

SYNOPSIS

During the course of our work on $\text{YBa}_2\text{Cu}_3\text{O}_7$ we, found that a softer heat treatment (ie, at lower temperatures and for smaller durations) gave much better products, in terms of homogeneity of the material, rapid reactivity, ease of oxygen pick up and also the sintering kinetics. Furthermore, by using this method we get many off-stoichiometric compositions into a single phase and thus we are able to get a host of new single phase compositions in our hands. It has indeed been interesting to study the detailed properties of these materials. This thesis presents the results of these studies.

The thesis is divided in four chapters. The first chapter gives a brief account of the physics of superconductors. In chapter II a detailed literature survey on high T_c oxide superconductors is presented. This chapter also includes a review on the different techniques of preparation that have been commonly used as also the literature on the study of phase equilibria in (Y-Ba-Cu-O) system and the role of oxygen intercalation in these materials. Chapter III describes the experimental techniques used in our studies and chapter IV includes the results obtained as well as discussions thereon.

Conclusions, references and the summary are given

in the end.

The materials under investigation have been prepared using the **ONE-STEP** method as described below:

In this procedure the required ingredients namely, Y_2O_3 (99.9%), $BaCO_3$ (99.9%) and CuO (99.9%) are weighed as per the required proportion. They are mixed in a ballmill for 15-20 hours by using an organic medium such as acetone or carbon tetrachloride. This homogeneous mixture is then dried in an oven at about $80^{\circ}C$. This mixed product is then pelletised as in the conventional preparation route (with or without using an organic binder). Pellets of diameter ranging between 6 mm and 50 mm and thickness between 2 mm and 6 mm are pressed in a hydraulic press by applying a pressure between 2-5 tons/inch².

These pellets are then mounted on a platinum foil or alumina tray on the bed of a thin layer of the powder of same composition as the pellet. This is then introduced in the furnace having an attachment to provide the required atmosphere (air/ O_2). It is worth noting here that unlike the conventional ceramic materials, the particle size does not have considerable impact on the sintering temperature of these new superconducting materials, possibly due to the fact that the sintering goes partially through a liquid phase. In this improved process the conventional prefiring step is

completely omitted instead, we heat the pellets slowly ($100^{\circ}\text{C}/\text{hour}$) till the required temperature. The furnace temperature is then arrested at the required temperature by using an Aplan temperature controller (accuracy $\pm 5^{\circ}\text{C}$). Furnace is then cooled in air/ O_2 atmosphere. The cooling rate is maintained between 60 and $100^{\circ}\text{C}/\text{hour}$. The cooling is arrested at about 450°C for 1-2 hours. The samples as prepared by the above mentioned technique were examined by

- (a) X-ray powder diffraction analysis
- (b) Resistivity versus temperature by the four probe technique
- (c) Paramagnetic Susceptibility
- (d) Photoelectron Spectroscopy
- (e) Scanning Electron Microscopy
- (f) Transmission Electron Microscopy
- (g) Oxygen determination by volumetric method

The most significant result is that we have been able to form single phase compounds at compositions other than the well-known 1:2:3 composition. The single phase region is shown shaded in the enclosed figure. The compositions which have been studied are given in the following Table(1). The letters A-J indicate their position in the figure.

TABLE-1

	CHEMICAL FORMULA	ABBREVIATED SYMBOL
A	$Y_2Ba_3Cu_5O_x$	2:3:5
B	$YBa_2Cu_3O_x$	1:2:3
C	$Y_5Ba_{11}Cu_{16}O_x$	5:11:16
D	$Y_4Ba_9Cu_{13}O_x$	4:9:13
E	$Y_3Ba_7Cu_{10}O_x$	3:7:10
F	$Y_2Ba_5Cu_7O_x$	2:5:7
G	$YBa_3Cu_4O_x$	1:3:4
H	$Y_3Ba_8Cu_{12}O_x$	3:8:12
I	$Y_2Ba_6Cu_9$	2:6:9
J	$YBa_4Cu_6O_x$	1:4:6

Out of these compositions listed in the above table three compositions were studied in greater details namely, (I) $Y_3Ba_7Cu_{10}O_x$ (3:7:10)

(II) $Y_2Ba_6Cu_9O_x$ (2:6:9)

(III) $YBa_4Cu_6O_x$ (1:4:6)

The following studies have been made on all these compositions :

(A) EFFECT OF SINTERING TEMPERATURE

All these compositions were sintered at different temperatures ranging from 880 to 1000°C. It is found that for each composition there is an optimum temperature range which is quite narrow. Below this, the

reaction rate is very slow and above this the composition starts melting incongruently. These temperature ranges are discussed and described in the thesis.

(B) EFFECT OF SINTERING TIME

The reaction as well as sintering improves with sintering time upto a point beyond which there is no significant improvement. This optimum time generally ranges between 10-15 hours for all these compositions.

(C) EFFECT OF QUENCHING TEMPERATURE

During the preparation of the sample, after the desired hours of sintering was complete the sample was slowly cooled ($2^{\circ}\text{C}/\text{min}$) to a temperature 'T' at which temperature the sample was suddenly dropped in liquid nitrogen bath to quench it. In this way samples quenched with different oxygen content and different crystal structures have been obtained. Their structural and electrical properties have been studied and the results are given in the thesis. Some typical results are reproduced below:

The lattice parameters and the unit cell volume for samples sintered for 13 hours and quenched at various temperatures are listed in Table(2) below.

TABLE-2

PHASE	TEMPERATURE (°C) FROM WHICH QUENCHING WAS DONE					
	900	800	700	600	500	400
	Tet	OrthII	OrthI	OrthI	OrthI	OrthI
a(A°)	3.852	3.825	3.825	3.829	3.816	3.802
b(A°)	3.852	3.868	3.895	3.894	3.894	3.871
c(A°)	11.740	11.708	11.684	11.682	11.682	11.613
V(A ³)	174.19	173.22	174.07	174.18	173.59	170.92

Tables(3) and (4) describe, respectively, the effect of quenching temperature and time of sintering on the electrical behaviour of the composition Y₃Ba₇Cu₁₀O_x prepared by sintering at 940°C.

TABLE-3

EFFECT OF QUENCHING TEMPERATURE

ELECTRICAL STATE	TEMPERATURE (°C) FROM WHICH QUENCHING WAS DONE					
	900	800	700	600	500	400
M/S* at RT	S	S	S	S+M	M	M
SC* above liq.N ₂	NO	NO	NO	NO	NO	YES
T _c (K)	---	---	---	---	72K	94.5K
R at RT (mΩ)	0.8	0.55	0.60	0.22	0.11	0.023

* M=Superconducting S=Semiconducting

SC=Superconducting

TABLE-4

EFFECT OF TIME OF SINTERING

ELECTRICAL STATE	TIME OF SINTERING (IN HOURS)							
	1	3	6	9	13	15	18	40
M/S at RT	S+M	S+M	S+M	M	M	M	M	M
SC.above liq.N ₂	YES	YES	YES	YES	YES	YES	YES	YES
T _C (K)	88.5	88.5	88.5	90.0	94.5	94.0	94.0	94.0
R at RT (mΩ)	0.72	0.70	0.60	0.58	0.24	0.24	0.24	0.24

The key observations of the extensive study are given below :

(A) Single phase compounds are possible at compositions other than the standard 1:2:3 if the preparation conditions are controlled appropriately.

(B) The solid state reaction involved in the formation of these single phase compounds seems to be 95% completed in as a short period as 1 hour. Another interesting observation is that some residual BaCO₃ which remains behind after heating at 940°C seems to go away on annealing at 400°C.

(C) An examination of the variation of the lattice parameters with composition reveals that compositions in the range of C to E (see figure) have lower 'c' and 'V' than the standard 1:2:3. This is known to be indicative of higher Cu³⁺ content and thereby better

superconductivity.

(D) The changes in the superconducting properties with changes in the O₂ concentration (as achieved by changing the quenching temperature) seems to be parallel with what is known for 1:2:3.

(E) The electrical properties of tetragonal + orthorhombic mixed phases as obtained by controlling the quenching temperature show interesting mixture of metallic, semiconducting and superconducting properties. This is strongly indicative of percolative conductivity with considerable amount of O₂ inhomogeneity in the samples. There are pockets of samples with intercalated oxygen ranging from nearly zero to 0.5 per formula unit.

(F) Attempts to form new Y-deficient structural phases have succeeded. $Y_{1/2}Ba_2Cu_3O_{7+}$ and $Y_{2/3}Ba_2Cu_3O_{7+}$ have been successfully prepared with structure isomorphous to 1:2:3. These compounds are superconducting with T_C between 90-92K. No ordering is, however, observed, instead Ba and Cu ions move and occupy the vacant Y sites.

(G) Photoelectron spectroscopic studies show that the oxygen gives three peaks more or less similar to 1:2:3. The first peak which appears at a binding energy of 529 eV is attributed to the lattice O²⁻. The second peak which is observed at 531.5 eV has been attributed to O¹⁻ by some authors while some have attributed it to the adsorbed (OH)⁻¹ ions or carbonate (CO₃)⁻² ions. This

assumption is based on the fact that some of the barium carbonate might have remained unreacted or some BaO might be picking up carbon dioxide or moisture from atmosphere. This carbonate may give rise to the above mentioned second peak. The third peak present at 533.3eV has been attributed to peroxy ions $(O_2)^{-2}$ by the majority of workers, however some authors have reported it to be due to the adsorbed foreign species.

It is widely reported that the peak III grows with decreasing temperature at the cost of peak I. However, our observation is that for a good superconductor the peak III grows at the cost of peak II and in a less oxygenated sample or a nonsuperconducting sample the peak III grows at the cost of peak I. However we are intrigued to find the presence of peak III in nonsuperconducting samples at room temperature as well as liquid nitrogen temperature.

XPS analysis of compositions 1:4:6 and 2:6:9 have also shown similar behaviour.

In regard to oxygen II peak we do not think that the experimental evidences are conclusive enough to attribute it to O^{1-} or for that matter oxygen III peak to peroxy ion $(O_2)^{2-}$. The subject is still open and needs further investigation. The position looks far more complicated more particularly in view of a recent finding in our laboratory that in case of superconducting $Bi_2Sr_2CaCu_2O_8$ there is only a single

oxygen peak (XPS).

However, the correlation between the intensities of the three oxygen peaks I,II,III may be an important factor, deciding the superconductivity in these oxide systems, and the reason for this may be worth exploring.

(H) In case of non isovalent substitution, the oxygen content in the unoxidised form is less than 6.5 e.g. 6.28 for 1:4:6 and 6.35 for 2:6:9. Following the behaviour of 1:2:3 it was expected that 1:4:6 would pick up 0.72 to come to [O]=7 in the fully oxidised form and 2:6:9 would pick up 0.65 to come to [O]=7. However this does not happen. In each case, the oxygen intercalated (Δx) is 0.5 only. So $Y_{0.55}Ba_{2.18}Cu_{3.27}O_{6.28}$ goes to $Y_{0.55}Ba_{2.18}Cu_{3.27}O_{6.78}$ only and $Y_{0.71}Ba_{2.12}Cu_{3.18}O_{6.35}$ goes to $Y_{0.71}Ba_{2.12}Cu_{3.18}O_{6.85}$ only although the structure can accommodate more oxygen to become isomorphous with 1:2:3. The $\Delta x=0.5$ means that the oxidation number goes up by 'one' per unit cell. The singular ion in the unit cell happens to be the Cu^{2+} in the chain. Thus an oxidation of $Cu^{2+} \xrightarrow{+h} Cu^{3+}$ in the chain is visualised to take up before the material becomes superconducting. This, however, does not imply that superconductivity takes place in the chain. To the contrary, we also feel that superconductivity takes place in the $(CuO_2)_\infty$ planes, but the initial oxidation takes place in the chain as shown above and this

triggers the superconductivity in the plane.

(I) Another point worth noting is that when full superconductivity is obtained at $[O] \approx 7$ then at that stage the Cu-O-Cu chains are not complete in the b direction and there would be several interruptions. In spite of that, we got superconductivity. This again underscores the fact that superconductivity indeed takes place in the $(CuO_2)_\infty$ planes and not in the $(CuO)_\infty$ chains.