalline and correspond to Hg1223 phase. The critical transition temperature Tc (126),(121 respectively, found a the best Tc value obtained for the compound in the sol-gel method because a significant rise in the peaks of the high phase (H-peak) 1223 and a significant decrease in the peaks of the low-phase (1212) (L-peak) in the mode of sol-gel than in the mode of solid state reaction, this is evidence that the structure obtained by the sol-gel method is more uniformly crystalline than the structure obtained from solid state reaction. There was also a change in the inertial properties of SSR-prepared samples compared to samples prepared by the sol-gel method, and they relied heavily on the frequency of the alternating electrode field and on the method of preparation.

References
[1] H. Kamerlingh Onnes1911; Commun. Phys.Lab.Univ. Leiden, 120b 3
[2] A. Maqsood and M.Maqsood 1996"proceeding of the international workshop held at Rajshahi university", Bangladesh, edited by AKMA Islam,28 Oct-1Nov
[3] M Irfan 2010 "Synthesis and characterization of Mg and Ge doped (Cu$_{0.5}$Tl$_{0.5}$)Ba$_2$Ca$\_n$Cu$_n$O$_{2n+4+\delta}$ " (n = 3, 4, 5)superconductors, PhD thesis, Quaid-i-Azam University
[4] E. K.Alwan Al-beyaty 2007" Effect of n Variation on Tc of(Hg0.8Tl0.2)Ba2Ca$(1-n)$Cu$n$O$_{2n+2+\delta}$ Compounds", University of Baghdad
[5] S. F. Oboudi, M. Q. M. AL-Habeeb 2016 "Dielectric and Transport Properties of Ag Nanoparticles added Bi$_{1.7}$Pb$_{0.3}$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$ Superconductor Compound", AARJMD,Vol.3,Issue.3
[6] K. A. Jassim, N. Q. Fadhil, Sh. H. Mahdi 2016 " Study the effect of (Y$_2$O$_3$, SbO$_2$) additives on the dielectrically properties of the[ Hg-1223] compounds".IJST,Vol.11-No.1-P.129
[7] K. A. Jassim, L. A. Mohammed, 2018"The partial replacement of the element of lanthanum (La) and its effect on the biodegradable properties of the BSCCO (Bi$_2$Sr$_2$Ca$_2$Cu$_3$-xLa$_x$O$_{10+\delta}$)", Karbala University Journal,Volume XV II/Scientific/, pp. 318-328