

## Superconductivity in compound $Y_{1-2x}Ce_xBa_{2+x}Cu_3O_{6.5+\delta}$ system

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**Abstract.** Partial substitution of Ce in place of Y has been achieved by taking care of charge compensation and compounds with the general formula  $Y_{1-2x}Ce_xBa_{2+x}Cu_3O_{6.5+\delta}$  have been successfully prepared. X-ray powder diffraction analysis reveals that this substitution gives orthorhombic single phase for  $0 \leq x \leq 0.3$ . The  $T_c$  remains nearly unchanged between 94-90 K.

**Keywords.** Charge compensation; X-ray diffraction analysis; oxygen content.

### 1. Introduction

Following the announcement of high  $T_c$  superconductivity in Y-Ba-Cu-O system (Wu *et al* 1987) and identification (Raychaudhari *et al* 1987) of the superconducting phase to be  $YBa_2Cu_3O_7$ , many attempts have been made to substitute Y ion by other trivalent ion and see the effect of such a substitution on the superconducting properties. Y has been successfully replaced by several rare earth ions such as La, Nd, Sm, Eu, Gd, Ho, Er, Lu (Hor *et al* 1987). A few exceptions like Ce, Pr, Tb etc. were recorded.

Liang *et al* (1987) investigated the effect of substitution of  $Ce^{4+}$  at Y site so as to increase the oxygen content due to the tetravalent nature of Ce. However, they have come to the conclusion that more than 5% Ce could not be substituted. They further observed that even 5% cerium suppresses  $T_c$ . Investigations by Pena *et al* (1988) also indicate non-superconducting phase (up to 77 K) in the Ce-substituted Y-Ba-Cu-O system. The results on soft X-ray absorption spectroscopy by Sladeczek *et al* (1988) indicate that Ce is present in the  $4^+$  state.

These studies apparently indicate that one of the reasons for our inability to replace Y by Ce in the orthorhombic 1:2:3 phase due to the tendency of Ce to be present as  $Ce^{4+}$ . It was therefore thought that a better chance of forming the desired compound with Ce substitution is by balancing the charge by substituting two trivalent ions by one tetravalent and one divalent ion e.g.  $2Y^{3+}$  substituted by  $1Ce^{4+} + 1Ba^{2+}$ . Correspondingly, the general formula after such a substitution would be  $Y_{1-2x}Ce_xBa_{2+x}Cu_3O_y$ . A series of compounds with  $0 \leq x < 0.5$  were investigated and the results of this investigation have been reported in this paper.

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## 2. Experimental

The samples were prepared using the standard ceramic technique. Ultra-fine powders of yttria, barium carbonate, copper oxide and cerium oxalate used for the preparation of the samples were weighed in the proper stoichiometric ratios on a single pan balance with an accuracy of 0.01 mg. Different stoichiometric compositions were prepared in batches of 8–10 g. The powders were thoroughly mixed using an agate pestle and mortar in an organic medium such as acetone and dried under IR lamp to remove traces of organic liquid. The powders were pre-fired in platinum crucibles at  $860 \pm 10^\circ\text{C}$  for 6 h in air in an electric furnace. The reacted mass was pulverized and again ground to a fine powder using an agate pestle and mortar. This pre-firing cycle was repeated thrice to get better reaction and the fine powders were pelletized in the form of discs of (8 mm diameter, 2 mm thickness) under a pressure of  $8 \times 10^6 \text{ kg/m}^2$ . The pellets were heated slowly to  $400^\circ\text{C}$  and the temperature was raised to  $930 \pm 10^\circ\text{C}$  in 3 h. This was maintained for 9–13 h and then cooled slowly at the rate of  $60^\circ\text{C/h}$ . Sintering and annealing were done in air atmosphere.

The following compositions were systematically studied:

Table 1. Compositions under investigation.

No.	X	Composition
A	0.1	$\text{Y}_{0.8}\text{Ba}_{2.1}\text{Ce}_{0.1}\text{Cu}_3\text{O}_{6.5+\delta}$
B	0.2	$\text{Y}_{0.6}\text{Ba}_{2.2}\text{Ce}_{0.2}\text{Cu}_3\text{O}_{6.5+\delta}$
C	0.3	$\text{Y}_{0.4}\text{Ba}_{2.3}\text{Ce}_{0.3}\text{Cu}_3\text{O}_{6.5+\delta}$
D	0.4	$\text{Y}_{0.2}\text{Ba}_{2.4}\text{Ce}_{0.4}\text{Cu}_3\text{O}_{6.5+\delta}$

X-ray powder diffraction analysis was carried out using a Philips X-ray diffractometer with  $\text{CuK}_\alpha$  radiation as a source. The diffraction was scanned for  $2\theta$  from  $22^\circ$  to  $50^\circ$  to see the monophasic 1:2:3 nature and to calculate the lattice parameters.

As is known the superconducting properties of these oxide materials critically depend on the oxygen content of the material and therefore it was necessary to determine this parameter. This was done by using volumetric method (Sinha *et al* 1987). The powdered material, when treated with dil- $\text{HNO}_3$ , reacts with it and Ba and Cu become  $\text{Ba}(\text{NO}_3)_2$  and  $\text{Cu}(\text{NO}_3)_2$  whereas Y and Ce precipitate as  $\text{Y}_2\text{O}_3$  and  $\text{CeO}_2$  resulting in a gaseous evolution of  $\delta/2$  moles of  $\text{O}_2$ . From the volume of the evolved oxygen one can calculate the total oxygen content per formula unit. Measurements were done at a constant ambient temperature and pressure in a calibrated glass volumetric unit.

Resistivity was measured as a function of temperature using the standard four-probe technique. A Keithley 220 instrument was used as a constant current source and the voltages at different temperatures were measured using a Keithley 181 Nanovoltmeter. A Pt-100 platinum resistance thermometer was used for temperature measurement.

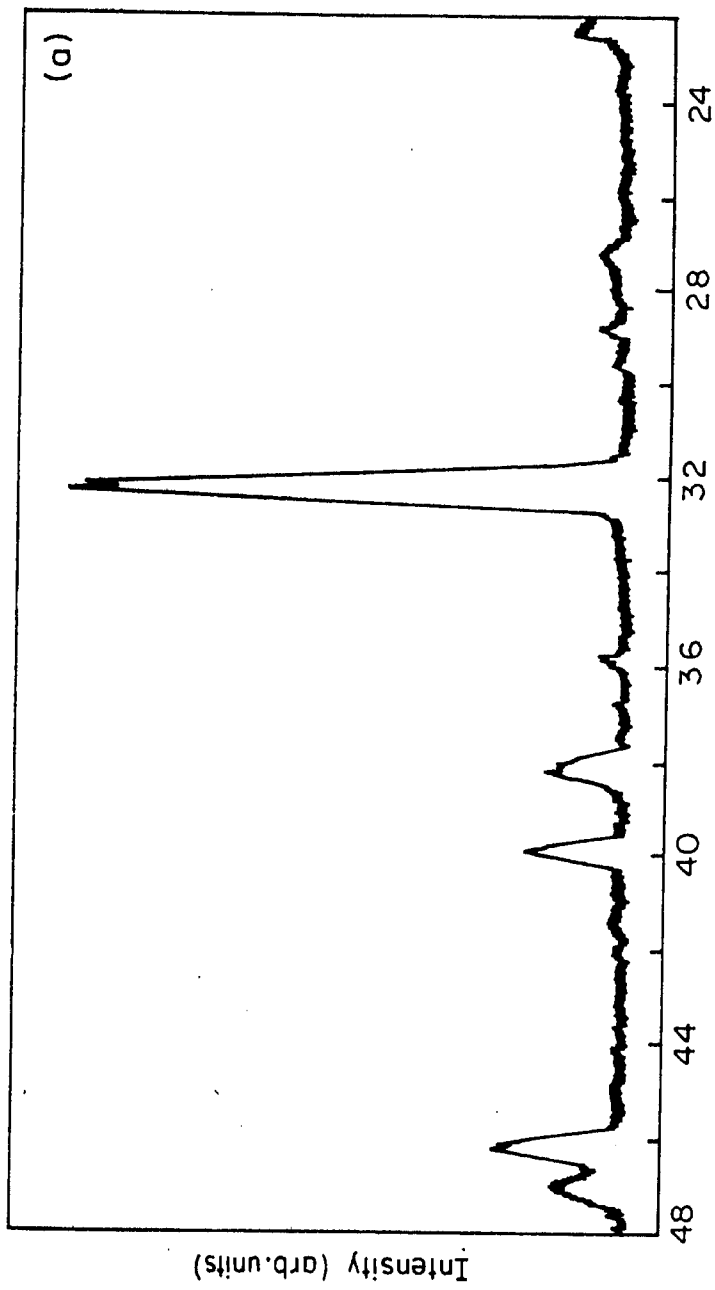


Figure 1. Powder X-ray diffraction pattern for a.  $Y_{0.8}Ba_{2.1}Ce_{0.1}Cu_3O_{6.5+\delta}$ .

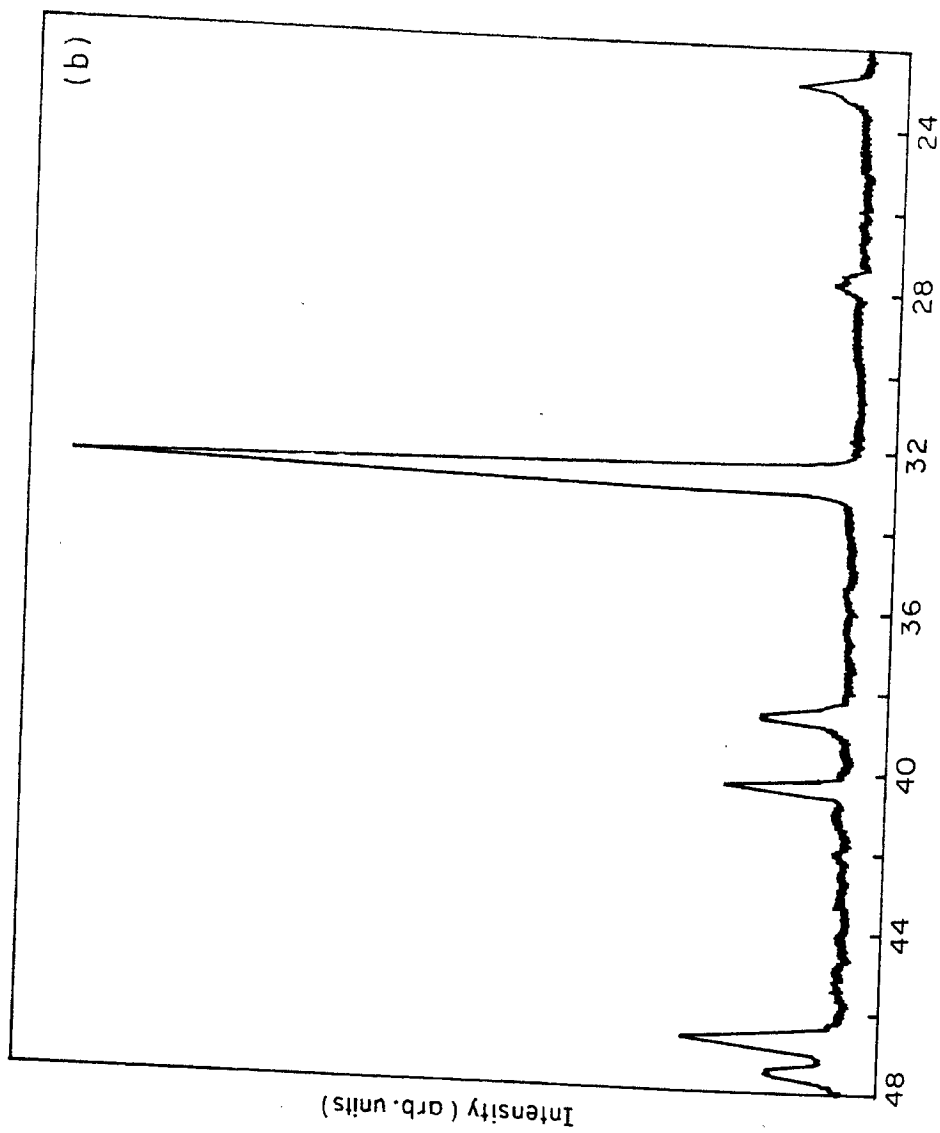


Figure 1b.  $Y_{0.6}Ba_{2.2}Ce_{0.2}Cu_3O_{6.5+x}$

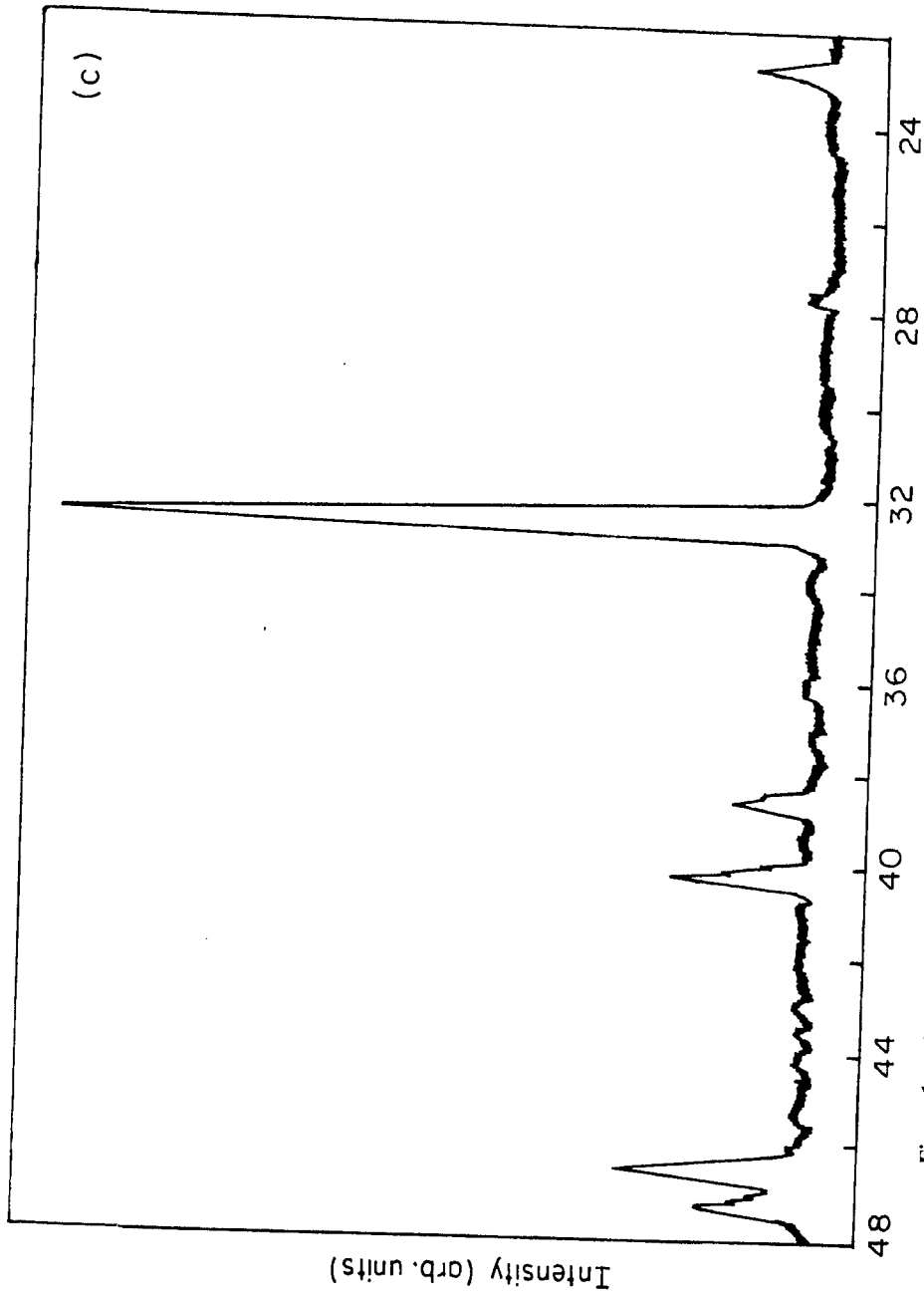


Figure 1c.  $Y_{0.4}Ba_{2.3}Ce_{0.3}Cu_3O_{6.5+\delta}$

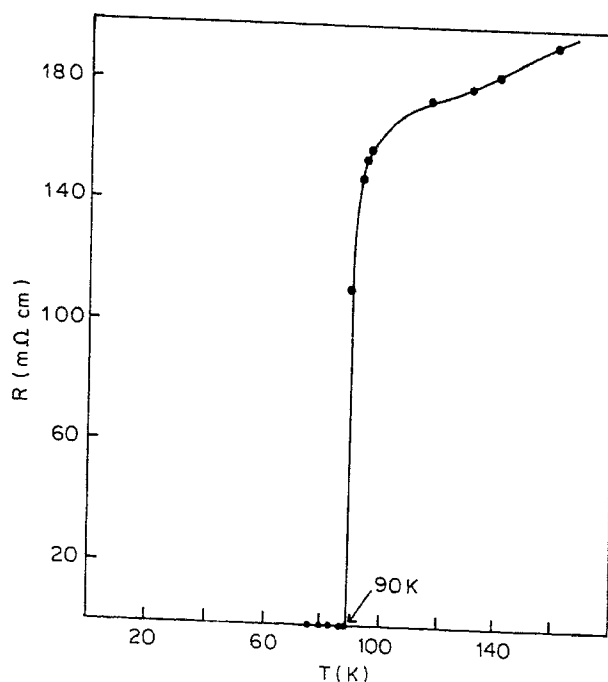
### 3. Results and discussion

X-ray powder diffraction patterns for samples A, B and C are shown in figure 1. The patterns corresponding to compositions A, B and C (i.e.  $0.1 \leq x \leq 0.3$ ) can be indexed on the basis of a single-phase orthorhombic 1:2:3 compound with lattice parameters as indicated in table 2. However, the composition corresponding to  $x = 0.4$  (sample D) shows the presence of additional phases. The diffraction lines for all samples are somewhat broader and therefore a separation between (110), (103) and (013) is not visible but that between (006), (020) and (200) is clearly seen. A progressive decrease of intensity of 005 is consistent with the progressive occupation of Y site by higher atomic number atom which in this case is most possibly Ce. This would support that Ce has indeed gone in solid solution. The unit cell parameters are found to decrease with increasing Ce concentration in the range of  $0.1 \leq x \leq 0.3$ .

The oxygen content per formula cell is also found to decrease with increasing Ce concentration (table 2).

**Table 2.** Oxygen content and unit cell parameters for  $Y_{1-x}Ce_xBa_{2+x}Cu_3O_y$ , with  $0.1 \leq x < 0.4$ .

No.	Composition	Oxygen content per formula cell			
		Unit cell parameter			
A	$Y_{0.8}Ba_{2.1}Ce_{0.1}Cu_3$	6.9	3.84	3.90	11.71
B	$Y_{0.6}Ba_{2.2}Ce_{0.2}Cu_3$	6.85	3.84	3.90	11.71
C	$Y_{0.4}Ba_{2.3}Ce_{0.3}Cu_3$	6.7	3.83	3.90	11.69



**Figure 2.** Resistivity as a function of temperature for  $Y_{0.4}Ba_{2.3}Ce_{0.3}Cu_3O_{6.5+\delta}$ .

The transition temperatures as noted in the resistivity data show that it decreases very slightly from 94 to 90 on going from  $x=0$  to  $x=0.3$ . A specimen resistivity vs temperature graph for  $x=0.3$  sample is shown in figure 2. The transition temperature is noted to be  $90^{\circ}\text{K}$ .

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