Tunable excitation x-ray fluorescence spectroscopy in phase analysis of high-T_c superconductors

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Abstract. O $K\alpha$ x-ray fluorescence of $YBa_2Cu_3O_{7-\delta}$ and $Sr_{0.85}Nd_{0.15}CuO_2$ samples containing CO_3^{2-} impurities, as well as pure $BaCO_3$, have been studied using tunable monochromatic synchrotron radiation excitation. When the excitation energy is set to the most intense features in the O 1s absorption edge of cuprates and to bound states above this edge the O $K\alpha$ spectra recorded are very similar to those of pure $BaCO_3$ even if the admixture of CO_3^{2-} is small. The observed changes in the O $K\alpha$ profiles of multi-phase $YBa_2Cu_3O_{7-\delta}$ and $Sr_{0.85}Nd_{0.15}CuO_2$ samples are discussed in terms of different x-ray absorption cross sections for O in the main phase and in the CO_3^{2-} fraction.

1. Introduction

It is established that high-T_c superconducting compounds are not stable in the presence of normal atmospheric contaminants H_2O and CO_2. The chemisorption and hydroxylation, ion exchange reactions and OH^- penetration cause a surface degradation of the specimen [1]. On the other hand, the use of carbonate as a precursor is a source of possible CO_3^{2-} impurity in the bulk of sintered materials [2]. It has also been shown for $YBa_2Cu_3O_{7-\delta}$ that C can be incorporated into the cuprate lattice during sintering due to the absorption of CO_2 onto the surfaces of finely ground powders [3]. Therefore, an investigation of the presence of C and other impurities is needed when making a spectroscopic analysis of the electronic structure of high-T_c superconducting oxides.

The dynamics of the surface degradation of high-T_c superconductors has been studied by photoemission spectroscopy [4] and by x-ray absorption spectroscopy using total electron yield [5]. High-spatial-resolution electron energy loss spectroscopy (EELS) has been employed for studies of grain boundaries [6] and the presence of extra phases on these boundaries [7]. EELS has also been used by Batson *et al* [8] to analyse the involvement of C in the electronic structure of $YBa_2Cu_3O_{7-\delta}$ and its effect on the superconducting properties.

In this paper we present studies of some cuprates containing CO_3^{2-} impurities using soft x-ray fluorescence spectroscopy with tunable monochromatic synchrotron radiation excitation. We demonstrate the sensitivity of this technique to impurities by taking advantage of the spectral variations with excitation energy and the difference in the O $K\alpha$ spectral profile between the main phase and the carbonate.

2. Experimental details

The $YBa_2Cu_3O_{7-\delta}$ specimen was prepared according to the standard procedure [9]. Oxygenation was performed at 475 °C in pure O_2. The sample turned superconducting at 90 K and the x-ray diffraction pattern, obtained soon after sintering, did not exhibit any impurity lines. However, the soft x-ray fluorescence spectra for this sample, presented in this article, were measured a long time (~one year) after preparing the sample.

The preparation and characterization of the $Sr_{0.85}Nd_{0.15}CuO_2$ sample is described elsewhere [10]. The material produced has a ~ 26% superconducting volume fraction and T_c^{onset} was found to be ~ 40 K. The x-ray diffraction analysis showed the presence of ~ 10% unidentified phases.

The measurements on the $YBa_2Cu_3O_{7-\delta}$ and $BaCO_3$ samples were made at the wiggler beamline W1 [11] and at the undulator beamline W3 [12] of the Hasylab, DESY, Hamburg. O $K\alpha$ x-ray fluorescence spectra were recorded using a high-resolution grazing incidence grating spectrometer with a two-dimensional detector [13]. The incidence angle of the photon beam was about 20° (36°) to the sample plane in the case of $YBa_2Cu_3O_{7-\delta}$($BaCO_3$). The fluorescence was detected at a 90° angle with respect to the incidence beam. The resolution of the monochromator was set to ~ 2 (0.7) eV in the case of the $YBa_2Cu_3O_{7-\delta}$ ($BaCO_3$) sample for 530 eV photon energy. O $K\alpha$ x-ray emission spectra were recorded using a 1200 lines mm^{-1} grating ($R = 5$ m) in the first order of diffraction with the spectrometer resolution set to 0.5 eV. Zn $L_{2,3}$ x-ray emission lines (1011.7 and 1034.7 eV [14]) were recorded in the second order of the diffraction for energy calibration.

O 1s x-ray absorption spectra were measured in total electron yield mode with the resolution of the monochromator set to ~ 1 (0.5) eV for the $YBa_2Cu_3O_{7-\delta}$ ($BaCO_3$) sample.

O $K\alpha$ x-ray fluorescence spectra of the $Sr_{0.85}Nd_{0.15}CuO_2$ sample were recorded at beamline 10-1 of the Stanford Synchrotron Radiation Laboratory. This beamline is equipped with a wiggler and a spherical grating monochromator. The monochromator uses a movable entrance slit and a fixed exit slit. The beam from the wiggler is focused onto the entrance slit by an adjustable horizontal collection mirror. Another adjustable mirror, vertically mounted, provides horizontal steering and focusing onto the sample. Vertical refocusing after the exit slit of the monochromator is provided by one of two *in situ* interchangeable mirrors. These mirrors have different coatings (Au and Ni) and their radii can be changed slightly in order to optimize the size of the spot on the sample. The entire energy range covered by the monochromator is ~ 200–1300 eV and the flux after the exit slit was estimated to be of the order of 5×10^{12} photons s^{-1} at 400 eV and 2.5 eV bandpass. The same type of spectrometer as used in the experiments on $YBa_2Cu_3O_{7-\delta}$ and $BaCO_3$ was used in these measurements. For energy calibration the Cr L_ℓ (500.0 eV) [15], V $L\alpha$ (511.3 eV) [14] and Mn L_ℓ (556.4 eV) [15] emission lines of pure metals were recorded. To facilitate setting the excitation energy the O 1s x-ray absorption spectra were recorded in both total electron and fluorescence yield modes. For the x-ray absorption and emission measurements the resolution of the monochromator was set to ~ 0.5 and ~ 1.5 eV, respectively.

3. Results and discussion

In figure 1 O 1s x-ray absorption spectra of some specimens are displayed. In order to analyse the spectral contributions of various contaminants, samples with degraded or/and contaminated surface were also used. The absorption spectrum labelled as 'surface of MgO' was recorded for an MgO single crystal using the total electron yield mode after keeping
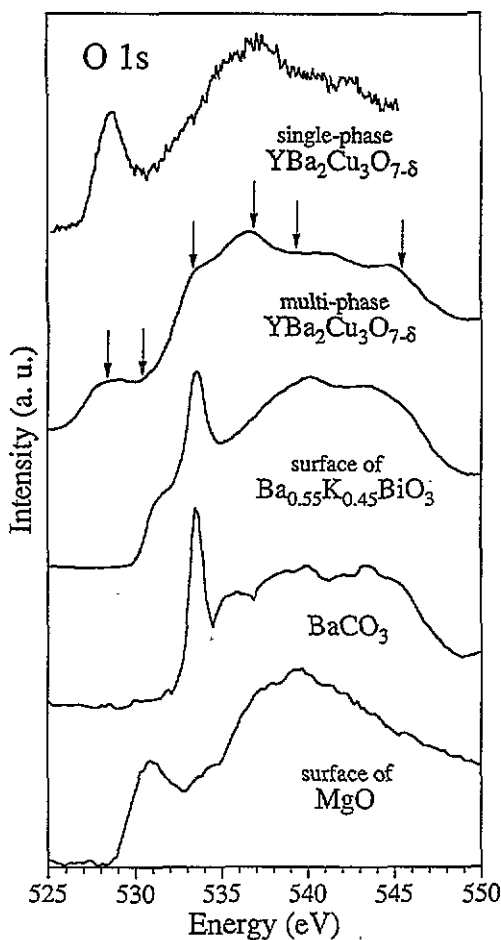
Figure 1. O 1s x-ray absorption spectra of some compounds. All spectra except for single-phase YBa$_2$Cu$_3$O$_{7-\delta}$ (total fluorescence yield) where recorded in the total electron yield mode. The arrows indicate the excitation energies used for O Kα x-ray flourescence spectra.

the sample in a vacuum of $\sim 10^{-7}$ Torr for ~ 250 h. This spectrum is completely different from one obtained just after mounting the sample in the chamber (not shown) which in turn was similar to the O 1s absorption spectrum of MgO reported elsewhere [16]. Therefore, the absorption spectrum for the surface of an MgO single crystal displayed in figure 1 can be attributed to surface contamination. However, this spectrum is dissimilar to that of BaCO$_3$ (figure 1), indicating the difference in the chemical composition between the contamination and CO$_3^{2-}$. On the other hand, the O 1s x-ray absorption spectrum for the surface of the Ba$_{0.55}$K$_{0.45}$BiO$_3$ thin film (figure 1) can be considered as a superposition of those for the MgO surface and BaCO$_3$, which suggests the presence of a large carbonate fraction in the surface layers. In order to obtain the bulk related spectrum of the O 1s absorption edge, it is necessary to use the total fluorescence yield mode.

One can see from figure 1 that the O 1s x-ray absorption spectrum from the multi-phase YBa$_2$Cu$_3$O$_{7-\delta}$ sample differs, even though it was scraped in vacuum, from that (recorded by the total fluorescence yield method) from single-phase YBa$_2$Cu$_3$O$_{7-\delta}$ [17]. For the former, enhancements in the relative intensity are observed around 533.5 eV, 540 eV and

545 eV, energies which correspond to main features in the O 1s absorption spectrum of $BaCO_3$. However, the origin of these differences is not obvious since similar variations in the spectral profile and, especially, the smearing of the first prepeak have in the past been attributed to O depletion of the sample [5].
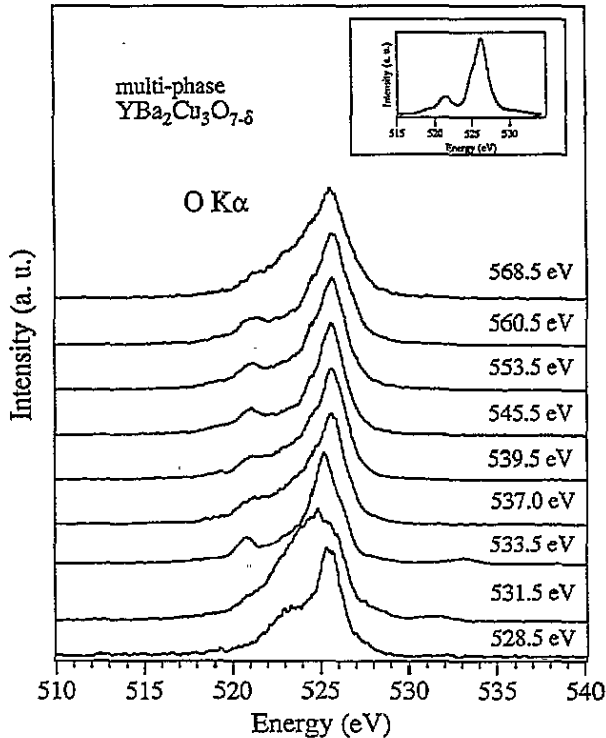

Figure 2. O $K\alpha$ x-ray fluorescence spectra of the $YBa_2Cu_3O_{7-\delta}$ sample with CO_3^{2-} impurities recorded at various excitation energies. The inset shows the O $K\alpha$ spectrum of Li_2CO_3 taken from [18].

In figure 2 O $K\alpha$ x-ray fluorescence spectra of the multi-phase $YBa_2Cu_3O_{7-\delta}$ sample recorded at different excitation energies are shown. For some excitation energies these spectra differ from those of single-phase $YBa_2Cu_3O_{7-\delta}$ [17]. This large discrepancy suggests that there are substantial contributions from contaminants. The main line at ~ 526.2 eV and the well separated low-energy structure at ~ 521.5 eV are characteristic of the O $K\alpha$ emission spectrum of CO_3^{2-} (figure 3; see also [18]). This is evidence of CO_3^{2-} impurity in the bulk of the sample (the contribution from the surface layers should be small since the penetration depth of ~ 500 eV photons in cuprates is ~ 2000 Å).

Inspection of figure 2 shows that for an excitation energy far above the O 1s absorption edge the O $K\alpha$ emission band of the multi-phase $YBa_2Cu_3O_{7-\delta}$ sample is similar to the corresponding spectrum of single-phase $YBa_2Cu_3O_{7-\delta}$ [17], except for a weak feature at ~ 521 eV, which is a sign of the CO_3^{2-} impurity. The 528.5 eV excited O $K\alpha$ spectrum should also originate mainly from O 2p states of the Y123 phase since the excitation energy is below the O 1s threshold for O in CO_3^{2-} groups (figure 1). For excitation energies falling in the range 537.0–560.5 eV the spectra look very similar to the 'pure' spectrum of $BaCO_3$
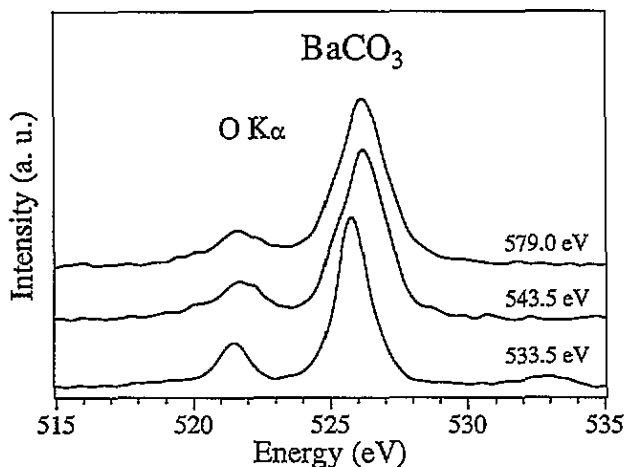
Figure 3. O $K\alpha$ x-ray fluorescence spectra of $BaCO_3$ recorded at various excitation energies.

(figure 3) (note that the measurements on $YBa_2Cu_3O_{7-\delta}$ and $BaCO_3$ were performed at different times; therefore, there might be a small shift between energy scales). The large spectral weight from the CO_3^{2-} fraction for these energies is surprising because judging from the 568.5 eV excited O $K\alpha$ spectrum the admixture of the CO_3^{2-} phase is small. A possible reason for this is found in the difference in relative x-ray absorption cross section for O in Y123 and $BaCO_3$. Using values calculated by Henke *et al* [19] for atomic absorption coefficients we estimate the relative O absorption cross sections for 540 eV photons to be $\sim$ 20% and 40% in Y123 and $BaCO_3$ respectively. The larger x-ray absorption cross section leads to predominant excitation of O atoms of the CO_3^{2-} fraction, when tuning the excitation energy to the main features of the O 1s edge and to bound states above it.

An additional reason for the observed O $K\alpha$ behaviour is that the impurity CO_3^{2-} phase may all be concentrated in the layers close to the surface. This will enhance the relative contribution of the CO_3^{2-} groups to the emission spectra because of the finite penetration depth of the photons.

Let us discuss the O $K\alpha$ x-ray fluorescence spectrum of the multi-phase $YBa_2Cu_3O_{7-\delta}$ sample recorded with an excitation energy of 533.5 eV. This spectrum is different from the series of spectra recorded with higher excitation energies. It is shifted to lower energies and the features are narrower. To clarify the origin of this difference we performed selectively excited O $K\alpha$ measurements on $BaCO_3$. Indeed, when tuning the excitation energy to the most intense peak (533.5 eV) in the O 1s absorption spectrum of the carbonate, we observe the same spectral behaviour (figure 3). The very narrow width of the 533.5 eV peak in the absorption spectrum suggests a localized, 'exciton like' character of the vacant states at this energy. This is also supported by the appearance of the recombination peak in the 533.5 eV excited O $K\alpha$ emission spectrum. Therefore, the coupling between the excited O 1s electron and the valence band electrons gives rise to the observed distortion of the spectral profile for the spectator emission. A similar low-energy shift observed for B K soft x-ray emission spectra of B_2O_3 and hexagonal BN, when exciting into the core exciton state, has been discussed in terms of differences in initial and final state electronic screening and phonon relaxation [20]. Thus, the behaviour of the 533.5 eV excited O $K\alpha$ spectrum of the multi-phase $YBa_2Cu_3O_{7-\delta}$ sample is consistent with that of pure $BaCO_3$.

We have shown that in the case of $K\alpha$ x-ray emission spectra of O the contribution

of CO_3^{2-} can be easily identified due to the difference in the spectral profile between $YBa_2Cu_3O_{7-\delta}$ and $BaCO_3$. Note, however, that one could not in this situation use the $K\alpha$ emission spectrum of C, because it is difficult to distinguish the signal from the surface and the bulk of the sample, even if there is no CO_3^{2-} on the surface but only adsorbed CO_2. The C $K\alpha$ profiles for the two are similar [18, 21].
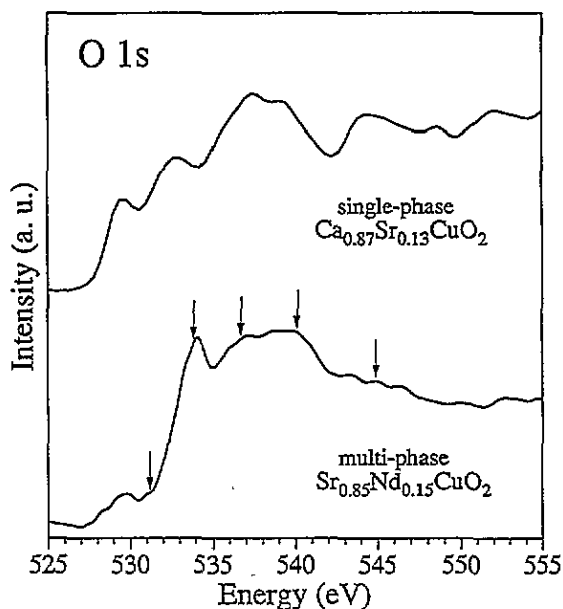

Figure 4. O 1s x-ray absorption spectra of the $Sr_{0.85}Nd_{0.15}CuO_2$ sample with CO_3^{2-} impurities and single-phase $Ca_{0.87}Sr_{0.13}CuO_2$ recorded in the total fluorescence yield mode. The arrows indicate the excitation energies used for O $K\alpha$ x-ray fluorescence spectra.

In the $Sr_{0.85}Nd_{0.15}CuO_2$ sample the presence of 10% of an admixture of unidentified high-pressure phases has been found using an x-ray diffraction method. In turn, the O 1s x-ray absorption spectrum (figure 4), recorded in the total fluorescence yield mode, exhibits a distinct peak at ~ 534 eV, which can be attributed to CO_3^{2-}. However, two other intense features at ~ 540 eV and 545 eV, characteristic of CO_3^{2-}, are not clearly observed in this spectrum and the fine structure is similar to that in the O 1s absorption spectrum of single-phase $Ca_{0.87}Sr_{0.13}CuO_2$ (figure 4).

The existence of the CO_3^{2-} fraction in this $Sr_{0.85}Nd_{0.15}CuO_2$ sample is supported by the results of O $K\alpha$ measurements using tunable excitation. As in the case of the CO_3^{2-} contaminated $YBa_2Cu_3O_{7-\delta}$ in the $Sr_{0.85}Nd_{0.15}CuO_2$ sample in the O $K\alpha$ profile changes in some characteristic way with variation of the excitation energy. The 531.3 eV excited O $K\alpha$ spectrum originates from the contribution of O atoms in the main phase. Again, at excitation energies tuned to the structures of the O 1s edge itself, O $K\alpha$ spectra are similar to those of CO_3^{2-}. In spite of the broadening, the shift to the low-energy side and an enhancement of the low-energy shoulder of the 569.3 eV excited O $K\alpha$ spectrum, this still indicates an appreciable contribution of O atoms from CO_3^{2-} groups. Therefore, one can conclude that even for a high excitation energy the x-ray absorption cross section for these atoms is still higher than that for the main phase.
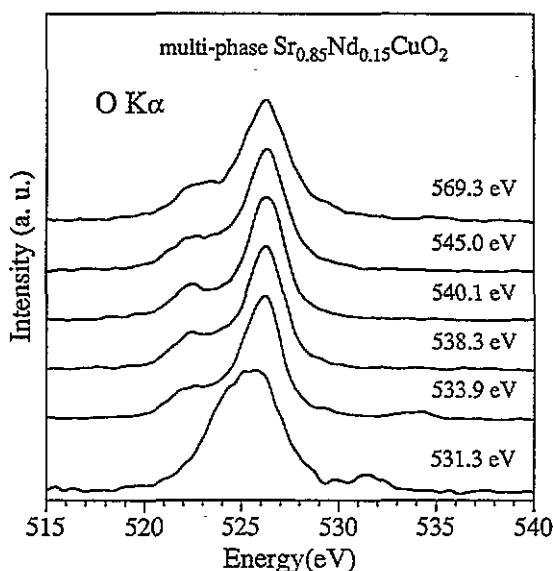
Figure 5. O $K\alpha$ x-ray fluorescence spectra of the $Sr_{0.85}Nd_{0.15}CuO_2$ sample with carbonate impurities recorded at various excitation energies.

Acknowledgments

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