Core level XPS studies on Zn-doped YBa$_2$Cu$_3$O$_{7-y}$

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Abstract : A systematic study on Zn-doped YBa$_2$Cu$_3$O$_{7-y}$ has been initiated to understand the electronic structure of these cuprates using core-level X-ray Photoelectron Spectroscopy (XPS). The core level spectra is related to site selective occupied density of states. This is due to the change in the chemical environment, albiet to some extent with the changes of interatomic distances of ion species. These aspects have been employed to explain the changes in the normal state electronic structure with Zn-doping.

Keywords : XPS. Zn-doped YBCO, electronic structure

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1. Introduction

The new perovskite superconductors are anomalous in their normal state properties [1]. Much emphasis has been placed on the following aspects to explain the normal and superconducting state properties : (1) low dimensionality in the crystal structure, (2) the mixed valency of Cu and (3) oxygen order-disordering [2,3]. Furthermore, some of the well estimated facts on the interplay between magnetism and superconducting state needs careful attention. According to Arbrikosov-Gorkov theory [4] that when magnetic impurities are added or substituted to superconducting systems, Tc decreases a fact well established in BCS type but fails to account in high Tc systems [5]. All these aspects have been extensively discussed in literature [6,7]. Incorporating the experimental results, one is left with the possibility of looking at an explanation based on electronic contributions as the cause for many anomalous properties of oxide superconductors.

In all high Tc superconductors discovered so far, Cu–O networks play a crucial role since the superconducting electrons are found in these layers [7]. Numerous

investigations have been carried to probe this aspect appeared in literature especially in YBCO system with $3d$ metals doping at Cu site [8]. All such substitutions decrease Tc irrespective of their magnetic properties. The structure of $YBa_2Cu_3O_{7-y}$ (YBCO) compounds consists of an orthorhombically distorted perovskite with triple unit cells stacked along the c-axis or a closely tetragonal form, depending on the oxygen stoichiometry [8]. The physical properties of this compound depends much on the oxygen-stoichiometry. Cationic and anionic substitutions in this cuprates at various lattice sites are found to affect differently for their superconducting and normal state properties [8,9].

By far, the most extensive doping at Cu sites in YBCO systems performed are Fe, Co, Ni and Zn. Tc suppression is more pronounced with zinc doping whereas Co, Fe have a little effect. At larger values of Ni substitution affect the Tc marginally in YBCO. The orthorhombic and tetragonal structural transformation is happening with small substitution of Fe and Co. In case of Zn and Ni, no structural phase transformations take place as revealed by XRD and supported by numerous reports [10]. The rich variety of reported behaviours as well as much of the experimental disagreement, arise primarily from the preferential occupancy of the two inequivalent copper sites [9]. Much effort has therefore been directed towards identifying the way in which the dopants are distributed between these sites. Consideration of the relative substitutional occupancies of the Cu (1) chain and Cu (2) plane sites is central in the interpretation of primary features such as the degree of depression of superconducting properties, the apparent orthorhombic-tetragonal phase transformation, oxygen site occupancy, substitutional solubility and annealing effects [11,12].

This report details the studies on the effect of Zn substitution in $YBa_2(Cu_{1-x}Zn_x)_3$ O_{7-y} (x = 0%, 3%, 5%, 10%, 15%) compounds at the Cu site. The effects of Zn substitutions are understood in terms of change in electronic structure using XPS core-level spectra.

2. Experimental Details

The YBCO and Zn doped YBCO samples were prepared by standard solid state technique reported elsewhere [13]. All the synthesised samples were characterised for structural properties by X-ray diffraction (XRD) and superconducting properties by a.c susceptibility. Room temperature resistivity was also measured. Oxygen content was determined by iodometry [13].

To see the valence state of Cu, core-level XPS was carried out. XPS measurements were performed in Ultra High Vacuum (UHV) using Mg K_α X-ray source. Electrons were monitored by a VG CLAM-2 hemispherical analyser. The FWHM was 0.85 eV at 100,000 cps for Mg K_α radiation on $Ag_{5/2}$ peak. To ascertain the surface stability, before each set of measurement, sample was scraped repeatedly *in situ* to expose the fresh superconducting grains. Spectra after fresh scrapings were found to be reproducible.

3. Results and discussion

XRD patterns recorded to determine phase purity and lattice parameters for Zn doped and undoped YBCO system. The values of lattice parameters for doped and undoped YBCO are in general agreement with values reported in literature. As the Zn concentration is increased the orthorhombicity is maintained in contrast to the situation observed with Fe, Co doping. Zn doped samples show small variation in structural parameters but almost close to undoped YBCO structural parameters reported elsewhere [13]. Annealing in oxygen at 500 C ensures optimum oxygen stoichiometry. The Tc's are respectively 92 K, 59 K, 45 K for Zn = 0%, 3% and 5%. For Zn = 10% and 15% no superconductivity was observed down to 12 K. No appreciable change in oxygen content was observed within the error limit of ± 0.02 and consistent with other reports in literature [10].

XPS spectra of Cu-2p, O-1s, Ba-3d, Ba-4d and Y-3d were recorded for both Zn-doped and undoped YBCO. Cu-2p and O-1s XPS spectra of CuO was also recorded for comparison. *In situ* scrapping was done to remove the contaminated surface layer so as to look at only the pure material surface as far as possible. This allowed the gradual suppression of the O-1s feature at 531 eV and other higher binding energies assigned to OH$^-$ and CO$_3^{2-}$ anions, present in the surface layer.

It is commonly admitted that there is considerable difficulty in the interpretation of the XPS experiments of superconductors. This is due to superconducting properties arise from bulk whereas XPS probes only surface properties. Existence of a thin passivation layer formed on the core of the crystallines by the reaction with atmospheric moisture and carbon dioxide obscure the electronic structure of bulk YBCO. High temperature annealing and argon bombardment are inappropriate as they are destructive.

(a) Cu-2p spectra :

Figure 1 shows Cu-2p XPS core-level spectra for pure YBCO and Zn doped YBCO. Also included is Cu-2p XPS spectrum of CuO for comparison. The spectra obtained show the typical double peak shape of divalent Cu compounds. It is known that for the divalent Cu compounds, the main peak at 933 eV corresponds to a Cu2$p^5$3d^{10}O2p^5 state, *i.e.* a configuration where the Cu core hole is shielded by a charge transfer from O. Besides the main line, there is a satellite at 943 eV correspondingly to a Cu 2p^5 3d^9 state. The interaction of the 2p core hole with the hole in the 3d shell leads to a multiplet splitting which is clearly indicated by the trapezoidal form of the satellite. The shift to higher energy by about 9 eV is caused by the Coulomb repulsion of the two holes reflecting change of the chemical environment [14].

There have been many discussions on trivalent nature of Cu ions in the high Tc superconductors. By simple valency counting arguments, one would expect YBCO to have formally 30% trivalent Cu ions. Cu^{3+} (3d^8) may give the following final states in the Cu-2p XPS spectra; Cu 2$p^5$3d^8, Cu2p^5O 2p^5 and Cu 2p^5 3d^{10} (O-2p^5)^2. No XPS satellites due to Cu 2$p^5$3d^8 final states, which would be at very high binding energy with respect to the main line, have been observed in this study or reported by others [15]. Since, the Cu-2p main

peak position is same for all these samples indicating that salient feature of typical divalent compounds is observed in all these compounds, one may consider that Cu is in divalent state irrespective of $3d$ metal doping.
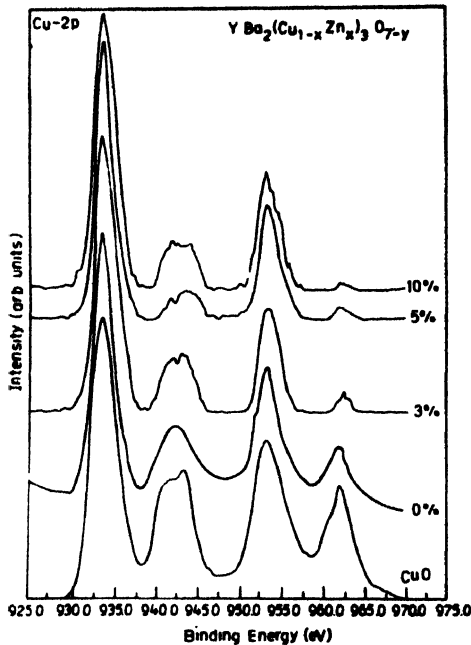

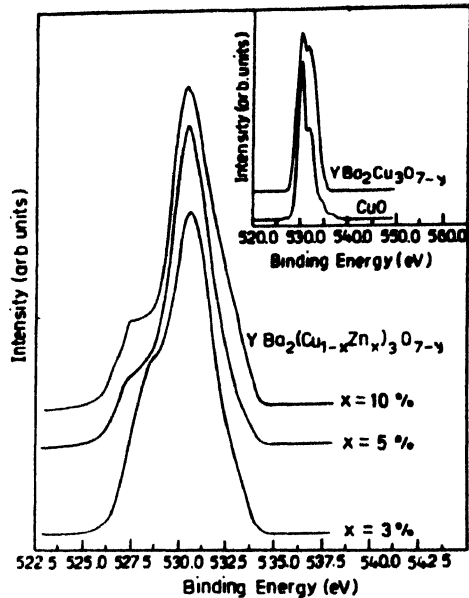**Figure 1.** Cu $2p_{3/2}$ XPS core-level spectra of CuO, Zn-doped and undoped YBCO.

Figure 2. O-$1s$ XPS spectra Zn-doped YBCO. Inset shows O-$1s$ XPS of CuO and YBCO.

The ratio of area of the satellites to main peak in the Cu-$2p_{3/2}$ XPS spectra is often related to charge fluctuations between O and Cu atoms. For the high Tc superconductors this value is similar so that found for CuO. Qualitatively, it appears that as one dopes Zn, this ratio reduces considerably which may be understood by considering the filling of $3d_{x^2-y^2}$ states and thus reducing charge fluctutations. In contrast, Ni and Fe doped spectra reported elsewhere [13] shows that there is appreciable change meaning that the charge fluctuations are significant. Note that from these spectra it is not possible to identify whether the dopants have occupied Cu (1) or Cu (2) site.

(b) O-1s spectra :

Figure 2 shows the O-$1s$ spectra of all the samples. Inset is O-$1s$ of CuO and pure YBCO. Note that there are at least two components in the spectra with a peak at 529 eV and another at 531 eV. It is known that there exists considerable controversy about the interpretation of this spectra [17,18]. But the consensus is that the higher binding energy peak is attributed to the impurity phases or surface contributions. The Bismuthate superconductors appear to exhibit only one peak at ~529 eV. While the peak at 529 eV is unambiguously assigned to O^{2-} ions. The situation is more complex for the peak at 531 eV where the influence of both surface and bulk contributions should be considered [19]. It is difficult to decide whether

oxygen monomers O⁻ or dimers O_2^{2-} contribute to the observed feature but in principle, both appear, to be possible.

As all doped and undoped YBCO compounds invariably exhibit a significant contribution at 531 eV, it gives rise to a question, whether at all it is due to impurity phases alone.

(c) Ba-3d and Ba-4d spectra :

Interest in the Ba-4d photoemission spectra (Figure 3) derives from the dependence of its line shape on the oxygen stoichiometry. Ba-4d measurements were made on all doped YBCO sample to see whether its line shape changes with dopant concentration. The Ba-4d level for the 92 K superconductor sample consists of two sets of spin orbit doublets giving
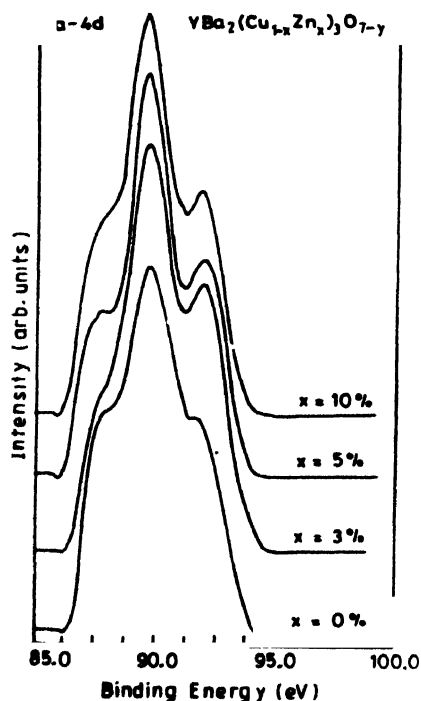

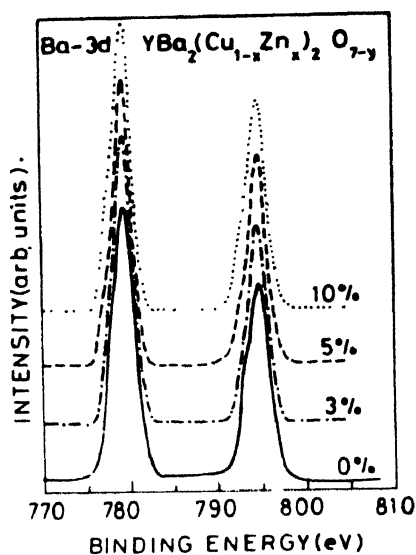**Figure 3.** Ba-4d core-level XPS spectra of Zn-doped and undoped YBCO.

Figure 4. Ba-3d core level XPS spectra Zn-doped and undoped YBCO.

rise to characteristic spectra with three peaks. In contrast to Ba-4d doublet reported overwhelmingly by others [20]. Presence of three components in the Ba-4d spectrum may be attributed to disorder crept in the lattice due to varied reasons discussed before. Moreover, in a polycrystalline sample, Ba-O layers are affected because of surface contamination and/or modified due to scrapping. Since XPS is a surface sensitive technique, this is reflected on the outermost core-level which is Ba-4d. No significant changes in case of Ba-3d spectrum observed in both doped and undoped samples (Figure 4) consistent with measurements done by others [20].

(d) Y-3d spectra :

The analysis of the Y-3d spectra shows the presence of two bonding states of the yttrium ions, corresponding to a chemical shift of 1.3 eV. The spectra did not reveal a sensitivity either to temperature variations or the oxygen stoichiometry [8,21]. We have recorded the core-level Y-3d of YBCO and Zn doped YBCO compounds to see whether there is any change due to doping in them. Figure 5 shows the 3d core-level of Y in doped YBCO samples. Note that there is no appreciable change in binding energy of peak positions but the spectral features doped YBCO shows some qualitative change when compared with the YBCO sample. This may be perhaps to the fact that Zn preferentially occupying Cu (2) site [16]. In otherwords, no charge transfer is taking place between two copper sites *via* Y site. This is reflected in the core-level sqectra of Y-3d.
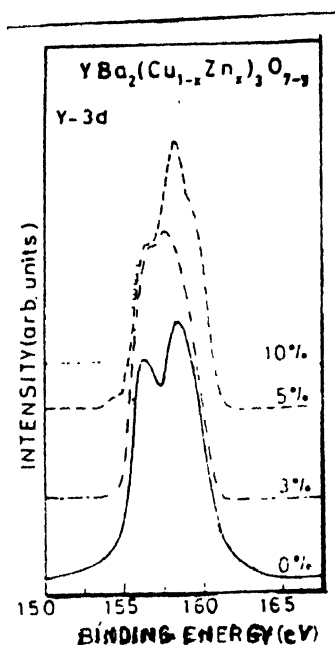

Figure 5. Y-3d core level XPS spectra of Zn-doped and undoped YBCO.

Based on above experimental results on doped and undoped YBCO samples and also from other high energy spectroscopic results have clearly established that there is no appreciable change in the valence state of Cu due to self-doping of oxygen and Zn-doping [8]. This has been corroborated by Electron Energy Loss Spectroscopy (EELS) measurements on Zn-doping on O 1 s edge has indicated no change in the EELS spectra [18]. Our results of XPS especially Cu-2p and O-1s did not reflect any changes. So based on these one may conclude that no charge transfer is taking place because Zn being closed 3d^{10} configuration leading to localisation of holes without reducing the density of holes.

In general, doping any site in a cuprate modifies the crystal field wave function leading to an appreciable change in Cu-3d, O-2p or O-2s contributions to the conduction band which can be empirically represented as below [3] :

The relevant crystal field wave function is

$$\psi_{x^2-y^2} = N_\sigma\left\{f_{x^2-y^2} - \lambda_\sigma\phi_\sigma - \lambda_s\phi_s\right\}, \tag{1}$$

where N_σ is the normalisation constant. $f_{x^2-y^2}$ is Cu 3d orbital. ϕ_σ and ϕ_s are appropriately symmetrised O-2s O-2p orbitals and λ_σ and λ_s are the covalent mixing parameters [3]. The electronic structure of this cuprate may be understood by considering the CuO$_2$ layers where a strong covalent bonding between Cu and O atoms is existing. Due to the crystal field effects, Cu 3d e_g level splits into 3$d_{x^2-y^2}$ and 3$d_{3z^2-r^2}$ states. On the CuO$_2$ planes, the 3d hole at a Cu^{2+} ion is ordered into orbitals of Cu3$d_{x^2-y^2}$ parentage and O with 2p_σ and 2s parentage [3,8]. In this, the most important part of the states at the fermi level is formed by electrons in the two dimensions of CuO$_2$ planes. The hybridisation with the O-2p states is strongest for the 3$d_{x^2-y^2}$ states in the CuO$_2$ plane [3,8].

To the first approximation, one may assume that there is no appreciable change in the $f_{x^2-y^2}$ contribution since our core-level Cu-2p spectra does not show any change in the binding energy due to Zn doping. However, the sub-satellites are narrowing down due to doping. By doping, we are essentially making Zn-O layers where the hybridization of Zn-4s and O-2p takes place rather than involving Zn-3d and O-2p states.

One may now understand the normal state properties of these doped YBCO in the following ways : Substitution of Zn in Cu site induces strong hybridisation between Zn 4s and O-2p states. There is no contribution from the O-2s states. Further, based on electronic configuration one has to account the filling of 3d states by Zn doping. This results into metallic state rather than ordering into an antiferromagnetic insulator. It is well known that unfilled 3d electrons are responsible for magnetic properties of cuprate.

EELS studies give valuable information about the changes in the O-2p states. Since EELS probes O-2p states which now has hybridised with Zn-4s rather than Cu-3d due to the electropositive nature of Zn. In otherwords one does not see the change in O-2p states due to Zn-doping. den Boer *et al* [22] investigated Zn-doped samples by using EELS. They found that there is no change in the O-2p contribution to the fermi level. From hindsight, one may tempted to look at Mossbauer studies for finding out whether there is any change in the O-2s contribution to the conduction band or fermi-level. This is due to isomer shift and hyperfine interaction which is independent in nature of the doping and temperature involved in Mossbauer measurements [23]. Yet another technique that may help us to understand whether there is any change in O-2s contribution due to

doping is pressure effect studies. Application of pressure may significantly affect O-2s states because these are spherically symmetric. Surprisingly, Zn-doped YBCO samples give zero pressure effect which is consistent with the picture evolved from Mossbauer studies above [24].

4. Conclusions

We have carried out a systematic study to understand the electronic structure of Zn-doped YBCO. It was pointed out that the doping results may be understood in terms of change in the electronic contributions of 3d states of cations or change in O-2s and O-2p to the conduction band. Doping Zn in YBCO compounds may induce Zn 4s-O 2p covalent hybridisation in the conduction band and there may not be any contribution of O-2p and O-2s for fully oxygenated Zn-doped YBCO compounds.

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