

## On the effects of Ti, Zr and Ce substitution in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ : transport, XRD, XPS and XANES studies

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**Abstract.** Results of the XRD, XPS, XANES, iodometric titration and transport studies on freshly prepared Ce, Zr and Ti substituted 1–2–3 samples are reported here. It is argued that at least 2% of Ce, Zr and Ti ions go into the 1–2–3 lattice. It is found that Zr, Ti ions exist in 4<sup>+</sup> valence state, Ce is in predominantly 4<sup>+</sup> (mixed valence) state and valence of Cu remains unaffected on substitution.

**Keywords.**  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ; XRD; iodometric titration; XPS; XANES.

### 1. Introduction

A survey of the available reports reveals that the substitutional aspects of Sc, Ti and V ions of the 3d transition group and Ce, Pr and Tb ions of the lanthanide series in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  system are not yet clear. Unlike other lanthanide ions substituted at Y-site, Ce, Pr and Tb exhibit anomalous behaviour attributed partly to the tetravalent (or mixed valent) character of these ions (Schneemeyer *et al* 1987; Liang *et al* 1987; Matsuda *et al* 1988; Kinoshita *et al* 1988; Narlikar *et al* 1989; Chen *et al* 1989). Further the incorporation of Sc, Ti and V in the 1–2–3 lattice is also a subject of controversy (Xiao *et al* 1987; Venkataramani *et al* 1988; Mehta *et al* 1989; Narlikar *et al* 1989). Similar controversy exists regarding the substitution of Zr in 1–2–3 system (Qadri *et al* 1987; Venkataramani *et al* 1988; Jayaram *et al* 1988; Narlikar *et al* 1989).

In a broad programme of work being carried in our laboratory on the 1–2–3 system (Padalia and Mehta 1989), an attempt has been made to look into the problem of substitutional aspects of Sc, Ti, V (3d), Ce, Pr and Tb (4f) and Zr (4d) ions in 1–2–3 system. In the present paper, we report the results of XRD, iodometric titration, transport, XPS and XANES studies on the freshly prepared Ce, Zr and Ti-substituted samples. Preliminary findings of electron probe micro analysis (EPMA) are also reported.

### 2. Experimental

Samples of composition  $(\text{Y}_{1-x}\text{M}_x)\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ ; M = Ce, Zr;  $0.00 \leq x \leq 0.10$  and  $\text{YBa}_2(\text{Cu}_{1-x}\text{Ti}_x)_3\text{O}_{7-\delta}$ ;  $0.00 \leq x \leq 0.06$  were prepared by the standard ceramic

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technique using proportionate quantities of  $Y_2O_3$ ,  $MO_2$  ( $M = Ce, Zr$  and  $Ti$ ),  $BaCO_3$  and  $CuO$  of  $\geq 99.9\%$  purity. The samples in pellet form were sintered in two stages at  $930^\circ C$  for 36 h in flowing oxygen. The final sintered samples were subjected to extended oxygenation for several hours from  $700^\circ C$  to  $400^\circ C$ . The samples were characterized by XRD method. The oxygen concentration was estimated by iodometric titration. Resistivity was measured on the sintered pellets using the four-probe method. EPMA in scanning mode was carried out with Cameca Camebax-R instrument. X-ray photoelectron spectroscopy (XPS) measurements were made with a VG ESCA-3(II) machine using  $AlK_\alpha$  radiation. X-ray spectroscopic set-up with laboratory source of continuous radiation was used for X-ray absorption near edge structure (XANES) studies. The sample surface was cleaned gently with an alumina scraper.

### 3. Results and discussion

Figure 1 shows the XRD patterns for the Ce, Zr and Ti-substituted 1-2-3 samples. For comparison XRD spectrum of pure 1-2-3 ( $x = 0.00$ ) is included in the same figure. The computed lattice parameters are given in table 1. The XRD patterns reveal the formation of orthorhombic 1-2-3 phase for all these compositions. Analysis of these spectra indicates that at least 2% of Ce, Zr and Ti ions go into the lattice. The preliminary EPMA data support the XRD results. A detailed analysis of the XRD data, taking into account the weighted average of the impurity phases present, provides clear indication of the formation of  $BaCeO_3/CeBa_2Cu_3O_x$  for Ce-substituted compositions with  $x \geq 0.05$ . The presence of  $BaZrO_3$  phase has also been detected in the Zr-substituted samples with  $x \geq 0.05$ . However, the intensities of the XRD lines for the impurity phases are not in proportion to the amount of Zr substituted. In the case of Ti-substituted samples with  $x \geq 0.04$ , the XRD lines present due to impurity phases are difficult to index as these lines do not match with the lines corresponding to  $TiO_2$  or  $BaTiO_3$  phases.

**Table 1.** Lattice parameters, oxygen concentration ( $O_{7-\delta}$ ) and  $T_c$  for  $(Y_{1-x}M_x)Ba_2Cu_3O_{7-\delta}$ ;  $M = Ce, Zr$  and  $YBa_2(Cu_{1-x}Ti_x)_3O_{7-\delta}$

$x$	$a$ $\pm 0.005 \text{ \AA}$	$b$ $\pm 0.005 \text{ \AA}$	$c$ $\pm 0.005 \text{ \AA}$	$V(abc)$ $(\text{\AA})^3$	$b/a$	$O_{7-\delta}$ $\pm 0.03$	$T_c(\rho = 0)$ $\pm 1 \text{ K}$
<b>Ce</b>							
0.000	3.819	3.886	11.667	173.15	1.017	6.92	91
0.025	3.820	3.889	11.675	173.44	1.018	6.90	82
0.050	3.821	3.890	11.677	173.56	1.018	6.92	—
0.075	3.823	3.890	11.678	173.66	1.017	6.93	—
0.100	3.822	3.889	11.678	173.58	1.017	6.93	82
<b>Zr</b>							
0.000	3.819	3.886	11.667	173.15	1.017	6.92	91
0.050	3.826	3.885	11.657	173.27	1.015	6.89	89
0.100	3.820	3.889	11.666	173.31	1.018	6.90	91
<b>Ti</b>							
0.000	3.819	3.886	11.667	173.1	1.017	6.92	91
0.020	3.823	3.882	11.665	173.1	1.015	6.90	82
0.040	3.825	3.883	11.664	173.2	1.015	6.92	74
0.060	3.828	3.881	11.663	173.2	1.014	6.93	72

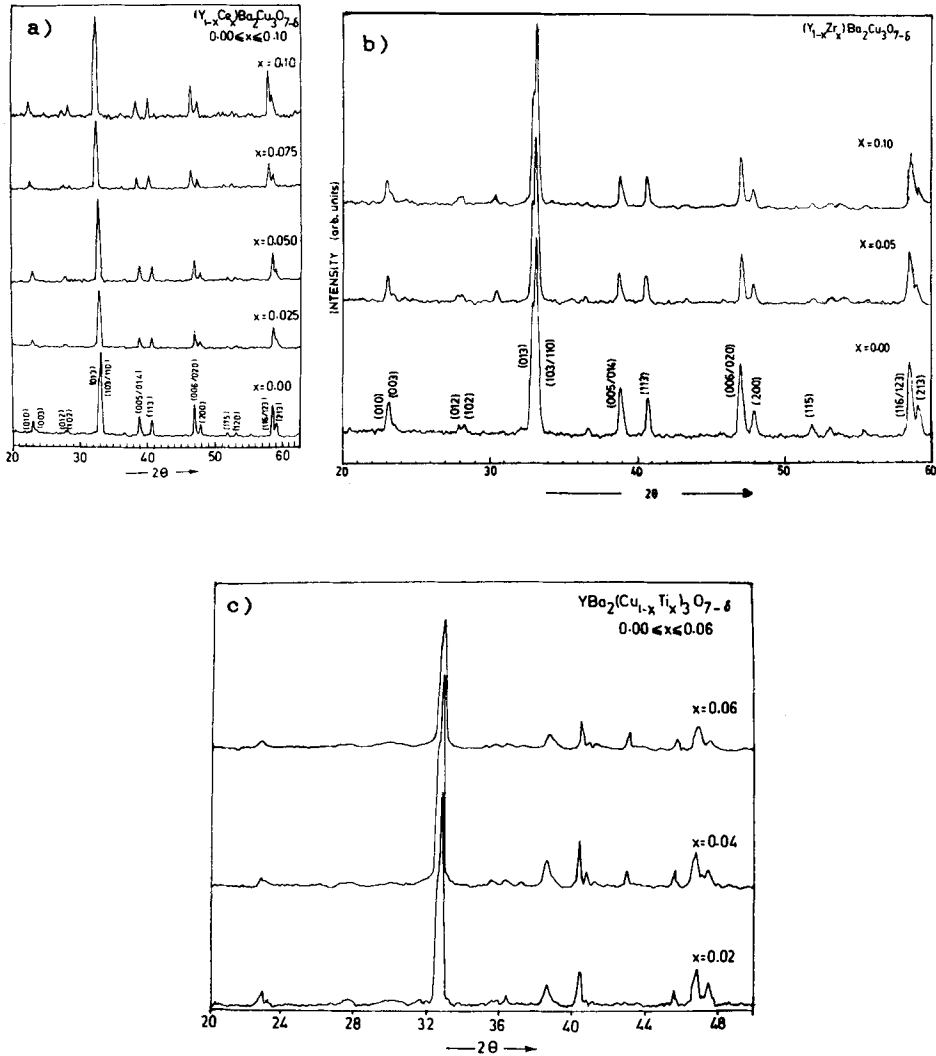


Figure 1. XRD patterns for (a) Ce-, (b) Zr and (c) Ti-substituted 1-2-3 system.

The oxygen content in the substituted samples estimated by the iodometric titration method is given in table 1. It is noted that the values of  $\delta(O_{7-\delta})$  do not show large variations on substitution. The value of  $\delta$  is 0.1 which is a characteristic feature of orthorhombic ( $Pmmm$ ) structure. This result lends support to the observed XRD patterns.

The superconducting transition temperatures ( $T_c$ ) measured for the substituted samples (table 1) show no change in  $T_c$  for Zr, some step change in  $T_c$  from 91 K to 82 K for Ce and significant fall in  $T_c$  from 91 K to 72 K for Ti-substituted samples. This is apparent from the resistance vs temperature plots for Ce and Ti-substituted samples shown in figure 2 (plot for Zr-substituted samples has already been published by Venkataramani *et al* 1988). A narrow transition width (3 K) for the Ce-substituted

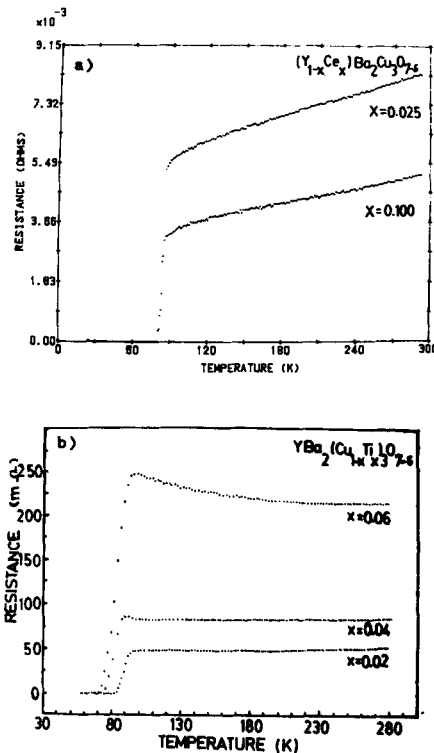
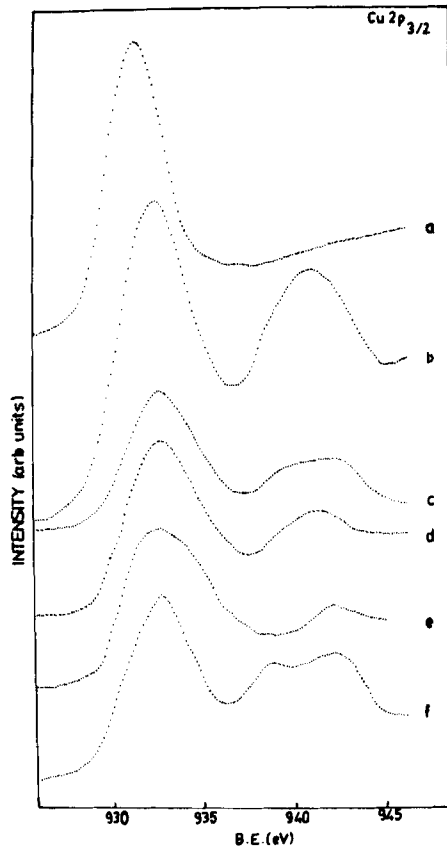


Figure 2. Resistivity (m ohm) vs temperature (K) plots for (a) Ce- and (b) Ti-substituted 1-2-3 system.

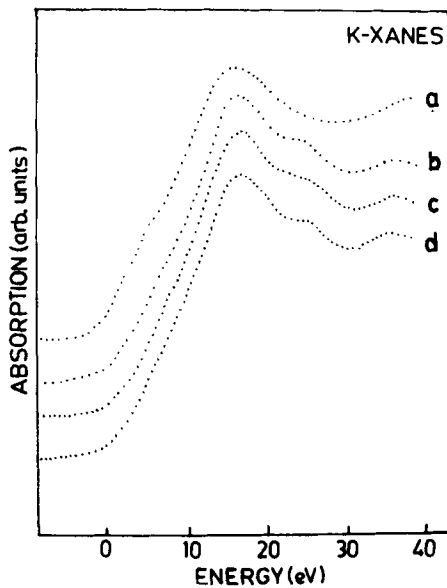
sample with  $T_c$  onset at  $85 \pm 1$  K (figure 2a) is a clear indication of Ce going into the lattice. Such a behaviour of  $T_c$  onset is not reflected in oxygen-deficient pure 1-2-3 compound wherein  $T_c$  onset is invariably 95 K. Support to this is provided by the fact that the estimated oxygen content in 2.5% Ce-substituted sample is 6.90 (table 1).

It appears that Ti prefers  $T_c$ -sensitive Cu site while both Ce and Zr go to the Y-site in the 1-2-3 system. On the basis of the ionic radii ( $r$ ), preference of  $Ti^{4+}$  to Cu site and  $Ce^{4+}$  to the Y-site is conceivable while that of  $Zr^{4+}$  to Y-site is rather difficult to explain. It is likely that  $Zr^{4+}$  ( $r = 0.80$  A.U.) is not accepted at the Cu-site ( $Cu^{2+}$   $r = 0.69$  A.U.) and a fraction of  $Zr^{4+}$  ( $\leq 2\%$ ) is accommodated at the Y-site ( $r = 0.93$  A.U.). This argument is consistent with the observation of no change in  $T_c$  on Zr substitution. In order to support the above argument based on the tetravalent (or mixed valent) behaviour of Ce, Zr and Ti, it was thought desirable to determine the valence states of these substituent ions. The 3d XPS of Ce and Zr and 2p XPS of Ti in the substituted 1-2-3 samples have, therefore, been recorded. The results show that Zr and Ti are present in pure tetravalent state while Ce ions exist in mixed valent ( $Ce^{3+}$  and  $Ce^{4+}$  predominant) state. These XPS results are consistent with our contention.

It is important to state that the 2p XPS and K-XANES of Cu in the Ce-, Zr- and Ti-substituted 1-2-3 samples when compared with those recorded for the pure 1-2-3 compound reveal no change in their spectral features (figures 3 and 4). This implies that the valence state of Cu is not affected on substitution of Ce, Zr and Ti ions in 1-2-3 system.



**Figure 3.**  $2p_{3/2}$  core level XPS of Cu in (a)  $\text{Cu}_2\text{O}$ , (b)  $\text{CuO}$ , (c)  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , (d)  $\text{YBa}_2(\text{Cu}_{0.96}\text{Ti}_{0.04})_3\text{O}_{7-\delta}$ , (e)  $(\text{Y}_{0.95}\text{Zr}_{0.05})\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  and (f)  $(\text{Y}_{0.925}\text{Ce}_{0.075})\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ .



**Figure 4.** K-XANES of Cu in (a)  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , (b)  $\text{YBa}_2(\text{Cu}_{0.96}\text{Ti}_{0.04})_3\text{O}_{7-\delta}$ , (c)  $(\text{Y}_{0.95}\text{Zr}_{0.05})\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  and (d)  $(\text{Y}_{0.925}\text{Ce}_{0.075})\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ .

#### 4. Conclusions

The results of the present multiple technique approach lead to the following conclusions: (i) the iodometric titration shows no change in oxygen concentration; (ii) XRD study reveals no change in orthorhombic structure; (iii) the XRD, EPMA and transport data analysis shows that at least 2% of Ce, Zr and Ti ions go into the 1–2–3 lattice; it is most likely that the Ti ions go to Cu-site while Zr and Ce ions occupy the Y-site; and (iv) the XPS and XANES studies reveal that Ti and Zr are in tetravalent state, Ce is in predominantly tetravalent (mixed valent) state and the valence state of Cu remains unaffected on Ce, Zr and Ti substitution in the 1–2–3 system.

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