

## Effect of substitution at the barium site in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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**Abstract.** The oxygen content in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  has been varied by substitution at Ba site with Sr or K and its influence on the structural and superconducting properties has been studied. These properties are compared with that of unsubstituted  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  prepared by quenching. The increase in  $\delta$  value of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  decreases the  $T_c$  drastically, whereas in  $\text{YBa}_{2-x}\text{K}_x\text{Cu}_3\text{O}_{7-\delta}$  system increase in the  $\delta$  value (as high as 0.92) does not affect the superconducting transition temperature, which remains above 77 K. In the  $\text{YBa}_{2-x}\text{Sr}_x\text{Cu}_3\text{O}_{7-\delta}$  system, as Sr content increases there is marginal decrease in the oxygen content as well as in the superconducting transition temperature.

**Keywords.**  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ; structural properties; superconducting properties.

### 1. Introduction

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and related oxides have been extensively studied to understand the superconducting phenomenon (Rao 1988a; Holland and Stacy 1988; Beyers and Shaw 1989). The crystal structure and superconducting transition temperature ( $T_c$ ) are controlled by the oxygen non-stoichiometry ( $\delta$ ) in these 123 oxides. Orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_7$  is a superconductor with  $T_c$  of 90 K. It has an oxygen vacancy ordered triple perovskite structure. The tripling of the  $c$ -axis occurs because of the ordering of the Y and Ba atoms (figure 1a). There are two Cu sites, the Cu(1) being four coordinated making chains of corner shared square-planar  $\text{CuO}_4$  units running along the crystallographic  $b$ -axis, and the Cu(2) are five coordinated forming layers of  $\text{CuO}_5$  square-pyramids (corner shared) perpendicular to the  $c$ -axis. The Cu–O–Cu bonds are bent in these layers. The Y atoms are placed between these puckered Cu–O

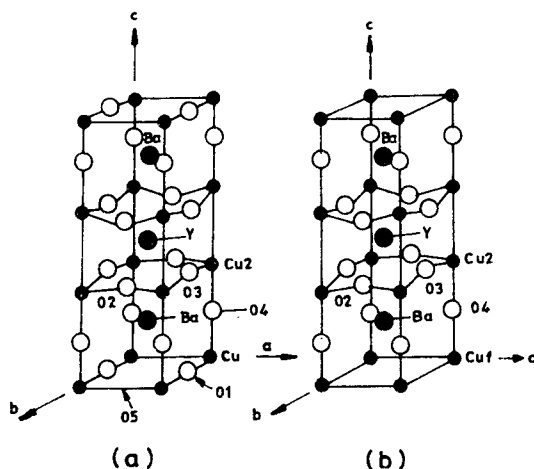


Figure 1. Crystal structure of (a)  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (orthorhombic) and (b)  $\text{YBa}_2\text{Cu}_3\text{O}_6$  (tetragonal).

layers. The orthorhombicity in this oxide is attributed to the ordering of the oxygen atoms preferentially on the O(1) sites leaving the O(5) sites empty. The  $\text{YBa}_2\text{Cu}_3\text{O}_6$  oxide has oxygen atoms neither at O(1) nor at O(5) sites (figure 1b) and crystallizes in a tetragonal structure. The structure of the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  oxides, having intermediate oxygen content, depends crucially on the order/disorder of oxygen between the O(1) and O(5) sites which influences the superconducting behaviour (Jorgensen *et al* 1987; Rao 1988b). The preparation condition influences the ordering/disordering of oxygen atoms at the O(1) and O(5) sites (Gallagher *et al* 1987; Farneth *et al* 1988).

It is known that the oxygen content in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  can be varied (Kanno *et al* 1987; Kwok *et al* 1988; Liang and Nakamura 1988). The effect of oxygen content on the structural and superconducting properties is well established (Cava *et al* 1987; Gallagher *et al* 1987). In the present study the oxygen content in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  has been varied by substitution at Ba site which is proximate to Cu–O planes and chains with Sr or K, and its influence on the structural and superconducting properties has been studied.

## 2. Experimental

The 123 oxides were prepared by solid state reaction from the corresponding stoichiometric amounts of  $\text{Y}_2\text{O}_3$ , CuO,  $\text{BaCO}_3$  ( $\text{SrCO}_3$  or  $\text{K}_2\text{CO}_3$ ). The Sr substituted systems were given heat treatment using an alumina crucible at 1203 K in air for 24 h. The pellets of the resulting compound were heated at 1153 K in oxygen for 24 h.

Stoichiometric amounts of  $\text{Y}_2\text{O}_3$ , CuO,  $\text{BaCO}_3$  and  $\text{K}_2\text{CO}_3$  were mixed thoroughly and made into pellets. These pellets were heated at 1153 K for 24 h in air with intermittent grinding and repelletizing. The final heat treatment was carried out at 1103 K in oxygen for 24 h. (To avoid potassium diffusion into the alumina crucible, the crucible which was used for the preparation of pure  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  was used again, i.e. the crucible was coated with  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ).

The systems  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  with different  $\delta$  values were prepared by quenching method. The stoichiometric amounts of  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$  and CuO were thoroughly mixed and heated at 1223 K for 24 h with intermittent grinding. After cooling to room temperature, the powder samples were pelletized. The pellets were heated at 1173 K in flowing oxygen for 6 h and then cooled to different quenching temperatures ( $T_q$ ): 673, 773, 873, 973, 1073 and 1173 K. After heating at these temperatures in flowing oxygen for 12 h the samples were quenched to liquid nitrogen temperature. All the samples were kept in a desiccator, since these oxides are sensitive to moisture and  $\text{CO}_2$ .

Powder X-ray diffraction studies were carried out on a Phillips diffractometer (model PW1140). Lattice parameters were obtained by a least squares fitting procedure. The oxygen contents were evaluated by oxygen evolution (Kawamura and Hiratani 1987) and iodometric (Harris and Hewston 1987) methods. Superconducting transition temperatures of the sintered pellets were obtained from d.c. four probe resistivity method (Pragasam *et al* 1990).

### 3. Results

The lattice parameters and orthorhombicity ( $\epsilon$ ), which is defined as  $\epsilon = 2(b - a)/a + b$  (where  $a$  and  $b$  are the lattice parameters), are given in table 1. The variation of lattice parameters and cell volume with strontium content  $x$ , is shown in figure 2. The lattice parameters decrease with increase in Sr content. There is drastic decrease in the lattice parameter  $c$  compared to  $a$  and  $b$  especially for Sr content  $x \leq 0.6$ . This is due to geometrical considerations. A similar observation was made by Ono *et al* (1987), where the lattice parameter  $c$  was found to decrease drastically for  $x \leq 0.5$ , but was nearly constant for systems with  $x > 0.5$ . This was attributed to smaller size of  $\text{Sr}^{2+}$  (1.12 Å) compared to  $\text{Ba}^{2+}$  (1.35 Å) which has pronounced effect on  $c$  parameter because the lattice parameter  $c$  is approximately three times  $a$  or  $b$ . It appears that the system attains maximum contraction at Sr content  $x \approx 0.6$ .

The oxygen non-stoichiometry ( $\delta$ ) measured by oxygen evolution and iodometry are given in table 1. The  $\delta$  values are found to be  $0.17 \pm 0.02$  but for the system with  $x = 1.0$ , where the  $\delta$  value is 0.33. The resistivity versus temperature plots for the Sr substituted systems are shown in figure 3. The  $T_c$  values, also given in table 1, decrease marginally with increase in Sr content.

The  $\text{YBa}_{2-x}\text{K}_x\text{Cu}_3\text{O}_{7-\delta}$  system forms a single phase for  $x \leq 0.6$ . Felner *et al* (1988) also made a similar observation for the compounds  $\text{LnBa}_{2-x}\text{K}_x\text{Cu}_3\text{O}_{7-\delta}$ , where  $\text{Ln} = \text{Y, Eu or Pr}$  and  $x = 0.5$  or  $1.0$ . They observed that only oxides with  $x$  value 0.5 form a single phase. However, Rajarajan *et al* (1988) have reported maximum solubility up to  $x = 1.4$  for the compound  $\text{YBa}_{2-x}\text{K}_x\text{Cu}_3\text{O}_{7-\delta}$ .

The values of lattice parameters and orthorhombicity are given in table 2. These oxides crystallize in orthorhombic symmetry but the extent of orthorhombicity decreases with increase in K content. This variation is seen in figure 4, where the lattice parameters are plotted against the K content,  $x$ . It is seen that the lattice parameter  $a$  increases with increase in  $x$  and approaches  $b$  at  $x \approx 1.0$ . This indicates a phase transition from orthorhombic to tetragonal symmetry. However the lattice parameters  $b$  and  $c$  remain unchanged.

The oxygen non-stoichiometry values of these oxides are given in table 2. There is considerable increase in the  $\delta$  value with potassium content. This is attributed to the electronic effect, i.e. charge compensation for the monovalent potassium since it decreases the total cationic charge. Therefore, total oxygen intake decreases with increase in potassium content. The resistivity versus temperature for the K substituted systems are shown in figure 5. The  $T_c$  values for these oxides are found to decrease with increase in potassium content but, interestingly, remain above liquid nitrogen temperature (77 K). These results suggest that such a drastic increase in the value of  $\delta$  does not seem to affect the superconducting transition temperature.

The lattice parameters and orthorhombicity ( $\epsilon$ ) values of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  with different  $\delta$  values prepared by quenching are given in table 3. The variation in lattice parameters and cell volume with temperature of quenching ( $T_q$ ) is shown in figure 6. The lattice parameters and hence cell volume increase with increase in  $T_q$  indicating dilation of the unit cell. These oxides are orthorhombic and orthorhombicity remains constant. This is expected since the orthorhombic to tetragonal phase transition occurs only for samples with  $\delta$  value greater than 0.60 (Specht *et al* 1988).

Table 1. Structural parameters of  $\text{YBa}_{2-x}\text{Sr}_x\text{Cu}_3\text{O}_{7-\delta}$ .

Compounds	Lattice parameters (Å)			Cell volume (Å) <sup>3</sup>	Orthorhombicity $\epsilon = 2(b-a)/a+b$	Oxygen non-stoichiometry ( $\delta$ ) by		Superconducting transition temp. $T_c$ (K)
	a	b	c			O <sub>2</sub> evolution	Iodometry	
$\text{YBa}_{2-x}\text{Sr}_x\text{Cu}_3\text{O}_{7-\delta}$								
x = 0.2	3.8298	3.8816	11.6830	173.68	0.0134	0.17	0.15	92
0.4	3.8254	3.8788	11.6364	172.66	0.0138	0.16	0.19	88
0.6	3.8227	3.8782	11.6149	172.19	0.0144	0.14	0.15	85
0.8	3.8225	3.8741	11.6149	172.00	0.0134	0.18	0.19	84
1.0	3.8210	3.8712	11.6134	171.78	0.0131	0.33	0.35	82

Table 2. Structural parameters of  $\text{YBa}_{2-x}\text{K}_x\text{Cu}_3\text{O}_{7-\delta}$ .

Compounds	Lattice parameters (Å)			Cell volume (Å) <sup>3</sup>	Orthorhombicity $\epsilon = 2(b-a)/a+b$	Oxygen non-stoichiometry ( $\delta$ ) by		Superconducting transition temp. $T_c$ (K)
	a	b	c			O <sub>2</sub> evolution	Iodometry	
$\text{YBa}_{2-x}\text{K}_x\text{Cu}_3\text{O}_{7-\delta}$								
x = 0.2	3.7935	3.8994	11.7308	173.53	0.0275	0.31	—	87
0.4	3.8623	3.9076	11.7308	177.05	0.0116	0.46	—	83
0.6	3.8886	3.9021	11.7308	178.00	0.0034	0.68	—	80
0.8	3.8967	3.9129	11.7308	178.86	0.0041	0.78	—	79
1.0	3.9021	3.9129	11.7308	179.11	0.0028	0.92	—	78

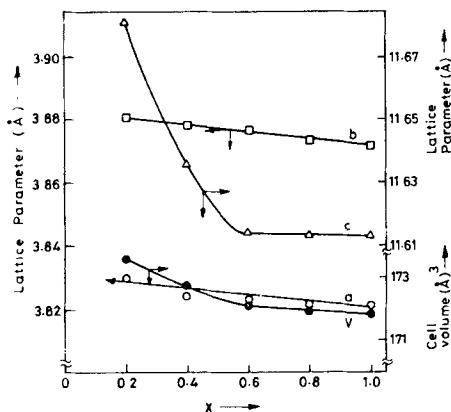


Figure 2. Variation of lattice parameters ( $a$ ,  $b$  and  $c$ ) and cell volume ( $V$ ) with Sr content ( $x$ ) in  $\text{YBa}_{2-x}\text{Sr}_x\text{Cu}_3\text{O}_{7-\delta}$ .

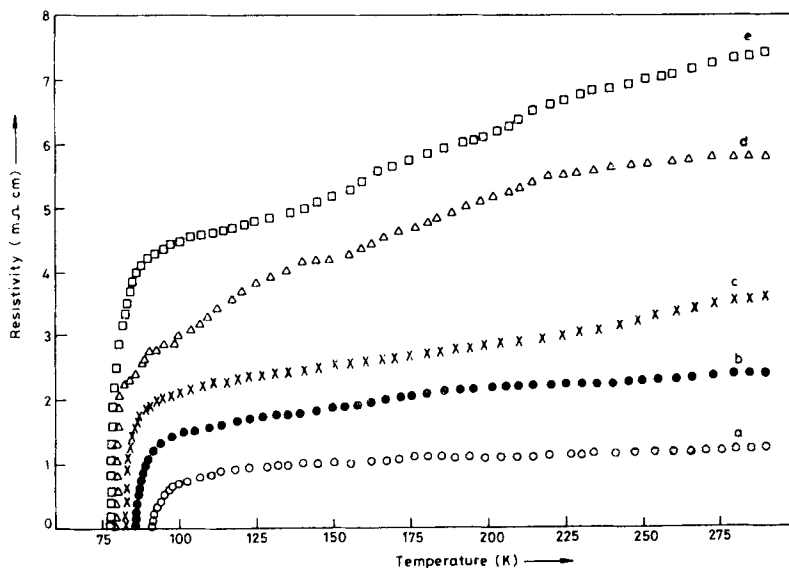


Figure 3. Resistivity vs temperature plot for  $\text{YBa}_{2-x}\text{Sr}_x\text{Cu}_3\text{O}_{7-\delta}$ , where  $x =$  (a) 0.2, (b) 0.4, (c) 0.6, (d) 0.8 and (e) 1.0.

The  $\delta$  values in these oxides are found to be in the range 0.10 to 0.42. The increase in the  $\delta$  value is expected, since these samples are quenched from high temperatures. The resistivity vs temperature plot is shown in figure 7. It is seen that only the samples quenched from temperatures less than 873 K are superconducting at  $\approx 90$  K. However the samples quenched from 973 K seem to show superconductivity at less than 77 K. But the samples quenched from temperatures greater than 973 K show increase in resistivity with decrease of temperature suggesting metal to semiconductor transition.

The oxygen non-stoichiometry ( $\delta$ ) controls both the crystal structure and superconducting transition temperature. In figure 8 the oxygen non-stoichiometry ( $\delta$ ) in

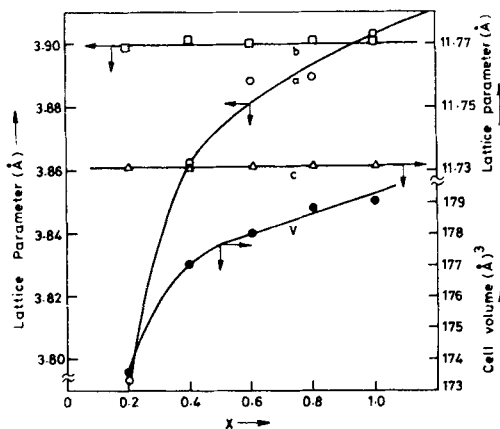


Figure 4. Variation of lattice parameters (*a*, *b* and *c*) and cell volume (*V*) with K content (*x*) in  $\text{YBa}_{2-x}\text{K}_x\text{Cu}_3\text{O}_{7-\delta}$ .

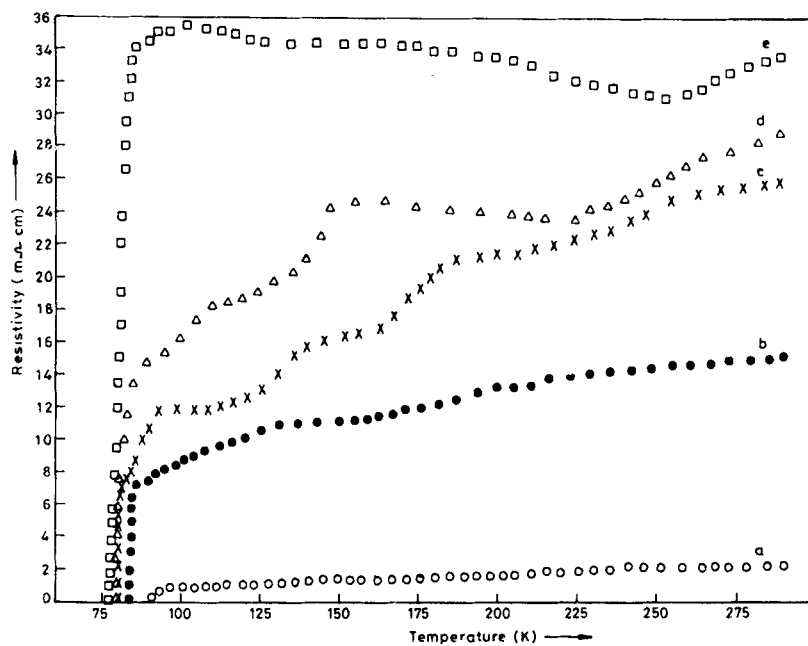


Figure 5. Resistivity vs temperature plot for  $\text{YBa}_{2-x}\text{K}_x\text{Cu}_3\text{O}_{7-\delta}$ , where  $x =$  (a) 0.2, (b) 0.4, (c) 0.6, (d) 0.8 and (e) 1.0.

$\text{YBa}_{2-x}\text{K}_x\text{Cu}_3\text{O}_{7-\delta}$  is plotted against orthorhombicity ( $\epsilon$ ) and  $T_c$ . In figure 9 the oxygen non-stoichiometry ( $\delta$ ) in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  is plotted against orthorhombicity ( $\epsilon$ ) and  $T_c$ . The  $T_c$  for  $\text{YBa}_{2-x}\text{K}_x\text{Cu}_3\text{O}_{7-\delta}$  decreases with  $\delta$  but remains above 77 K, whereas for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$   $T_c$  decreases drastically. The orthorhombicity ( $\epsilon$ ) decreases with  $\delta$  for  $\text{YBa}_{2-x}\text{K}_x\text{Cu}_3\text{O}_{7-\delta}$ , but it remains unchanged for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ .

Table 3. Structural parameters of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> prepared by quenching from high temperatures (T<sub>q</sub>).

Compounds	Lattice parameters (Å)			Cell volume (Å) <sup>3</sup>	Orthorhombicity $\varepsilon = 2(b - a)/a + b$	Oxygen non-stoichiometry (δ) by		Superconducting transition temp. T <sub>c</sub> (K)
	a	b	c			O <sub>2</sub> evolution	Iodometry	
YBa <sub>2</sub> Cu <sub>3</sub> O <sub>7-δ</sub>								
T <sub>q</sub> (K) = 673	3.8230	3.8924	11.6772	173.76	0.0180	0.12	0.11	93
773	3.8230	3.8924	11.6772	173.76	0.0180	0.15	0.16	90
873	3.8244	3.8972	11.6916	174.26	0.0189	0.18	0.19	89
973	3.8276	3.8988	11.6964	174.55	0.0184	0.30	0.28	—
1073	3.8306	3.9018	11.7054	174.95	0.0184	0.36	0.38	—
1173	3.8320	3.9018	11.7054	175.02	0.0181	0.41	0.42	—

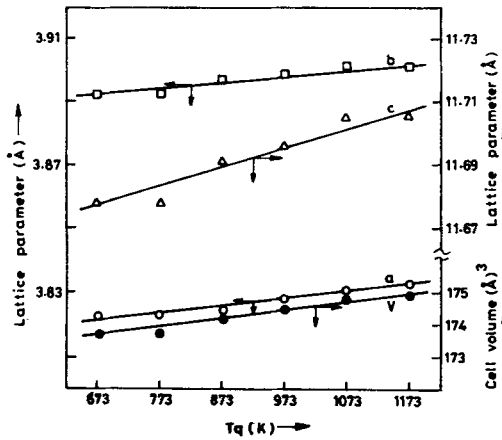


Figure 6. Variation of lattice parameters (*a*, *b* and *c*) and cell volume (*V*) with temperatures of quenching ( $T_q$ ) of  $YBa_2Cu_3O_{7-\delta}$ .

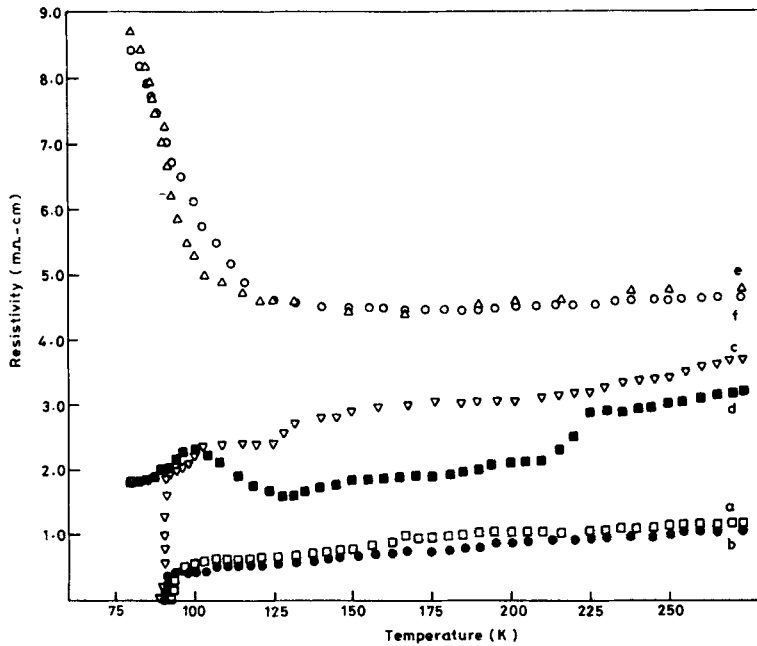


Figure 7. Resistivity vs temperature plot for  $YBa_2Cu_3O_{7-\delta}$  prepared by quenching from high temperatures ( $T_q$  in K): (a) 673, (b) 773, (c) 873, (d) 973, (e) 1073 and (f) 1173.

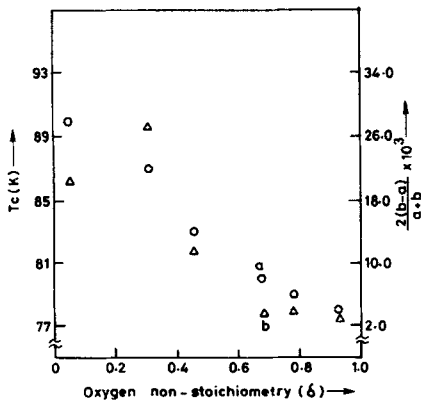


Figure 8. Variation in  $T_c$  (o) and orthorhombicity  $\epsilon$  ( $\Delta$ ) with oxygen non-stoichiometry ( $\delta$ ) of  $YBa_{2-x}K_xCu_3O_{7-\delta}$ .



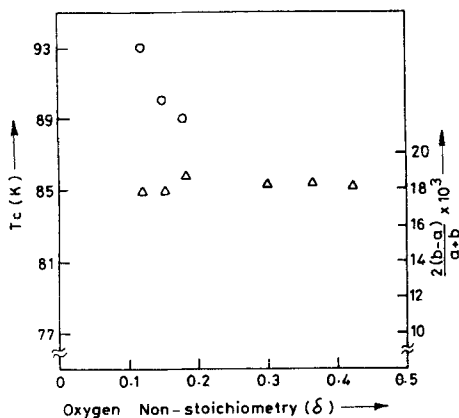


Figure 9. Variation in  $T_c$  (o) and orthorhombicity  $\epsilon$  ( $\Delta$ ) with oxygen non-stoichiometry ( $\delta$ ) of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ .

#### 4. Discussion

The cause for the decrease in  $T_c$  in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  is attributed to the increase in the  $\delta$  value as reported (Beno *et al* 1987). The increase in  $\delta$  in these systems is due to vacancies created at O1 site. This is established from powder neutron diffraction studies (Santoro *et al* 1987).

The decrease in  $T_c$  in the substituted systems may be due to chemical pressure induced in the lattice by substitution of smaller Sr or monovalent K at Ba site. It is known that the Ba–O4 (2.7408 Å) distance along  $a$ – $b$  plane is less than that of  $c$ –direction i.e. Ba–O2/O3 (2.984/2.960 Å) or Ba–O1 (2.874 Å) distances (Santoro *et al* 1987). Therefore, substitution of Sr at the Ba site would have decreased the effective bonding with the oxide ions in the neighbouring Cu–O planes or chains, i.e. along  $c$ –direction. This causes further weakening of Ba(Sr)–O1 and (Ba)Sr–O2/O3 bonds. Because of this chemical pressure some of the oxide ions at O1 could have escaped leading to marginal increase in the  $\delta$  value. This could have influenced the Cu–O2/O3 plane, probably by increasing the electron density and thus restricting the hole movement. This could have led to marginal decrease in the value of  $T_c$ .

In the case of monovalent K substitution the effective coordination number of Ba is reduced. Among the oxide ions coordinated to Ba, oxide ion at O1 site is weak [ $\Delta H$  for O1 removal and insertion is  $\approx \pm 90$  kcal/mol which is far less than for other lattice oxide ions present, which have  $\Delta H$  values of  $> 300$  kcal/mol (Marucco and Gledel 1989)]. Therefore oxide ion from O1 site would have escaped due to chemical pressure because of electronic effect. This is evident from increase in  $\delta$  value as high as 0.92 for K content  $X = 1.0$ . However, an interesting question arises as to how such a drastic increase in  $\delta$  does not decrease the superconducting transition temperature,  $T_c$ . It still remains above 77 K.

The increase in the oxygen vacancies or oxygen non-stoichiometry ( $\delta$ ) in these oxides is attributed to loss of oxide ion from O1 site. Increase in  $\delta$  value in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  decreases the  $T_c$  drastically, whereas increase in  $\delta$  value (as high as 0.92) in potassium substituted system,  $\text{YBa}_{2-x}\text{K}_x\text{Cu}_3\text{O}_{7-\delta}$ , does not decrease the  $T_c$  below 77 K. It induced phase transition from orthorhombic to tetragonal symmetry. This means loss of almost all the chain oxygen (O1) does not decrease the  $T_c$  in these

systems. These results indicate that presence of oxide ion at O1 position is not always a necessary condition for the 123 oxide to superconduct. Therefore, the role played by copper–oxygen planes (Cu2–O2/O3) in superconductivity is crucial compared to copper–oxygen chains (Cu1–O1) in 123 oxides. This is observed in the bismuth and thallium based superconductors, where only copper–oxygen planes are present, not chains.

The 123 oxides are more promising than other high  $T_c$  oxides. However, the stability of these oxides poses problems. The lack of stability in these oxides is mainly due to copper–oxygen chains. The results in this study suggest that the copper–oxygen chains can be monitored by making suitable substitution at Ba site. Therefore, by making suitable modification at the copper–oxygen chain the stability of the 123 oxides can be improved.

## 5. Conclusions

The increase in  $\delta$  value for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  prepared by quenching decreases the  $T_c$  drastically. In  $\text{YBa}_{2-x}\text{K}_x\text{Cu}_3\text{O}_{7-\delta}$  system as K content increases the value of  $\delta$  increases, which leads to a likely phase transition at  $x = 1.0$ . However, such an increase in the  $\delta$  value does not affect the superconducting transition temperature, which remains above 77 K. In  $\text{YBa}_{2-x}\text{Sr}_x\text{Cu}_3\text{O}_{7-\delta}$  system as Sr content increases there is marginal decrease in the oxygen content as well as superconducting transition temperature.

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