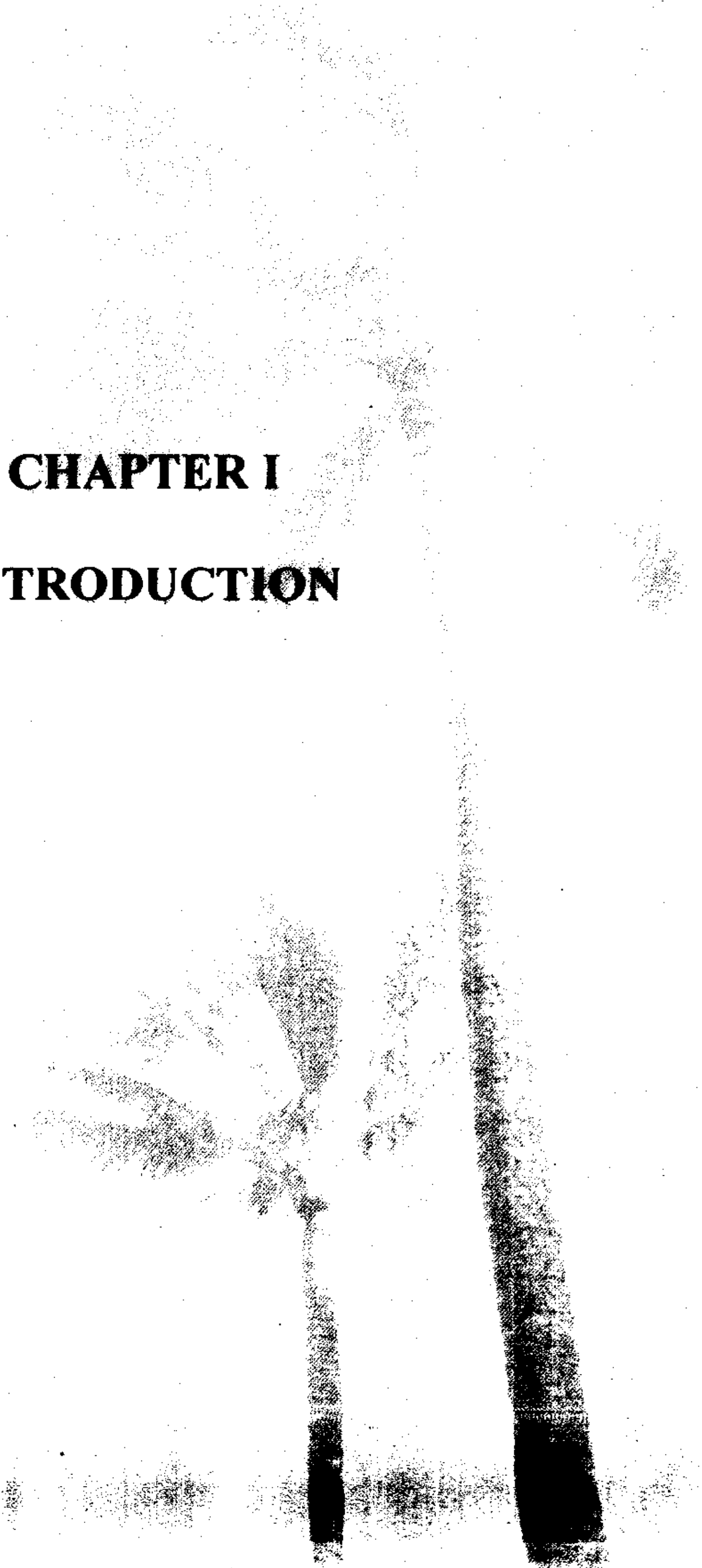
CHAPTER I

INTRODUCTION



INTRODUCTION

I.1- **General introduction**:

Superconductivity is a multi-faceted-phenomenon that offers many advantages over current technology. Superconductors are materials that conduct electricity with practically no resistance at all at very low temperature. None of the electrical is lost when flowing through a superconductor. The field of superconductivity has many aspects. For most materials, which are normal conductors, whenever electrical current flows, there is some resistance to the motion of electrons through the materials. It is necessary to apply a voltage to keep the current going to replace the energy dissipated by the resistance. Electronic is based on components in which the resistance changes under control of an input voltage; these components are made of semiconductors. In a conductor, a current would quickly diminish due to resistance. However, in a superconductor, a current can continue to flow forever because there is nothing to stop it.

Superconductivity is the name given to a remarkable combination of electric and magnetic properties, which appears in certain metals when they are cooled to extremely low temperatures. The temperature at which a superconductor loss resistance is called its superconducting transition temperature or critical temperature; this temperature, T_c is different for each metal. The first metal discovered to be a superconductor was mercury by a Dutch physicist, Onnes,[1] in 1911. He discovered that the mercury lost all the resistance to the flow of electricity when cooled to about 4°K. Also he induced a current in a superconductor that was formed in the shape of a ring , and cooled it in liquid helium.[1] The first concept that comes to mind upon hearing the word superconductor is zero resistance. However, there is another equally significant aspect of superconductors that is less widely recognized the unique magnetic properties of superconductors. The important discovery about the superconductors is the Meissner effect,[2] which was found experimentally in 1933 without any theoretical basis. The Meissner effect is the expulsion of a magnetic field from within a superconductor. A metal expels any magnetic field inside it when it cools through T_c and becomes superconducting. By expelling the field and thus distorting nearby magnetic field lines, a superconductor will create a strong enough force field to over come gravity. This gives rise to the memorable photos of a small magnet floating freely above a cooled block of superconductor.

Since a superconductor has no resistance, it carries current indefinitely without requiring voltage or expenditure for electricity. Once the current is started, it continues, provided that the superconductor is kept cold. For many years it was thought that all superconductors behaved according to a basically similar pattern. However, it is now realized that there are two kinds of superconductor, which are known as type-I and type-II. Most of elements which are superconductors exhibit type-I superconductivity, whereas alloys generally exhibit type-II superconductivity. The two types have many properties in common but show considerable difference in their magnetic behavior.

I.2- **High temperature supercoductors**:

The history of high-temperature superconductivity as a field distinct from ordinary superconductivity is very brief. It began in late 1986, Bednorz and Muller[3] had reported the observation of supercondctivity in lanthanum copper oxides doped with barium or strontium at temperatures up to 38 K. This caused tremendous excitement because 38 K was above the ceiling of 30 K for superconductivity that had been theoretically predicted almost 20 years earlier. Once the barrier was broken, hundreds of scientists rushed to try various chemical compounds to see which one would give the highest T_c. In 1987, Wu et al.[4] reported that they discovered a superconductor with a critical temperature of 92 K for the compound yttrium barium copper oxide (YBCO). This discovery excited the entire research community because a significant barrier had been broken. Subsequently, attention was focused on copper oxides, and before long the bismuth strontium calcium copper oxide (BSCCO) system was found[5] with T_c = 105 K. That was followed by the discovery[6] in 1988 of thallium barium calcium copper oxide, (TBCCO), with T_c =125 K. The thallium compounds were given very little attention prior to 1991, because of fears that thallium was extremely toxic, and therefore was dangerous to have in the laboratory. Almost five years elapsed before the mercury barium calcium copper oxide compound,[7] (HgBaCaCuO), boosted the T_c record to 133 K. Under extremely high pressure,[8] T_c can be pushed over 150 K. The discovery of oxides with a superconducting transition temperature (T_c) above the boiling point of liquid nitrogen has revitalized the study of superconductivity and has stimulated a large volume of research in this area.

I.3- The bismuth strontium calcium copper oxide (BSCCO) system:

The bismuth strontium calcium copper oxide (BSCCO) system has been chosen for this work because it has many advantages: the row materials is sheep, has a good T_c and it is easy to handle in the laboratory than the thallium compounds and mercury compounds.

Michel et at.[9] were the first to find superconductivity in the Bi-Sr-Cu-O system and isolated a new superconductor compound, closed to the composition $Bi_2Sr_2Cu_2O_{7+y}$ midpoint critical temperature of 7-22 K. Akimitsu et al.[10] have also observed a superconducting transition with onset temperature near 8 K for the phase with copposition of $BiSrCuO_y$ in the same system.

Maeda et al.[5] discovered a new high-T_c oxide superconductor of the Bi-Sr-Ca-Cu-O system without any rare earth element. The oxide $BiSrCaCu_2O_x$ has T_c of about 105 K, higher than that of $YBa_2Cu_3O_7$ by more than 10 K. In this oxide, the coexistence of Sr and Ca is necessary to obtain high T_c. Also it should be noted that this oxide is extremely stable in water and moisture and that no change in the superconducting properties has been observed even after the thermal cycling between 4 K and room temperature or above. Furthermore, the oxide has two phases with different T_c and their structures. Tarascon et al.[11] have determined the crystal structure of the compound $Bi_4(Sr,Ca)_6Cu_4O_{16+y}$. It has a tetragonal unite cell with a = 0.3817 nm and c= 3.06 nm. The resistivity curves indicated that more than one phase is present. Adachi et al.[12] studied the superconducting properties in a Bi-Sr-Ca-Cu-O system. Two types of superconductors were observed: one has a transition temperature of 80 K and the other has two transitions at 80 K and 110 K. XRD measurements suggest that the latter superconductor has at least two phases.

Nobumasa et al.[13] reported that the high T_c superconducting phase above 100 K in a Bi-Sr-Ca-Cu-O superconductor was found to appear in proportion to the time of the sintering just below the melting temperature. Also the X-ray diffraction pattern indicated that the high T_c phase contains triple Cu-O layers sandwiched by two Bi_2O_2 layers. The mechanism of the high T_c phase formation is proposed such that a disproportionation into triple and single Cu-O layers occurs from 80 K phase with double Cu-O layers to form the high T_c and a semiconducting phase. It was reported that the 80 K phase in the Bi-Sr-Ca-Cu-O system has structure similar to the $Bi_4Ti_3O_{12}$ type structure[14] and the chemical composition is closed to $Bi_2(Sr,Ca)_3Cu_2O_y$.[15-20]

Subramnian et al.[21] reported a new superconductor has been identified as $Bi_2Sr_{3-x}Ca_xCu_2O_{8+y}$ with x ranging from about 0.4 to 0.9. It displays onset behavior near 120 K. Koinuma et al.[22] synthesized thin films of Bi-Sr-Ca-Cu-O superconductors on a polycrystalline YSZ (2.5% yttrium stabilized zirconia) substrate by the 50 Hz ac sputtering method. The films deposited without intentional heating were amorphous insulators. The superconductivity of these films depended on the annealing condition. Chatterjee et al.[23] have been investigated a superconductivity of low bismuth containing system, as compared with the standard $Bi_2Sr_2CaCu_2O_8$ system. Electrical resistivity and AC susceptibility data establish that the sample, with composition $BiSr_4Ca_2Cu_4O_y$,sustains bulk superconductivity below 74K with a large Meissner signal. It apperas from the X-ray diffrection pattern that the symmetry and the position of the atoms in the units cell of this sample are different from those of the $Bi_2Sr_2CaCu_2O_8$ system, though the unit cell dimensions are more or less the same.

A study by Kijima et al.[18] of the varying nominal composition in the Bi-Sr-Ca-Cu-O system indicated that the phase concerned with the superconducting transition near 75 K in this system has a composition of $Bi_2CaSr_{1.5}Cu_2O_y$ and a layered structure with an orthorhombic unit cell of a=5.40, b=27.0 and c=30.6 A°.

Kuroda et al.[24] obtained a superconducting film of Bi-Sr-Ca-Cu-O on a (100) MgO substrate by sequential deposition of Cu, Bi, CaF_2 and SrF_2, followed by annealing in oxygen at 1133-1163 K. All the films exhibited a strong preferred orientation, with their c-axis direction normal to the substrate surface with a length of 30.605 A°. The films annealed at 1143 K exhibited a large and sharp drop in resistance at 110 K.

Mori et al.[25] studied the effects of sintering temperature and of Cu and Ca contents for Bi-Sr-Ca-Cu-O system based on $BiSrCaCu_{2.2}O_x$ compound. A maximum T_c value of 85 K was obtained for the composition $BiSrCaCu_{2.2}O_x$, but its single phase was not obtained. Cava et al.[26] reported that a superconductivity above 100 K has been observed in a multiphase samples of Bi-Sr-Ca-Cu-O. They found three phases of Bi-Sr-Ca-Cu-O system showing a superconductivity at T_c's near 120, 105 and 80 K. Also they studied the crystal structure and the physical properties of single crystals, grown by a flux technique.

Pena et al.[27] showed the effects of annealing under various atmospheres on the superconductivity of Bi-Sr-Ca-Cu-O materials.

Samples of nominal composition 1112, 2212, 2202 were annealed under vacuum or nitrogen gas, then reacted under oxygen or NF_3 gas flows. Fully reversible and opposite effects on T_c are observed when the 110K and 85 K phases are annealed under the same conditions.
Sun et al.[28] reported that the phase decomposition of high quality $Bi_2Sr_2CaCu_2O_y$ single crystals annealed at 1023 K for 1h in air, vacuum, flowing oxygen or nitrogen atmospheres, is studied by X-ray diffraction. It is found that the decomposition of the $Bi_2Sr_2CaCu_2O_y$ phase is dependent on the annealing atmosphere. The variations of superconducting transition of crystals after annealing in different atmospheres were measured by AC susceptibility and could be explained by the oxygen configuration. The structural changes and oxygen diffusion influence each other and both act on the oxygen content and superconductivity of $Bi_2Sr_2CaCu_2O_y$ single crystals.

The effects of lead substitution in Bi-Sr-Ca-Cu-O system have been studied by several groups.[29-31] They reported that lead substituted for bismuth induces a new phase. Furthermore, the lead substitution also appears to affect the speed of reaction so that similar material can be produced in have the time. Tang et al.[32] reported that liquid nitrogen quenching of the compounds $Bi_{4-x}Pb_xSr_4Ca_2Cu_4O_y$ ($x = 0.7, 0.9, 1.0,$

1.1 and 1.2) is required to produce superconductors having T_c's well above the transition temperature of the host "2212" superconductor. The X-ray diffraction patterns of those compounds are those of the "2212" structure (with a few weak lines of the "2223" structure appearing). The resistivity curve for the higher doped compounds (x = 0.7 and 0.9) indicates the existence of two super-conducting phase transitions, one at around 105 K and another around 89K. For the heavier doped compounds (x =1.1 and 1.2), the resistivity curves show only a single transition. In general, the zero resistivity temperatures are seen to decrease with increased Pb doping. Imao et al.[33] synthesized the 110 K-phase Bi-Sr-Ca-Cu-O (Bi-based) superconductors using a variety of Pb-oxides (PbO, PbO_2, Pb_2O_3), also the superconducting properties for the samples were investigated. They found that the doping of Pb_2O_3 into Bi-based superconductors was effective in forming a 110 K-phase. The XRD results showed that the volume fraction of a 110 K-phase in the prepared samples increased by doping Pb_2O_3.

With regard to the role of the Pb substitution, Yamada et al.[34] synthesized new high-T_c superconductor Bi-Sr-Ca-Cu-O with additive of Pb. They found that increasing Pb content increased the zero resistivity temperature T_c. A maximum T_c value of 85.5 K was obtained for the composition $Bi_{0.5}Pb_{0.5}SrCaCuO_2O_y$. So Pb substitution may induce a mixed valence state also in Bi besides the Cu mixed valence state, and that may result in T_c enhancement. Kambe et al.[35] found that the increase in the hole concentration obtained by substitution Pb^{2+} ions for some Bi^{3+} ions in a bismuth superconductor (80 K) lowered the T_c to 77 K. Also Liu et al.[36] reported that the oxygen content in Pb-doped $Bi_2(Sr,Ca)_3Cu_2O_y$ superconductors does not remain constant as more lead is substituted, thus the changes of the copper valency with Pb substitution is not straight-forward matter. Jao et al.[37] found that the superconductivity of Bi-Sr-Ca-Cu-O sample is determined by both annealing environments and the Pb content. Oxygen annealing tends to degrade the superconductivity as Pb ≈ 0.3, while it improves the superconducting properties of samples with Pb ≈ 0.4.

Stephens et al.[38] have developed a solution route to bulk Bi-Sr-Ca-Cu-O superconductors based on triphenyl bismuth (Ph_3Bi), an extremely soluble Bi- organometallic. The results indicated that the Ph_3Bi-based solution method yields materials that are comparable to those produced by the common solid-state approach, while offering definite advantages over other solution routes to bulk superconducting materials.

Several groups have demonstrated the possibility to prepare thin films either of the 2212 phase, $Bi_2Sr_2Ca_1Cu_2O_8$, or of the 2223 phase doped with lead, $(Bi, Pb)_2Sr_2Ca_2Cu_3O_{10}$, by sputtering, with zero resistance below 85K for the 2212 oxide,(39-49) and below 110K for the 2223 phase.(50-58) Brousse et al.[59] have been prepared thin films of $Bi_2Sr_2Ca_1Cu_2O_8$ and $(Bi, Pb)_2Sr_2Ca_2Cu_3O_{10}$ on monocrystalline (100) MgO substrates, using a laser ablation method with post annealing treatment. The influence of substrate temperature and oxygen pressure during deposition were investigated. Electric and magnetic measurements have been used to characterize the films. A study by Flower et al.[60] shown the effect of substituting lead for bismuth superconductor and compared with the previous work. Two superstructures are observed with one being present only at lead concentration greater than 0.1. Analysis of X-ray diffraction patterns show that the unleaded and 0.1 Pb content material is tetragonal, whereas the samples containing higher amounts of lead are orthorhombic. The second superstructure is only found in orthorhombic material.

Sakai et al.[61] reported that micro-probed Raman scattering spectra of optic phonons in Bi-Sr-Ca-Cu-O have been observed as a function of temperature near the transition temperature T_c using both the as-grown and annealed samples. In Bi-Sr-Ca-Cu-O, phonon modes in the as-grown sample increase their peak frequencies monotonically with decreasing temperature. Also Shimada et.[62] observed phonon structures in the tunneling conductance of $Bi_2sr_2CaCu_2O_8$. There is no particular phonon-mode whose contribution to T_c is larger than 12 K. The resistivity and the nuclear-spin relaxation rate calculated using the spectral function. Several Group (63-68) have studied the properties and crystallization of Bi-Sr-Ca-Cu-O glasses, with some similarities in results. Glasses-transition temperatures (T_g) range from 643 to 703 K. Differential thermal analysis (DTA) shows a sharp exotherm at 723 K, typically followed by weaker transitions around 833 K. There is usually an endotherm around 1033 K, with overlapping exo- and endothermic events at higher temperatures. The superconducting glass-ceramics generally exhibit fine.

Komatsu et al.[63] obtained samples by quenching 1.5:1:1:2 (Bi:Sr:Ca:Cu:O) melts between iron plates. They observed no superconductivity after annealing these samples at 873 K for 4 hour. A glass-ceramic consisting mostly of 2212 with smaller amounts of CuO. Also Hinks et al.[64] obtained glasses from splat-quenched 2:2:2:3 melts. They observed no superconductivity after heat treatments below 800°C. However, after an unspecified heat treatment, they reported resistivity drops T_c at 110 and 85 K and zero resistivity at a T_c of ≈80 K. Skumryev et al.[65] splat-quenched 1:1:1:2 melts between copper plates, and obtained 2212 after heating at 1053 K for 4 hour in oxygen. This material showed a T_c of 115 K and a T_c of 45 K. Bi-Sr-Ca-Cu-O glass-ceramic have shown to be capable of yielding substantial amounts of the 110 K phase. Shi et al.[66] splat-quenched 2:2:2:3, 2:2:3:4, and 2:2:4:5 melts. Heating the 2:2:3:4 material at 870°C for 10 days resulted in zero resistivity at 105 K. however, a slight trace of the 80 K phase was evident in their magnetic susceptibility measurements. However the majority phase in the X-ray diffraction (XRD) pattern was still 2212. Heating any of these composition at 1123 K, or for a shorter times at 1143, always resulted in a substantial or long superconducting transition at 85 K. Tomy et al.[69] have examined several compositions and the effect of several heat treatments on the superconductivity in Bi-Pb-Sb-Sr-Ca-Cu-O system.

The onset and the zero resistance temperatures are dependent on the heat treatment.

Motoi et al.[70] studied the effect of annealing under various conditions of temperatures from 673 K to 1073 K and oxygen partial pressures from 0.0 atm. to 1.0 atm. on the superconductivity in $Bi_2Sr_2CaCu_2O_y$. The heat treatment under reducing conditions enhances the T_c of $Bi_2Sr_2CaCu_2O_y$ up to 94 K. Malachevsky et al.[71] have prepared samples of Bi-Sr-Ca-Cu-O with different compositions and heat treatments, replacing part of the bismuth by other heavy elements. They analyzed the presence of the different phases formed in each case by using X-ray diffraction. Also they reported the influence of the heat treatments and compositions in the quantity and stability of the phases.

Superconductors offer a lot of benefits[72] over normal conductors that might be exploited in applications. Superconductors conduct electricity without energy loss, so they might be used in place of conventional conductors to save energy. Because superconductors have no electrical resistance, They do not give off any heat. In a conventional conductor, the energy lost due to resistance is given off as heat. This heat has limited the degree to which electrical circuits can be packed together. Using superconductors, electrical circuits can be packed tightly together with no concern for heat built-up. Another advantage to superconductors is their ability to generate powerful magnetic fields. Very powerful fields can be generated from relatively small superconducting electromagnets.

I.4- **The lanthanum copper oxide system:**

High Temperature superconductivity in oxocuprates was first observed in the lanthanum copper oxide system,[3] and this system has remained of central interest for the understanding of the electronic properties of these phases due to its simplicity in structure and stoichiometry. The base material La_2CuO_4 is itself a semiconductor. However it can be converted to a superconductor either by partial isomorphous replacement (La^{3+}- M^{2+}) or by insertion of additional oxygen into interstitial positions at high oxygen pressure and elevated temperatures (La_2CuO_{4+x}).[73-77] In both cases, mixed valence systems of copper (Cu^{II}-Cu^{III}) in the CuO_2 planes result, which exhibit metallic behavior above the critical temperature T_c.

In 1986 Bednorz and Muller[3] were the first to give evidence of superconductivity near 35 K in these cuprates by partial substitution of barium for lanthanum. A similar phenomenon was later observed with substitution of strontium.[78,79] More recently, a highly interesting method of converting La_2CuO_4 at ambient temperature into a superconductor with T_c of 43 K was found simply by anodic oxidation of the ternary phase.[80]

The electrochemical oxidation technique provides direct access to highly oxidized phases as a route for the synthesis of high temperature superconductors. Summarized below are characteristics of this material produced from both electrochemical and chemical oxidation reactions. The intrinsic reactivity of La_2CuO_{4+x} and its precursor determine the surface chemistry of this copper oxide system.

Wattiaux et.al.[80-82] first reported that La_2CuO_4 can be oxidized in an aqueous base using the electrochemical technique. They observed electrochemical intercalation of oxygen at ambient temperature in cyclic voltammetry studies of La_2CuO_4 electrodes in aqueous KOH solution. It has been suggested that this reaction proceeds via insertion of oxygen into the La_2CuO_4 lattice during electrolysis; a formal description is given in Equation 1.

$$La_2CuO_4 + x\,O^{2-} \rightarrow La_2CuO_{4+x} + 2xe^- \qquad [1]$$

They found two intriguing physical properties of this new superconducting phase: (1) it shows a larger orthorohombic distortion compared with La_2CuO_4, instead of the smaller distortion found in the high pressure oxygenated samples [83,84] and (2) its Tc ≈ 44K surpasses the 35 K obtained by optimum Sr doping.[79] Subsequent experiments showed that controlled potential electrolysis of La_2CuO_4 results in the formation of a bulk La_2CuO_{4+x} superconductor.[85-90]

Rudolf et al.[91] reported galvanostatic oxidation data showing a continuous variation of the potential with the composition up to $x=0.07$ and indicated that the electrochemical deintercalation is reversible. They also described the reaction process of the anodic oxidation as an electron / hydroxyl ion transfer process leading to a mixed- valence state of copper.

A study by Chou et al.[92] reported very similar oxidation data with **a maximum oxygen content $x = 0.08$ obtained at potentials below the** oxygen evolution potential. They conclude that the electrochemical reaction forms La_2CuO_{4+x}, with two distinct bulk superconducting phases found at $x \approx 0.03$ ($T_c \approx 32K$) and $x \geq 0.08$ ($T_c \approx 45K$). The electrochemical oxidation of the La_2CuO_4 did not appear to be reversible. They were in strong disagreement with the interpretation of Rudolf et al.[91]

Bhavaraju et al.[93] have carried out galvanostatic and potential step experiments also showing that the oxygen atoms intercalated on oxidation are completely removed on reduction. Oxygen can be quantitatively added and removed from La_2CuO_{4+x} ($0 \leq x \geq 0.085$) electrochemically in 1 M KOH at ambient temperature. Their electrochemical data show, however, that intercalation and deintercalation of oxygen occur far from equilibrium. Samples prepared electrochemically show superconducting transitions with temperatures of ~ 30K and ~ 42 K, depending on the oxygen content. Takayama et al.[94] reported a chemical oxidation route to superconducting La_2CuO_{4+x}. The La_2CuO_4 obtained by the normal solid state reaction was oxidized in an aqueous solution of $KMnO_4$. The product included excess oxygen up to $x \approx 0.09$ and showed bulk superconductivity below about 40 K. Two different orthorhombic phases appeared upon increasing x; one had a smaller distortion while the other had a larger one, compared with the stoichiometric La_2CuO_4. Electron diffraction patterns suggested a complicated manner of ordering the interstitial oxygen atoms in the sample with $x \approx 0.09$.

The same group indicated that La_2CuO_{4+x} having various x values could be prepared by the $KMnO_4$ oxidation method with the aqueous solution heated to 333 K. Some samples oxidized in concentrated $KMnO_4$ solutions underwent spinodal decomposition resulting in products having x ~ 0.01 and x ~ 0.22. The former showed a superconducting transition at ~ 14K, the latter at 40 K.[95]

Rajaram et al.[96] also found that La_2CuO_4 becomes superconducting at T_c =44 K when subjected to an electrochemical oxidation in 1N NaOH at room temperature. However, they claimed that superconductivity in an electrochemically oxidized La_2CuO_4 pellet is not confined to the surface, as expected for a process with small diffusion coefficients.

Takeda et al.[97] carried out two means to dope the oxygen in La_2CuO_4 structure; one is annealing under high oxygen pressure at high temperature and the other, electrochemical oxidation in an aqueous alkaline solution at ambient temperature.

Electrochemical oxidation has thus been shown by many workers to be extremely efficient for doping oxygen into a La_2CuO_4 type compound. This method performed at near room temperature is now a standard technique for chemical processing giving a non-equilibrium state, which is difficulty realized by a normal bulk reaction. In effect, only a few hundred mV of electrode potential has a more oxidative power than considerable oxygen pressure.

Radaelli et al.[98] studied different samples of La_2CuO_{4+x} prepared by electrochemical oxidation with different x values using neutron diffraction. Also the miscibility gap of La_2CuO_{4+x} was investigated.[99] Feng et al.[100] reported a preparation of superconducting phase in La_2CuO_{4+x} at ambient temperature by electrochemical oxidation over the nominal composition range $0< x <0.1$. A stable superconducting phase with T_c ~32-34 K is observed for $x \leq 0.05$. In contrast, samples with $x > 0.05$ are found to be unstable either at room temperature or upon annealing between 298 K and 383 K..

Bennett et al.[101] demonstrated a new electrochemical process which is reversible to some degree and allows reproducible control over the superconducting properties of La_2CuO_4 at room temperature. They used an electrochemical cell of the type:

$$La_2CuO_4 \ / \ H^+ \ (0.005\ N\ H_2SO_4 \text{ in methanol}) \ / \ Pt$$

in which La_2CuO_4 is the working electrode and platinum wires served as the reference and counter electrodes. The cell anode was held at

+1.6 V with respect to the Pt electrode. The total duration of polarization, including the relaxation periods, ranged from 50 to 150 h.

In 1996 Chou et al.[102] synthesized large single crystals of La_2CuO_{4+x} by using an electrochemical process in 1M NaOH. The oxidation took place at room temperature and continued for two months. Neutron scattering studies of these crystals reveal that the oxygen- rich phases in these crystals have a structure different from that observed in undoped or Sr-doped La_2CuO_4.

Lees et al.[103] carried out room temperature chemical oxidation on four La_2CuO_4 thin films using an aqueous sodium hypobromite solution. They combined the seemingly disparate techniques of pulsed laser ablation and aqueous room temperature chemical oxidation to provide a versatile, facile method for producing superconducting La_2CuO_{4+x} thin films.

Scarfe et al.[104] reported an electrochemical oxidation technique was used to obtain bulk oxidized La_2CuO_{4+x} single crystals from the as grown crystals. Samples were prepared by galvanostatic oxidation with current in the range 5-10 μA and different charging times. Some samples were annealed at 383 K in flowing oxygen. The quality of the crystals was evaluated by transmission X-ray Laue photography, and by measuring rocking curves for several fundamental peaks.

Copper containing oxides with perovskite- related structures have been known where the oxygen atom (oxide ion) can be intercalated into the perovskite structures when they were used as an electrode for water electrolysis at room temperature.[105] So, electrochemists tried to dope the oxygen in $YBa_2Cu_3O_7$ when this 90K class superconductor was found in 1987. However, this oxide was too unstable to be dealt with in a wet atmosphere. La_2CuO_4, on the contrary, is relatively stable to water and incorporates oxygen in the lattice according to the electrode reaction.

Earlier studies of the aqueous electrochemistry and the dissolution behavior of $Ba_2YCu_3O_7$,[106] as typical of the cuprates, have clearly indicated this instability to attack in aqueous media and the ready reducibility of such cuprates.[107] Here, La_2CuO_4 surface reactions in the unoxidized compound have also been examined by electrochemical techniques in aqueous media under open circuit conditions at 298K. Rotating ring-disk electrode (RRDE) techniques were employed in both collection (detection of products) and shielding (monitoring removal of reactants) modes to follow the surface chemistry.

The ring results can lead to conclusions regarding the stoichiometry of the dissolution reactions.[106-108] Separately, in basic solution, the coulombic efficiency and rate of formation of the superconductor phases could be determined by monitoring the oxygen evolution rate which is in competition with superconductor formation.

The rotating ring-disk electrode (RRDE) is an extension of the rotating disk electrode in which the disk is encircled by a ring of conductive material that functions as a second working electrode. The disk is used to electrochemically generate or remove a reactive species which is electrochemically monitored as it is swept by laminar flow past the ring.

The RRDE, as originally conceived by Levich, Frumkin, and co-workers,[109-111] provides the chemist with a powerful methodology for studying complicated chemical as well as electrochemical reactions. The capability of a RRDE's ring electrode to detect, virtually simultaneously, species generated at the disk electrode provides an elegant and convenient solution to this analytical problem.[108] In addition, the rigorously defined mathematics of the RRDE geometry makes it possible to distinguish between faradic (electron transfer) and non-faradic processes. Also this system allows an accurate description of the rate of the electron transfer process occurring at the electrode surface as a function of measurable physical properties. This results from the rotating disk geometry permiting precise hydrodynamic control of the flux to and from a reacting surface, and thereby providing a unique experimental variable.

The advantage of using this technique is that a steady state is attained rather quickly and measurements can be made with high precision. In addition, at steady state, double-layer charging does not enter the measurement. Also, the rates of mass transfer at the electrode surface in this method are much larger than the rate of diffusion, so that the relative contribution of the effect of mass transfer to the electron transfer kinetics is both smaller and controllable.

In the RRDE, the current–potential characteristics of the disk electrode are unaffected in flow by the presence of the ring. Since RRDE experiments involved the examination of two potentials (that of the disk, E_D, and that of the ring, E_R,) and two currents (disk, i_D, and ring, i_R), the representation of the results involves more dimensions than that of experiments involving a single working electrode. RRDE experiments are usually carried out with a bipotentiostat , which allows separate adjustment of E_D and E_R. However, since most RRDE experiments involve steady-state conditions, it is possible in principle to use an ordinary potentiostat to control the ring circuit and a simple floating power supply in the disk circuit. Several different types of experiments are possible at the RRDE; the most frequently are used collection experiments, where the disk generated species is observed at the ring, and shielding experiments, where the flow of bulk electroactive species to the ring is perturbed because of the disk reaction.

The advantages of the RRDE shielding technique have been less exploited than those of collection, and there are a variety of difficult-to-follow heterogeneous chemical processes whose equilibrium and kinetic parameters become readily accessible by this means. We have used both in our study of the surface reactions in the La_2CuO_4 system.

I.5- Aim of the work:

The field of superconductivity has moved into the realm of applied science in recent years. Even more applications may become possible because of the discovery of high-temperature superconductors. This thesis studied two systems, first the Bi-Sr-Ca-Cu-O (BSCCO) system, which has many advantages than other superconducting compounds, and the second is the La_2CuO_4 system. The work was aimed to study different parameters, which may play important role in the preparation of Bi-Sr-Ca-Cu-O (BSCCO) system, to improve the T_c of the superconducting phase. Also understanding the chemical behavior of La_2CuO_4 system by using the electrochemical methods. To achieve these goals the next steps have been followed;

I.5-i- Bi-Sr-Ca-Cu-O system:

a- Different compositions of Bi-Sr-Ca-Cu-O have been prepared.

b- Different heat treatments were applied to study their effects on the formation of superconductor phase.

c- The effects of lead doping and barium doping have been studied.