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The influence of aluminum doping and oxygenation on the properties of $YBa_2Cu_{3-x}Al_xO_{6.5+\delta}$ ($0 \leq x \geq 0.045$) HTSC

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Abstract

The effect of Al_2O_3 particle addition on the crystal structure and superconducting properties of $YBa_2Cu_3O_{6.5+\delta}$ (YBCO) ceramics is systematically studied. Samples were synthesized using a solid state reaction to prepare $YBa_2Cu_3O_{7-\delta}$ and $YBa_2Cu_{3-x}Al_xO_{6.5+\delta}$ ($0 \leq x \geq 0.045$) samples by mixing the appropriate ratios of constituent oxides; BaO, CuO, Y_2O_3 and Al_2O_3. The mixtures were ground to fine power and then calcined at 870°C. The calcined powders were grounded again and molded into pellets by applying a hydrostatic pressure from (0.6) GPa. These pellets were sintered at 960°C. The structure of the prepared samples was characterized by X-ray diffraction (XRD). The crystal lattice parameters were found to change and the orthorhombicity decreased slightly with Al_2O_3 addition, and no change in the structural symmetry state was obtained. A series of $YBa_2Cu_3O_y$ (YBCO) samples with small amounts (0–0.45) wt.% of nanosized alumina particles (45 nm) are synthesized with the flow of oxygen gas of about (1.25) L/min. The microstructure has been characterized by Scanning Electron Microscopy (SEM) and the critical temperature has been measured by the standard four-probe method in the applied magnetic field at 77 K. SEM and (XRD) analyses have shown that alumina reacts with YBCO and the superconducting transition temperature (T_c) was 116 K and decreases with increasing alumina content from 108 K to 92 K for x= 0.01 and 0.045 respectively. The iodometric titration is used to determine the oxygen content in the samples and the value of O_2 varies from sample to another. The result of titration exhibited that the value of δ is increasing when increasing Al concentration.

Keywords: Al doping; Electrical resistivity; XRD; SEM.
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1. Introduction

For the cuprates showing high temperature superconductivity, there is much interest in how the superconducting properties of the Cu(2)-O planes and the Cu(2) based magnetic order evolve as a function of the doping level [1]. By doping, the electric state of the superconductivity will be more clarified and understood. The effect Al_2O_3 substitution on

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the superconducting properties of high -Tc superconductors (HTSCs) may improve the understanding some of the unusual normal state and superconducting properties of these materials [2-8]. By far the most extensive research preformed to date, has been for 3d transition – metals doped at the copper sites .It was established that in high –Tc oxides of ceramic materials critical temperature [Tc(R=0)] was suppressed with the doping of ferromagnetic impurities. Early studies showed that Al doping was possible in Y123 and that Al substitutes Cu in the CuO chains [9,10,11]. This substitution was more effective for the improvement of the critical current density, Jc, of YBCO at 77 K than the substitution of Cu in the CuO_2 plane [12]. In the case of YBCO bulk superconductors $YBa_2cu_3O_7\backslash Y_2BaCuO_5$ composites) fabricated by the top- seeded melt-growth (TSMG) process[13], the most difficult issue is pushing particles below some critical size (about 500 nm for Y_2BaCuO_5 (Y211) particles [14] during crystal growth. Nanosized non-superconducting regions can be introduced into YBCO bulk superconductors by neutron irradiation [15] or by chemical substitution of atoms in the $YBa_2cu_3O_{7-\delta}$ (Y123) lattice (mainly the Cu atoms in the CuO chains [16] or the CuO_2 planes [17,18]). These artificially created pinning centers can be effective for enhanced flux pinning in YBCO at intermediate magnetic fields and high temperatures. However, it is important to find an optimum concentration of these impurities in order to improve pinning without decreasing the critical temperature, Tc. Recently, successful Al doping in YBCO bulk superconductor was reported [19]. Moreover, it was also shown [20] that the method of oxygenation played a very important role in increasing the critical current density, J_c.

In this study the effect of Al_2O_3 particle addition on the crystal structure and superconducting properties of $YBa_2Cu_3O_{6.5+\delta}$ (YBCO) high temperature superconductor is explained.

2. Experiment Details

Al –doped YBCO samples were prepared by the solid state reaction technique. In the first step , the starting materials, high – purity (99.999%) powders of Y_2O_3, $BaCO_3$, CuO and Al_2O_3 according to the formula of $YBa_2Cu_{3-x}Al_xO_{6.5+\delta}$ (x=0.00,0.01,0.02,0.03,0.045) in an agate mortar followed by calcinations at 870^{o}C for 30 hours with two intermediate grindings .Then , after mixing of high purity at 99.999% ,the stoichiometric ratio. Then the mixture was re-grounded. Measuring the weight of reactants with the required amounts using sensitive balance with (4-digitals), type (STATON) 462AL. The second step is transferring the mixture into a programmable tubular furnace using an alumina crucible and with heat treatment up to 870^{o}C .The powder heated to temperature 870^{o}C for 22 hours by heating rate of 60^{o}C per hour then cooled to room temperature with rate 60^{o}C per hour and by means of programmable controlled type (EUROTHEM 818P) which is connected with the furnace. The powder grinding was carried out in agate mortar for about 60 min and sieving it to get powder or granular size of about (45μm) as maximum. After four intermediate grinding and calcinations of the precursors under air the obtained mixtures were re-ground and the resulted powder was then pressed into pellets using cylindrical die which has a stainless steel cylinder of 0.5 cm (13mm) diameter and (1.5-1.8) mm thick using manually hydraulic press type (PERKIN-ELMER) under pressure of 0.6GPa.

The pellets were heated in flowing oxygen for calcining and sintering where the temperature was raising at rate of 60^{o}C /hour. When the temperature of the pellets reached 600^{o}C, the pellets were held at this temperature for 7 hours under flow of oxygen [21].The temperature was then raised again to 960^{o}C in 2 hours time followed by cooling to ambient

temperature at the rate of 60^{o}C/h. An automated temperature controlled tubular furnace of ± 2^{o}C was used.

The samples were characterized by X-ray diffraction (XRD) and the purity was checked using the Rietveld method. The measurements were performed using a Shimadzu X-ray diffractometer with (Cu-kα) radiation and crystal analyses were performed using GSAS Program [22]. The significance of oxygen flow is to enhance the value of (δ) to reach the content of oxygen atoms in the sample to about (6.79-6.98). Scanning electron microscope is used to examine the morphology of the crystalline grains of the prepared samples.

The transition temperature Tc of the HTSC samples was determined using the four probe "resistive". The temperature resistivity measurement on Al_2O_3 added YBCO samples cooled slowly to room temperature were carried out by the four-Probe method. In this standard four–probe method, a small current is passed through a sample and the voltage drop across it. The terminals distinct from those used for passing the main part of the current through the specimen ,where voltage drop in both leads and contacts and the electrical contact to the sample were made with fine copper wires, adhered with silver paste. The cryostat system was used for the measurement of critical resistivity of the sample, with the presentence of liquid Nitrogen. Dc Technique with typical excitation current I = 100μA was used for the a-axic electric resistance measurement from which the value of Tc is determined. After polishing the surface layer of specimens, the electrical contacts were made by evaporating four point contacts of silver paste on the samples. For the electrical measurements a Keithley model 181 nano voltmeter and a Keithley model 221 current were used and the temperature was measured by a calibrated copper constant thermocouple with an accuracy of ±0.2 K.

3. Results and Discussion

3.1 X-ray Diffraction Studies

The X-ray powder diffraction (XRD) studies were carried out on Al_2O_3 added to YBCO samples sintered 960^{o}C and cooled slowly to room temperature at a rate 2 ^{o}C/min under oxygen flow. Figure 1 represents the powder diffraction patterns of YBCO specimens with 0.0%. The effect of substitution by Al with respect to Cu atoms in the studied concentration range will produce a compound of orthorhombic structure. It can be noticed that the volume of unit cell increases with the value x and it that is attributed to the effect of Al- substitution on the variation of the lattice parameters (a,b,c).

However, XRD patterns showed no impurity phase except for a few percent Y_2BaCuO_5, for the concentration of 0.045%. In particular, oxides of copper could cause significant errors in weight- loss and idometric titration measurement. However in the doped samples, a few additional peaks were observed at 2θ = 25.1^{o}, 28^{o}, 47.3^{o}. The intensities of these additional peaks were found the same with increasing Al_2O_3 addition. Figure 2 shows the superconducting transition temperature for Al-doped YBCO, $YBa_2Cu_{3-x}Al_xO_{6.5+\delta}$. It is noticed that the superconducting onset temperature decreases with higher Al content. The transition temperatures Tc were determined from the magnetic transition curves taken after zero-field cooling as the mid-point of these curves with an applied external magnetic field of 2 mT.

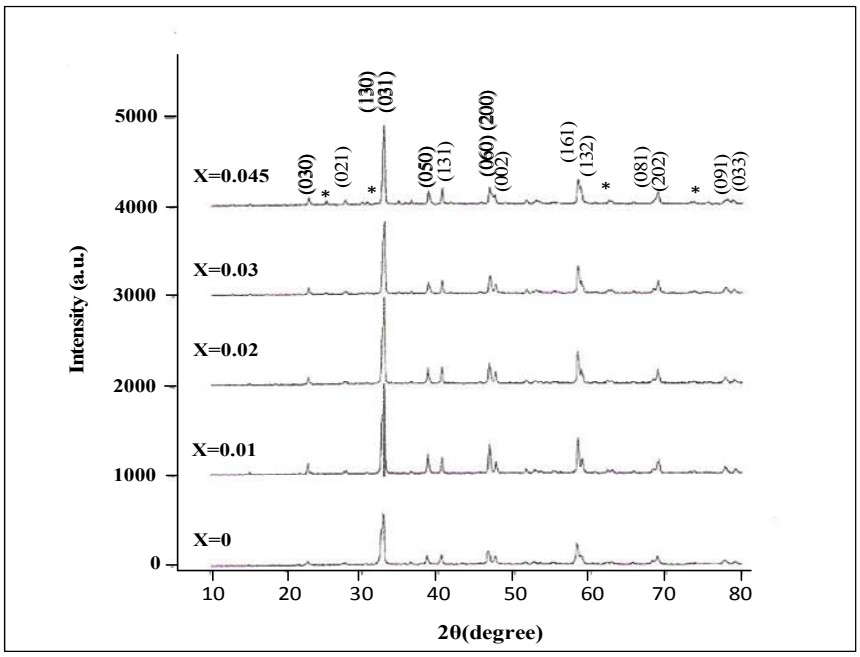

Figure 1: X-ray diffraction patterns for components $YBa_2Cu_{3-x}AlxO_{6.5+\delta}$.

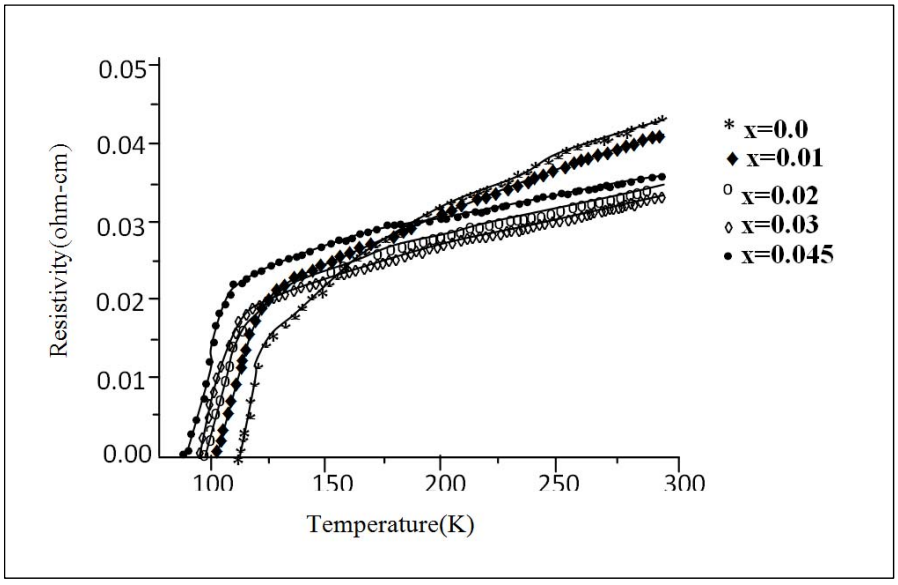

Figure 2: Resistivity versus temperature for $YBa_2Cu_{3-x}AlxO_{6.5+\delta}$ compositions.

The transition temperatures are obtained and listed in Table 1 and the decrease in their values (Tc vs x) is consistent with related published data [23]. With increasing the concentration of Al up to x = 0.045 as shown in Figure 1, the intensity of the diffraction peaks (030, 060, 002, 132) decreases. Table 1 reports the lattice constants (a, b, c) and the volume of the unit cell (a x b x c) of $YBa_2Cu_{3-x}AlxO_{6.5+\delta}$ (x=0.00, 0.01, 0.02, 0.03, 0.045). The effect of substitution by Al atom with respect to Cu atom in the concentration =0.00, 0.01, 0.02, 0.03, 0.045, will produce a compound of orthorhombic structure. It can be noticed that the volume of the unit cell increases slightly with the value of x and that is attributed to the effect of Al - substitution on the structure properties by the variation of a,b,c.

Table 1: Typical parameters and result obtained the values (Tc, Lattice Parameters , volume and δ) for all samples

Specimens	Tc (K)	Lattice Parameters (Å)	Volume (Å ^{3})	δ
$YBa_2Cu_3O_{6.5+\delta}$	116	a=3.8200 b=3.8855 c=11.4835	170.4451	0.382
$YBa_2Cu_{2.99}Al_{0.01}O_{6.5+\delta}$	108	a=3.8202 b=3.8854 c=11.4837	170.4526	0.383
$YBa_2Cu_{2.98}Al_{0.02}O_{6.5+\delta}$	102	a=3.8203 b=3.8855 c=11.4835	170.4584	0.389
$YBa_2Cu_{2.97}Al_{0.03}O_{6.5+\delta}$	95	a=3.8203 b=3.8855 c=11.4835	170.4584	0.42
$YBa_2Cu_{2.955}Al_{0.045}O_{6.5+\delta}$	92	a=3.8354 b=3.8813 c=11.4948	171.1115	0.44

The oxygen content was determined by idometric titration which is found to all samples of the $YBa_2Cu_{3-x}Al_xO_{6.5+\delta}$ superconducting [23]. Titration process is a simple chemical method used to determine the amount of oxygen content which is a function to the ratio of iodine content that was evolved from the mixture of samples substituted by Al in the composition of the $YBa_2Cu_{3-x}Al_xO_{6.5+\delta}$. It was found that, the content of oxygen in the samples under study slightly increases with increasing the Al substitution in the compound.

3.2 Temperature Resistivity Measurements

Figure 2 shows the resistivity versus temperature curves for YBCO with different contents of Al_2O_3 (0.0 to 0.045) wt% when the samples were slowly cooled at a rate of 2^oC/min under oxygen atmosphere. The electrical measurement represent by resistivity measurement of partially substituted rare earth material Al in Cu are reported in Figure 2. It is clear that a negative effect on Tc value happened by increasing (x-value) within the range (x = 0.0, 0.01, 0.02, 0.03, 0.045), the value of Tc has decreased from 116 K to (108, 102, 95, 92) K in superconductor $YBa_2Cu_{3-x}Al_xO_{6.5+\delta}$, respectively. This decrease may be related to the decrease in the density of state for charge carriers that caused by the presence of the element of superconductivity. The Al doping, therefore, seems to reduce the inter grain connectivity, which may possibly due to enhanced interaction of ferromagnetic spins of Al^{+3} with the mobile free carriers in conducting CuO_2 planes, and hence suppress the density of mobile carriers [24]. The superconducting properties such as transition temperature and critical current density are dependent on the concentration of the high oxide state, Cu^{+3} [or $(Cu\text{-}O)^+$], since superconductivity is related on the concentration of Cu^{+3} ions. This resembles that the current density generally increases with increasing Cu^{+3} concentration.

The superconducting properties of $Y_1Ba_2(Cu_{1-x}Al_x)_3O_7/Y_2BaCuO_5$ bulk superconductors with different Al contents (x = 0.0025–0.05) were studied by Antal1 et al [25]. They found that the critical current density at the lowest Al concentration (x = 0.0025) was higher in comparison to the un-doped reference sample. Thus, the critical current density Jc improves by Al doping. The increment of Jc was explained by the elimination of

the formation of a/c oxygenation macro cracks during the oxygenation process. The a/c-oxygenation macro cracks are formed during oxygenation by the tensile stresses in the oxygenated layer and are perpendicular to the direction of the current flow. These macro cracks directly reduce the effective cross section and consequently the measured critical current density.

It is found [25] that with increasing Al concentration, both *J*c and *T*c decrease, this confirmed that the Cu atoms in the Y123 lattice were partially substituted. The lowest Al concentration in our work essentially affected the value of *T*c although it remains above 90 K with the standard oxygenation. The transition width ΔTc was higher with increasing Al content .Increasing the transition width for Al doped samples has been ascribed to the microscopic in homogeneity of Al distribution dissolved in the Y123 phase [25]. The inhomogeneity could be lowered by Al diffusion, if the samples were kept at higher temperatures and for longer time.

3.3 Surface Morphology

Micrographs were taken using JOEL JSM 4600 scanning electron microscope (SEM) operating at 15 kV to compare the microstructure of pure and Al_2O_3 doped-YBCO samples. The samples were polished, etched using a dilute HCl solution then coated with metal to ensure better micro structural observations. Figure 3 shows (a) the microstructure of pure $YBa_2Cu_3O_{6.5+\delta}$ sample and Figures 3 (b,c,d,e) show the microstructure of $YBa_2Cu_{3-x}Al_xO_{6.5+\delta}$ samples (0.01,0.02,0.03,0.045) slowly cooled in O_2 atmosphere after sintering at 960^{o}C.The micrographs clearly show that the size of the plates shaped-particles are in the range of 20-11.6 μm. It was found that the grain growth of plate like-shaped increased rapidly with increasing Al substitution, reaching a maximum size at the interior region of the fracture surface.

X = 0.0

X = 0.01

X = 0.02

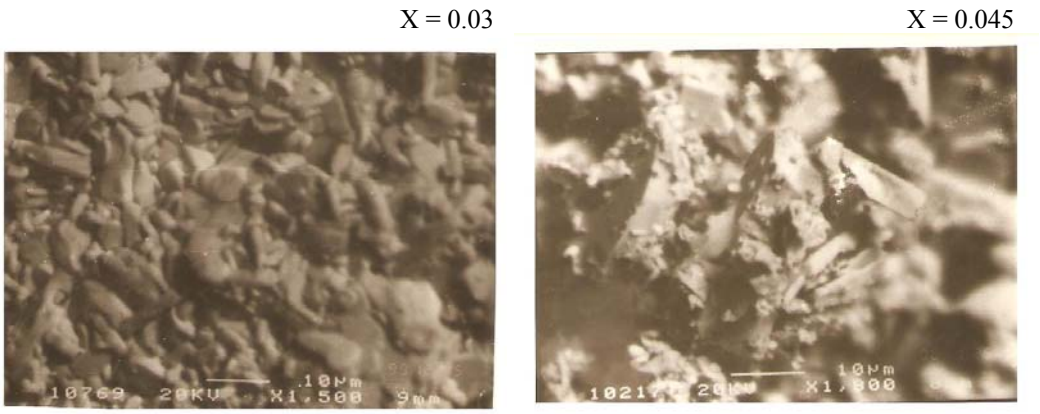

Figure 3: SEM observation of $YBa_2Cu_{3-x}Al_xO_{6.5+\delta}$ compositions.

3.4 Enhanced Oxygen Absorption in $YBa_2Cu_{3-x}Al_xO_{6.5+\delta}$ Samples

The determination of the oxygen content in $YBa_2Cu_{3-x}Al_xO_{6.5+\delta}$ sample was carried out using "Iodometrics titration" method. The effect of Al substitution in the parent compound tends to increase the oxygen content in the mixture to a maximum value (δ). The value of Tc is maximum at x = 0.01 and gradually decreases (increase in δ value) for higher x values, as shown in Table 1. Therefore processing atmosphere and annealing temperature are of great importance in obtaining high temperature superconductivity. In the case of YBCO materials, it has been extensively reported that slow cooling of the sintered $YBa_2Cu_{3-x}Al_xO_{6.5+\delta}$ samples under flow of oxygen or annealing at temperatures in the range of 600-650^{o}C for several hours, are essential requirement for obtaining orthorhombic phase [26-27]. It is important to note that tetragonal-orthorhombic phase transformation takes place below 700^{o}C by absorbing oxygen. It is also noticed that during the Al substitution in YBCO, that the widely accepted procedure of slow cooling at 2 ^{o}C/min or annealing at 650^{o}C for seven hours after high temperature sintering is not necessary to obtain high temperature superconducting in YBCO samples. Table 1 shows the values (δ) of oxygen content for all samples.

4. Conclusion

In this paper a systematic study on the ($YBa_2Cu_{3-x}Al_xO_{6.5+\delta}$) HTSC prepared by solid state reaction method is presented. X-ray diffraction analysis showed that all compositions crystallize within the orthorhombic structure and that there is no structure change in the superconducting YBCO compound due to Al addition, a few additional peaks located at 2θ = 25.1^o, 28^o, 47.3^o compared to the pure YBCO. Furthermore, the lattice parameters (a,b,c) and the unit cell volume were determined. For the composition x = 0.045, Y_2BaCuO_5 impurity was observed. Resistivity measurements show that the increase of Al concentration induces a decrease of Tc values. It turns out that it is not possible to unambiguously define the contributions coming from each of the two main phases in the samples or to precisely define the contribution coming from the back ground. Therefore, quantitative analysis is needed and this is especially the case at temperatures near and below the magnetic ordering temperature of Y_2BaCuO_5. The investigations of oxygen content showed the extensive procedure of flow cooling or annealing at 650^{o}C for seven hours for oxygenation is not essential to obtain superconductivity of Cu substitution by Al. The appearance of texture in SEM images for all samples under study such as plate –like is accompanied with the formation of superconducting phase.

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