New High T_c-Value Investigated in Superconducting System $YBa_2(Cu_3)_{1-x}Ag_xO_{6.5-2.5x+\delta}$

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Abstract: A ceramic superconductor compound with composition $YBa_2(Cu_3)_{1-x}Ag_xO_{6.5-2.5x+\delta}$ has been prepared experimentally by solid state reaction from principal roots of high purity materials like Y_2O_3, BaO, CuO and Ag_2O. The study was concentrated on the effect of partial substitution of Ag with respect to Cu atoms by the ratios (x = 0.1, 0.2, 0.3, 0.4 and 0.5) through different analysis and measurements. X-ray diffraction (XRD), Scanning Electron Microscope (SEM) and Resistivity measurement is play an important role to show the improvement on high superconducting phase. It was found that the best substituted value of (x = 0.5) investigated a favor value of T_c equal nearly to (123 K), due to more excess of Ag atoms in the structure. X-ray diffraction showed an orthorhombic structure related to high-T_c phase with high stability through diminishing some peaks related to low temperature superconducting phase, that was related to presence of multiphase derivative from YBCO-phase. SEM pictures give us more details on the surface morphology, grain and grain boundaries, it gives an indication on successful of sintering process, the last one is very important in forming superconducting phase.

Key words: Superconductor compound, 123-compound, resistivity measurements, X-ray diffraction.
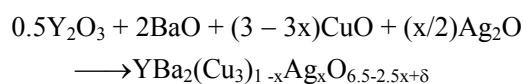
1. Introduction

After discovery of high-T_c superconductor compound with a temperature (90 K) in the system $YBa_2Cu_3O_{6.5+\delta}$ [1] most scientists condensed their activities on ability of increasing T_c-value as a function of different parameters. These parameters can be classified into two types, one of them related to synthesized procedure summarized by flow of oxygen, forming pressure, sintering temperature and time of sintering [2, 3]. The other classification related to variation of chemical composition as a partial substitution of isovalent elements for rare earth elements [4, 5], Barium element [6-8] and for copper atoms in the structure by different elements such as (Co, Ag) [7, 9]. The effect of Co-atoms in the structure was clear through the modification in the c-a-axis. There is

a re-orientation between c-a axis and the space group was Ima2 [10]. There is no effect of substitution of Ni-atoms with respect to Cu-atoms through the structure and magnetic properties [11]. The completely modification in a mixture toward new superconductor composition is a new event in recording higher (T_c) approach to room temperature [12].

2. Experiments

The components of our mixture were Y_2O_3, BaO, CuO and Ag_2O which has purity of about 99.99%. The dependent chemical reaction to produce a requested composition is follow:

$$0.5Y_2O_3 + 2BaO + (3 - 3x)CuO + (x/2)Ag_2O$$
$$\longrightarrow YBa_2(Cu_3)_{1-x}Ag_xO_{6.5-2.5x+\delta}$$

Appropriate amounts of these powders were mixed and grinding prescribed by agate mortar and pestle for 2 hrs in 2-propanol and dried. The calcination process performed at 940 °C for 18 hrs to evolve a volatile of light elements those might be presence in the mixture

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then crushed again into fine powder. The calcination and grinding procedure were repeated at least three times to investigate a chemical balancing through a color phase stability of resultant powder. The mixture was pressed into pellets in diameter of 15 mm under pressure of 8 ton. The pellets were sintered in a tube furnace at 940 °C for 18 hrs at a rate 60 °C/h and oxygen flow of about 1.25 l/min to enhance the nonstoichiometary in crystal structure that has direct effect on presence of high-T$_c$ superconductor. Then slowly cooled to 500 °C with a rate of 30 °C/h and holding time for 7 hrs before it returned to room temperature. It is very important on stability of high-Tc phase especially with the presence of oxygen flow [13].

3. Results and discussion

After successive preparation of high-T$_c$ superconductor compound YBa$_2$Cu$_3$O$_{6.5+\delta}$ with (T$_c$ = 89.5 K) [14] depends on preferable conditions represented by hydrostatic pressure, sintering temperature, time of sintering, and oxygen flow. These conditions have direct effect on abrupt variation in resistivity behavior. As well known that the magnetic susceptibility play an important role on appearance of high-Tc phase, then it is necessary to exam any testing sample roughly by Meissner experiment. It is a simple experiment and just gives us indication on diamagnetic behavior at a certain temperature. Four-probe technique is also used to find a resistivity behavior as function of temperature and determine T$_c$-value as shown in Fig. 1.

X-ray diffraction technique with simple software prepared for this purpose used to investigate the structural phase if it is orthorhombic or tetragonal as a function of (x) in comparable with pure one, which has lattice constants (a = 3.826, b = 3.894 and c = 11.702 Å) with orthorhombic phase [15]. The substitution of Ag for Cu atoms have ratios (x = 0.1-0.5) by step (0.1) in mixture YBa$_2$(Cu$_3$)$_{1-x}$Ag$_x$O$_{6.5-2.5x+\delta}$ that was prepared experimentally.

The resistivity behavior as function of Ag

substitution in a mixture as explains in Fig. 1. The results showed, in Table 1, the increasing in Tc-value as Ag increased in the mixture. Regarding to (x = 0.1) there is a sharp decreasing in resistivity creating T$_c$-value of about 90K for the sample YBa$_2$Cu$_{2.7}$Ag$_{0.1}$O$_{6.785}$. Whereas increasing of Ag to (x = 0.2) in the mixture tend to increase the critical temperature to T$_c$ = 97K for the sample YBa$_2$Cu$_{2.4}$Ag$_{0.2}$O$_{6.797}$. The effect of (x = 0.3) in composition YBa$_2$Cu$_{2.1}$Ag$_{0.3}$O$_{6.84}$ appeared sharp decreasing in resistivity behavior at Tc = 114K. The Ag-content in a sample at x = 0.4, 0.5 for YBa$_2$Cu$_{1.8}$Ag$_{0.4}$O$_{6.793}$ and YBa$_2$Cu$_{1.5}$Ag$_{0.5}$O$_{6.95}$, they showed a critical temperatures T$_c$ = 117, 123K, respectively, as shown in Table 1. There are two parameters have direct effect on T$_c$-value represented by oxygen and silver contents, those are attributed to increasing of (T$_c$) as confirmed by de Leeuw [16]. The variation of O-content has a limit effect on improvement of T$_c$ from literature review [17]. The insertion of Ag-atoms in the structure was the predominate effect on the enhancement of T$_c$-value, the effect of Ag substitution which might to be a limited elongation in forming Ag-O bond in stead of Cu-O bond that was appeared from a limited variation in lattice constants. Another thing, the increasing of Ag with respect to Cu in the mixture showed an increasing of normal resistivity, before an abrupt variation happened. That was return
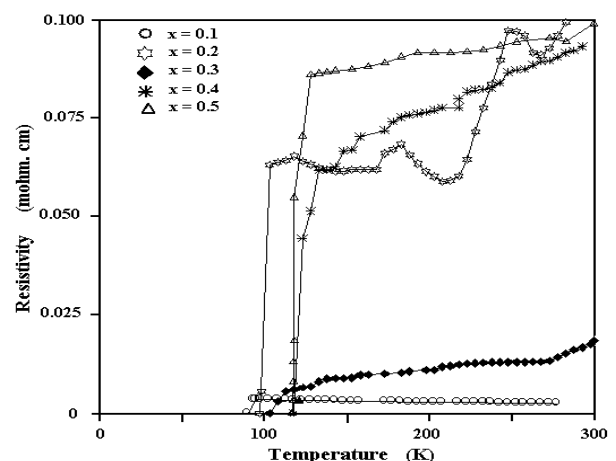

Fig. 1 **Indicates resistivity behavior as function of temperature.**

Table 1 Indicates the parameters affected as function to Ag-substitution in $YBa2(Cu3)1-xAgxO6.5-2.5x+\delta$.

The composition	δ	T_c (K)	a ($\overset{\circ}{A}$)	B ($\overset{\circ}{A}$)	C $\overset{\circ}{A}$
$YBa_2Cu_3O_{6.873}$ [14]	0.373	89.5	3.826	3.894	11.702
$YBa_2Cu_{2.7}Ag_{0.1}O_{6.785}$	0.285	90	3.805	3.892	11.67
$YBa_2Cu_{2.4}Ag_{0.2}O_{6.797}$	0.297	97	3.843	3.925	11.714
$YBa_2Cu_{2.1}Ag_{0.3}O_{6.84}$	0.34	114	3.835	3.884	11.645
$YBa_2Cu_{1.8}Ag_{0.4}O_{6.793}$	0.293	117	3.844	3.874	11.66
$YBa_2Cu_{1.5}Ag_{0.5}O_{6.95}$	0.45	123	3.825	3.889	11.689

to the enhancement of conductivity mechanism regarding to the density of Ag content in the composition. The abrupt variation in the resistivity curves around T_c-value showed a narrow width in temperature range of about ($\Delta T = 4K$).

X-ray diffraction patterns, Figs. 2-6, were analyzed by homemade software to determine the lattice constants and consequently exhibited the deviation in a structure form in comparable with pure one [13]. ASTM-data sheets 43-0269, 39-0486, 43-0545, 40-0411, 38-1433 and 44-0029 are requested to complete the analysis of X-ray pattern through definition of Miller indices. It was found that the effect

of Ag-content substituted in the mixture (x = 0.1) showed the appearance of some peaks labeled by (040) related to orthorhombic phase with elongation in
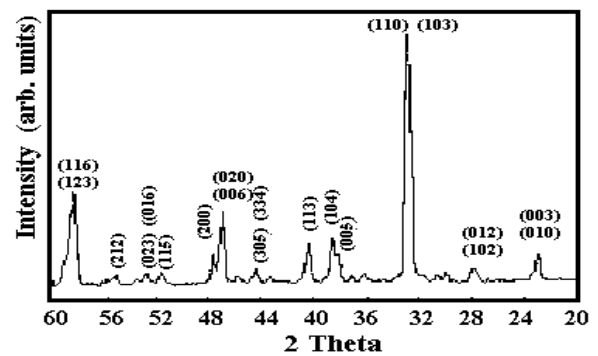

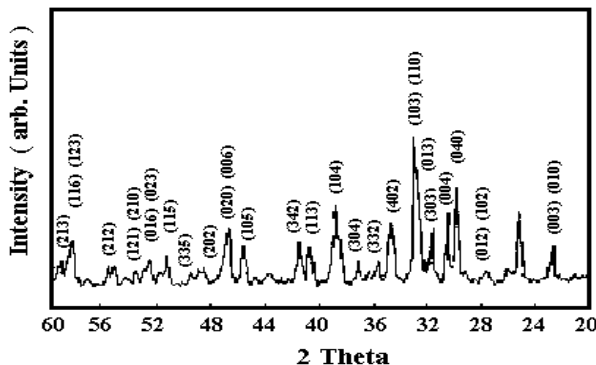**Fig. 4 Indicate x-ray diffraction pattern for Ag = 0.3.**

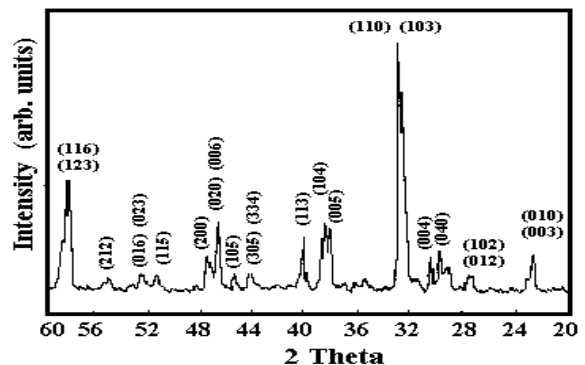**Fig. 2 Indicate x-ray diffraction pattern for Ag = 0.1.**

Fig. 5 Indicate x-ray diffraction pattern for Ag = 0.4.
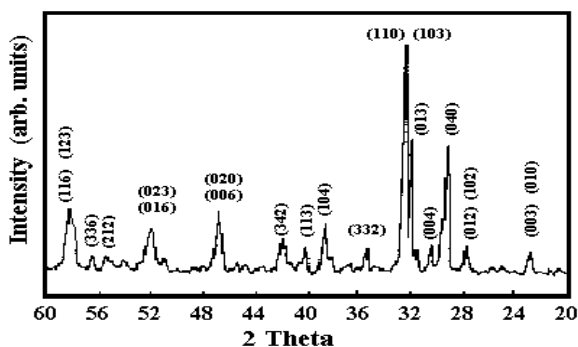

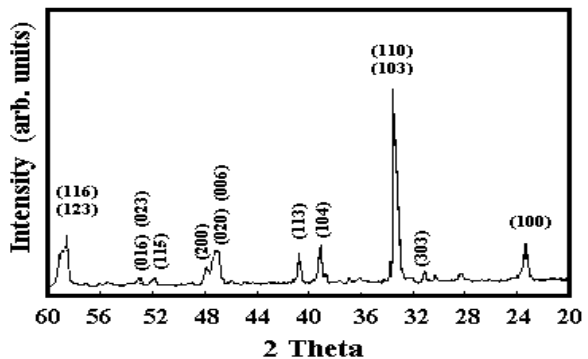**Fig. 3 Indicate x-ray diffraction pattern for Ag = 0.2.**

Fig. 6 Indicate x-ray diffraction pattern for Ag = 0.5.

b-axis, lattice constants are a = 3.885, b = 11.68, and c = 3.813. The others were (303), (402), (332), (304), (342), (335) have tetragonal phase with elongation in two axis, a = b = 11.76, and c = 12.04. The peak (202) related to YBa$_2$Cu$_3$O$_9$ whereas the peaks (121), (210) related to phase of YBa$_2$Cu$_3$O$_6$ as shown in Fig. 2. All these phases were present with low intensity peeks, which mean the presences of those multiphases might be with low density with respect to original phase. This is the reason of a slight variation in T$_c$.

The increasing of Ag substitution to (x = 0.2), as mentioned in Fig. 3, exhibited the enhancement of the peak (040), on the other hand the peaks related to tetragonal phase were limited on the peaks (332), (342) and (336). The low intensity of those peaks, their limited number, and the diminishing of the peaks related to YBa$_2$Cu$_3$O$_9$ phase and YBa$_2$Cu$_3$O$_6$ phase are the reason of the enhancement of orthorhombic phase. The second thing that was causing the improvement of high-T$_c$ orthorhombic phase is return to high intensity of the original peaks related to YBa$_2$Cu$_3$O$_7$.

The substitution of Ag at (x = 0.3), there are only two peaks (305), (334) related to tetragonal phase and diminishing all undesired peaks as shown in Fig. 4. On the other hand the increasing in the intensity of original peaks like (110), (103) and (200) tends to increase the density of orthorhombic phase. This result is enough to explain the increasing of T$_c$. Regarding to ratio of Ag at (x = 0.4), as shown in Fig. 5. There is a limited appearance to peaks like (040), (305) and (334) to enhance the orthorhombic phase. Most of original peaks have high intensities like (110), (103), (200), (116) and (123), which are the main reason of increasing T$_c$, in addition of vanishing the most undesired peaks.

The effect of substitution by Ag with x = 0.5 as shown in Fig. 6, there is a stability in the original peaks related to 123-phase with completely diminishing of undesired peaks except the peak (303), which has very low intensity. The conclusion from X-ray diffraction patterns was the exhibition of orthorhombic phase for all samples under study with a slightly variation in lattice constants, as mentioned in Table 1. There is a slightly shifting in the position of the peaks, which causes a slightly variation in the lattice constants.

In addition to interpretation of X-ray patterns in the enhancement of orthorhombic phase, this played an important role in increasing Tc values. As a point of view that the substitution of Ag in the composition is not equivalent to Cu content that means the substitution of Ag atoms is one to three of Cu. There is an important parameter represented by the defect density those were created as a result of substitution.

Regarding to the composition YBa$_2$(Cu$_3$)$_{1-x}$Ag$_x$O$_{6.5-2.5x+\delta}$, each part of Ag additive replaced by three part of Cu, such that the total amount of (Cu + Ag) should reduce from three in pure compound to two. Then we expect that there is abundance in defect related to the position of Cu atom, might be in basal plane or in the middle planes. The thing that enhanced our talk was the steady increase in the ratio of (O) atom as Ag ratio increase, as explain in Table 1. That tends to increase the non stoichiometary in the compound which is a role in creating orthorhombic phase.

The second thing, the radius of Ag is greater than the radius of Cu that means the strength of bond creating between Ag-O is smaller than the bond Cu-O, that make the extra O atom inserted to create O-O bond is favor than the creating of Ag-O bond especially in the basal plane, the last is responsible on the mechanism of conductivity below T$_c$. The though that we conclude that there is abundance in the O-O bonds creating, which increasing the negative ions with respect to positive ion. This is the reason of increasing T$_c$ as a function of Ag ratio increase. The thing that was emphasis our talk, shown in Fig. 7 and Table 1, it was clears that there is a slightly increasing of lattice constant (a), which return to the big radius of Ag inserted in Cu site.

It was clear that Ag-atoms may replace in the site of Cu(1) and Cu(2) where as oxygen atoms has a sites

O(1), O(2), O(3) and O(4) in the structure, as mentioned before the extra oxygen may takes some sites regarding to Cu(1) or Cu(2) producing O-O bends. Return to Fig. 7, the ration x = 0.1 creating a slight decreasing in the lattice constant that is normal related to the presence of multi phase created at this ratio such that there is no observable increasing in T$_c$ in comparable with pure one. The general conclusion was the remaining of orthorhombic phase with slightly variation in the lattice constant a, which was accompanied with developing of T$_c$-values.

SEM-pictures considered good tool in the determination of surface morphology as shown in Fig. 8. The plates-like appeared for all compositions with a smaller size than the pure compound and the grain size are elongated platelets with a size (22.53-8.25 µm). It was found that the grain growth of plate-like increased rapidly with increasing Ag substitution and reaches to maximum size at the interior of fractural surface, as
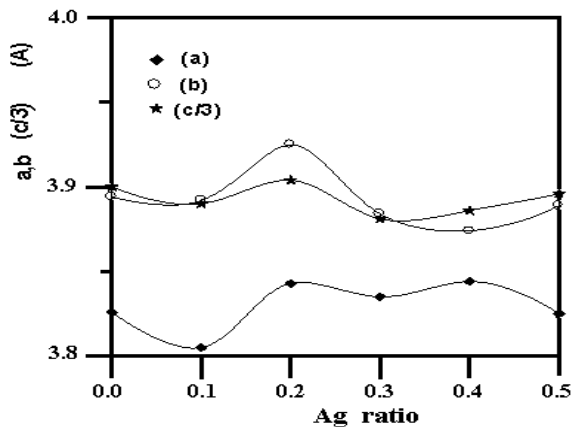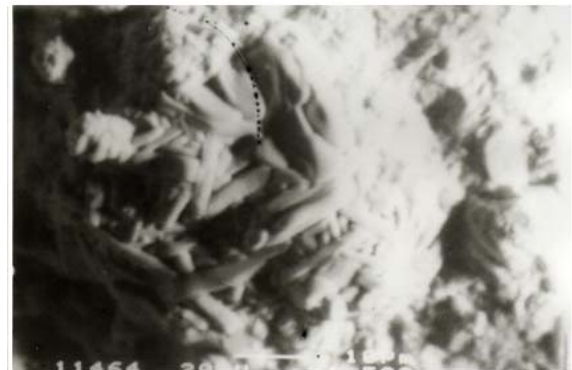

Fig. 7   indicate the variation of lattice constant as a function of Ag ratio.

(a)

(b)

(c)

(d)

(e)

Fig. 8   Indicates SEM picture for surface morphology of the samples for different ratio of Ag in the mixture, (a) x = 0.1, (b) x = 0.2, (c) x = 0.3, (d) x = 0.4, (e) x = 0.5.

shown in Fig. 8e that is return to large homogeneity of the chemical species agrees with the orthorhombic stability. The grain might be turns to grain cluster and appearance of grain size of about 19 μm, as shown in Fig. 8c. All SEM-pictures except picture (e) exhibited flak grains like that lead to decrease the weak link between grains those explain the increasing in rseistivity by increasing the Ag insertion in a mixture as shown in Fig. 1.

4. Conclusions

The composition YBa$_2$(Cu$_3$)$_{1-x}$Ag$_x$O$_{6.5-2.5x+\delta}$ showed high T$_c$ superconductor with increasing of T$_c$ as Ag increased. It was clear that the Ag-content (x = 0.5) give us the best result in critical temperature, this value may be attributed to a high insertion of O-content in the mixture. The second thing is the increasing of Ag-content has a direct effect for increasing the O-content in the mixture. This composition normally showed nonstoichiometaric due to the increasing of (O) atoms with respect to density of (Cu + Ag) from pure one. That means the mechanism of conductivity related to negative charges regarding to high excess of these charges rather than the positive charges represented by the accumulation of (Y, Ba, Cu, Ag) atoms. As a result of that there is a partial deviation in the lattice constants related to vacant site produced due to the partial substitution of Ag for Cu atoms. The reason for producing high density of positive vacant rather than negative vacant is return to the nature of substitution. There is one Ag-atom substituted instead of three Cu-atoms that is the reason for increasing the oxygen content in the mixture and tend to make the negative charges as a mobile charge in a superconducting behavior.

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