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Fingerprinting substitution sites in Pb,Dy-$Bi_2Sr_2Ca_1Cu_2O_{8+\delta}$ using X-ray Photoelectron Diffraction

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Abstract. The substitution sites of Pb and Dy dopants in the cuprate-type high temperature superconductor $Bi_2Sr_2Ca_1Cu_2O_{8+\delta}$ are determined by a direct comparison of the angle-scanned X-ray photoelectron diffraction (XPD) patterns. We demonstrate the power of XPD as a fingerprinting tool and conclude that Pb occupies Bi sites and Dy the Ca sites. The presence of the incommensurate lattice modulation is not visible in XPD, probably due to a Pb-induced, reduced modulation amplitude.

1 Introduction

The discovery of high temperature superconductors has triggered numerous studies of the details of their geometrical structure. The superconducting $Bi_2Sr_2Ca_1Cu_2O_{8+\delta}$ (Bi2212, $T_c = 85$ K) is the most extensively studied bismuth-containing superconductor. It has a layered structure and an incommensurate superlattice modulation with the period of 25.8 Å along the b axis. This modulation has been subject of many studies, both at the surface [1–3] and in the bulk [4–6].

Many different materials have been used to dope the pure Bi2212 in order to influence the charge around the Cu-O planes believed to be responsible for superconductivity or to modify the structure. In this context the question about the influence of dopants on the modulation is interesting as well. Pb substitution of Bi in Bi2212 has led to many studies [7–9], because sufficient Pb doping inhibits the modulation.

For the determination of the effects of dopants on the charge distribution it is very important to know what site the dopant atom is occupying and whether it is distributed homogeneously substituting mainly one element of the host compound or clustering together. Chemical knowledge can help to suggest the occupation site, but it remains difficult to prove it unambiguously.

X-ray photoelectron diffraction (XPD) [7,10–12] proves to be the method of choice for substitution site identification. We want to mention that this method may also be applied to other complex compounds, for instance minerals. In a previous study, Pillo et al. [11] have investigated Pb,Y-Bi2212 and demonstrated the power of the XPD method for investigating the substitution sites by a direct comparison of diffraction patterns. They find that Pb and Y occupy the Bi and Ca sites of the host material, respectively, and show that the lattice modulation is present again for Y-Pb-Bi2212 although it is absent in Pb-Bi2212 for similar Pb contents.

Here, the occupation sites of Pb,Dy-Bi2212 are studied. XPD is capable of providing the information about the substitution sites and we demonstrate that Pb occupies the Bi sites and Dy the Ca sites. The lattice modulation is not apparent in the XPD patterns as it is the case for pure Bi2212 [12] probably due to a Pb induced, reduced modulation amplitude.

2 Experimental

The experimental set-up represents an extended version of the Vacuum Generators ESCALAB Mk II spectrometer, operating with a base pressure in the low 10^{-10} mbar region. The spectrometer is equipped with a hemispherical electron-energy analyzer with a three-channeltron detection system. A motorized manipulator allows sample rotation with two degrees of freedom [13,14]. The angular resolution was better than 1° full cone acceptance. All the measurements were carried out at room temperature.

X-ray photoelectron spectroscopy (XPS) and XPD were performed with Mg $K\alpha$ ($h\nu = 1253.6$ eV) or Si $K\alpha$ ($h\nu = 1740$ eV) radiation. The spectra have been

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measured with a pass energy of 100 eV corresponding to an energy resolution of approximately 1 eV.

In XPD, the emitted photoelectron wave from a chosen core-level scatters at the surrounding atoms and interferes with the directly emitted wave to give an interference pattern as a function of emission angle. For photoelectrons emitted with kinetic energies above approximately 500 eV, this strongly anisotropic angular distribution of photoelectrons gives the possibility to obtain a basic picture of the local, real-space environment of the emitter [14], due to the "forward focusing" phenomenon along the emitter-scatterer axis (for review see Ref. [15]). Prominent intensity maxima in full hemispherical XPD patterns (diffractograms) can often be immediately identified with near-neighbor directions. The photoelectron angular distribution is, to a first approximation, a forward-projected image of the atomic structure around the photoemitters. Its sensitivity to local order and chemical species makes XPD a powerful technique for surface structural investigations. XPD can be used to characterize near surface structure [16], substitution sites [11], film growth [17–19] and even phase transitions [20].

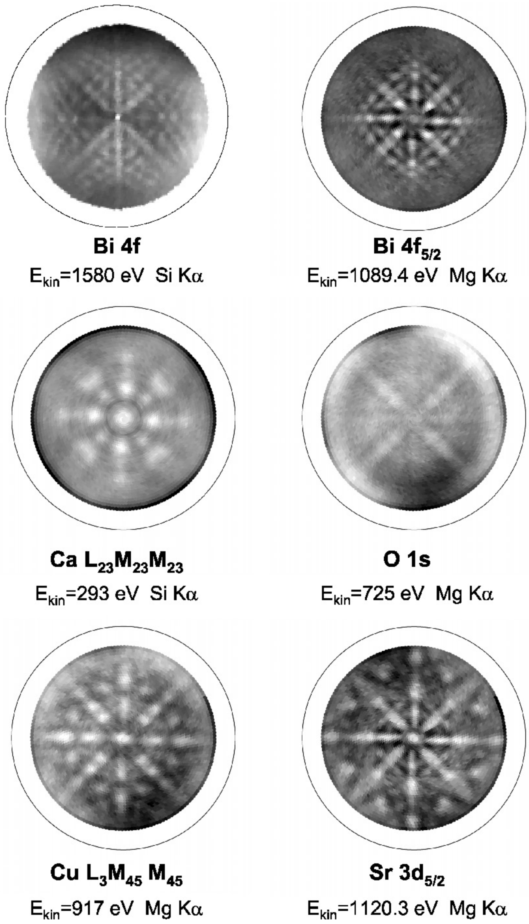
A typical XPD diffractogram consists of intensity at a given core level binding energy for about 5500 angular settings (θ, ϕ) of photoelectron emission angles θ (polar) and ϕ (azimuthal). Measured intensities are represented in a stereographic projection (see Fig. 1). The center of each plot represents normal emission and the outer circle corresponds to grazing emission, $\theta = 90°$. Along each imaginary circle with the center in the center of the plot, theta is constant and phi varies from 0° to 360°. The intensity is represented in a grey-scale plot, with high intensity in white.

Diffractograms presented in this paper are background corrected, i.e., a smooth polar angle dependent background has been subtracted in order to flatten the images and to enhance the contrast.

The samples were grown from nonstoichiometric systems consisting of solute and flux which form a high temperature solution [21]. The single crystals are 2×3 mm^2 large and less than 0.5 mm thick. They were mounted onto the sample holder with silver epoxy. For the measurements the crystals were cleaved in situ at a pressure in the lower 10^{-10} mbar region, yielding clean mirrorlike surfaces with (001) orientation. The cleanness was checked by XPS.

3 Results and discussion

The near surface composition of the Pb,Dy-Bi2212 was determined by XPS. The Pb:Bi ratio is found to be 0.15. This is below the critical value of about 0.25 for removing the modulation [8,9]. The Dy:Ca ratio is 1.1, showing that large quantities of Ca have been substituted. It is know that XPS results considering composition are not necessarily the same as the ones obtained by other techniques, however the ratios are mostly relevant. Furthermore, they will be used here for comparison with our previous study, which has been performed using the same technique.



Bi 4f E_{kin}=1580 eV Si Kα

Bi 4f$_{5/2}$ E_{kin}=1089.4 eV Mg Kα

Ca L$_{23}$M$_{23}$M$_{23}$ E_{kin}=293 eV Si Kα

O 1s E_{kin}=725 eV Mg Kα

Cu L$_3$M$_{45}$ M$_{45}$ E_{kin}=917 eV Mg Kα

Sr 3d$_{5/2}$ E_{kin}=1120.3 eV Mg Kα

Fig. 1. Shown are measurements on the core levels or Auger transitions (Ca and Cu) of elements present in pure Bi2212: Bi $4f$ (top right), Ca $L_{23}M_{23}M_{23}$, O $1s$, Cu $L_3M_{45}M_{45}$ and Sr $3d_{5/2}$. Measurements have been performed with Si-$K\alpha$ radiation (1740 eV) on Pb-Bi2212 for Ca and on Bi2212 for Bi (top left) [12] and with Mg-$K\alpha$ radiation (1253.6 eV) on Pb,Dy-Bi2212 for all the others. Background corrected data (see text) are shown as a linear gray scale plot in stereographic projection.

In Figure 1 we present a set of XPD patterns showing emission from the atomic species of the host material Bi2212: Ca, Bi, O, Cu and Sr. One observes a clear fourfold symmetry of all patterns (except for Fig. 1 (top left) taken from [12] for comparison). This is in contrast to the previous work of Osterwalder et al. [12], where the strong modulation along the b axis in pure Bi2212 causes a considerable deviation from the four-fold symmetry, i.e., where the XPD diffractograms become two-fold symmetric, clearly distinguishing between the crystals a and b axis, as can be seen by comparing the Bi $4f$-diffractograms in Figure 1 (top left and right). Modulation is present in our system as well, (as confirmed by low energy electron diffraction (LEED), not shown) but apparently with a weaker amplitude as for the pure Bi2212.

On the other hand, the four-fold symmetry is consistent with the previously published data of Pillo et al. [11]

where the Pb and Y doped Bi2212 has been studied. The concentration of Pb in their crystal (0.27) was large enough to cause the disappearance of the modulation in Pb-Bi2212. However, doping with Y *re*-introduced the modulation, although weaker than the one of the pure Bi2212. In our case the concentration of Pb is well below 0.25 and the modulation is present (because of lack of Pb), as evidenced by LEED, which lets us conclude that Dy can not have a strong influence on reestablishing the modulation. In both studies the modulation appears in LEED images for two different reasons and is in both studies not strong enough to change the XPD-measurements. The overall fine structure in the XPD images is identical for both crystals.

We can conclude that the intensity of the modulation in our system is diminished and probably does not exceed in amplitude the one of Pb,Y-Bi2212, which is significantly smaller than the one for pure Bi2212, but larger than zero. It is very likely that the cause for the reduction of the modulation amplitude is the presence of Pb. Its concentration, however, is not large enough to totally remove the modulation.

The kinetic energies of all the measured core levels or Auger lines are in the vicinity of each other, except for Ca. The measurement of the Ca diffractogram was difficult due to the overlap of the core level lines of the different elements and the small concentration of Ca. In order to obtain a measurement with better statistics, we have investigated Ca in Pb-Bi2212, where it is present in a larger quantity. The Auger transition was the only available emission line for Ca, where, at the same time an emission line of Dy was available close by (within some 100 eV kinetic energy distance). Low kinetic energies (less than approximately 500 eV) are known for the shorter inelastic mean free paths and diminished electron wave anisotropy leading to forward focusing peaks. For a direct comparison of XPD patterns, using XPD as a fingerprinting technique without a detailed understanding of the different interference features, it is therefore important to choose similar kinetic energies.

The structure of the presented diffractograms is quite complicated, but the images are distinctly different from each other. Therefore, instead of trying to understand the details of the fine structure due to interference and forward focusing, the individual patterns can be used as a fingerprint for the respective local real-space environment of the corresponding element, i.e., for the crystallographic site, as previously suggested [11]. Thus, we do not proceed with the structural analysis which can be performed using the measured patterns, but rather use them for the identification method, which demands only the measurements of the diffractograms of the dopants. A comparison with the fingerprints leads directly to the identification of the substitution site. In this sense, the diffractograms in Figure 1 represent characteristic fingerprints for the local real space environment of the different elements and therefore for the different sites.

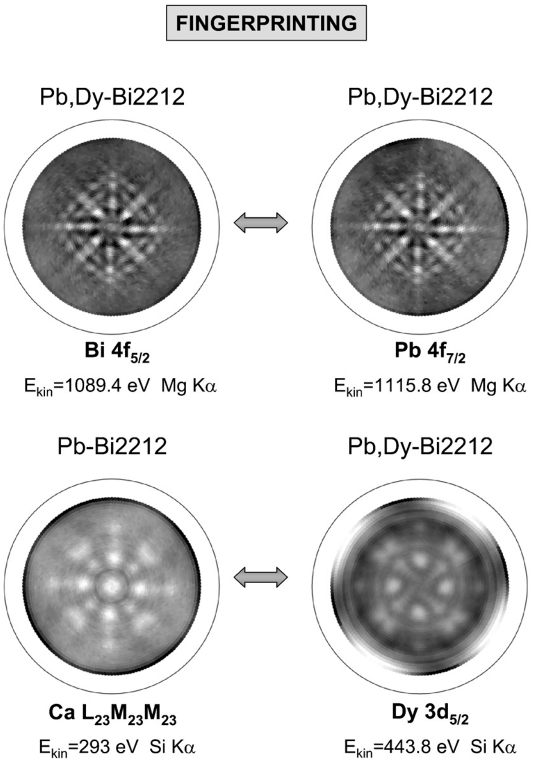


Fig. 2. Fingerprinting: direct comparison of the XPD patterns of Bi $4f_{5/2}$ with Pb $4f_{7/2}$ and Ca $L_{23}M_{23}M_{23}$ (Auger transition) with Dy $3p_{3/2}$. All data are background normalized (see text). In addition, the Dy diffractogram has been four-fold symmetrized.

In Figure 2, the XPD of the dopants, i.e., emission patterns from Pb $4f_{7/2}$ and Dy $3d_{5/2}$ are presented in the right column. On the left side in Figure 2, the most similar diffraction patterns to the ones on the right side have been chosen among the XPD data of the host material presented in Figure 1. One observes a striking coincidence of the Pb pattern with the one of Bi and of the Dy pattern with the one of Ca. Pb and Bi diffractograms are taken at approximately 1000 eV. In this kinetic energy region forward focusing effects are dominant and we could say that we are comparing projected real-space images of the two elements. Dy and Ca are, on the other hand, measured at lower kinetic energies. This means that the diffractograms are not necessary dominated by the forward focusing effects, and that one can probably not resolve directly the atomic structure from forward focusing directions. However, these lower energies do not hinder fingerprinting, i.e. substitution site identification. From the identical appearance of the two patterns at the similar energies, we can conclude about identical local environments, i.e., chemical sites. We can conclude unequivocally, that Pb and Dy dopant atoms occupy Bi and Ca sites, respectively.

In this study, a simple case of a single element substitution has been treated. By no means the applicability area of the fingerprinting method is limited to single site substitution. Multiple site substitution would lead to a pattern which is a linear combination of the diffraction patterns of those host elements, which are being substituted. One would accordingly simulate the measured XPD-pattern of the dopant as a linear combination of the patterns of the host in order to determine quantitatively which sites have been substituted and to which extent. This wide range of application possibilities makes fingerprinting one of the most comfortable methods for the investigations of doping and element substitution, as long as the detection limit of XPS (typically a few percent) is respected.

4 Conclusion

We have shown that XPD represents a direct tool to determine substitution sites of dopants, even in very complex materials with many constituents with low concentrations. It is demonstrated that XPD can, for these purposes, be used at low kinetic energies – the presence of forward focusing is not a requirement for the fingerprinting. In Pb and Dy doped Bi2212 we have demonstrated that the Pb atoms occupy the Bi sites and the Dy atoms the Ca sites. The substitution sites are similar to the previously published case of Pb,Y-Bi2212 [11]. The modulation along the crystal *b* axis is present, according to the composition of Pb,Dy-Bi2212. However, the four-fold symmetry of all the XPD patterns indicates that the lattice modulation is weaker than in pure Bi2212, which is assigned to the Pb doping.

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