X-ray photoelectron diffraction for pure and Nb-doped KTaO$_3$: site determination for the Nb atoms

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Abstract. We present a set of polar-angle-dependent x-ray photoelectron spectra (XPS) obtained from *in situ* cleaved single-crystalline pure KTaO$_3$. The variation of the intensity for different angles can be explained by the diffraction of the emitted electrons by the surrounding atoms of the emitter and thus may be used as a 'fingerprint' for the location of emitting impurity atoms. Measurements were carried out on niobium-doped KTaO$_3$. The atomic position of the niobium atoms was deduced from the comparison of the angle-dependent spectra, giving a clear hint that tantalum is replaced by niobium.

1. Introduction

Potassium tantalate–niobate mixed crystals (KTN, i.e. KTa$_{1-x}$Nb$_x$O$_3$ with $0 < x < 1$) are photorefractive with a very high sensitivity [1]. Therefore, this material is of special interest for many applications, e.g. optical signal processing or holographic storage [2]. In the experiment presented it is used as a testing material for an application of x-ray photoelectron diffraction: the site determination for elements that occur in host materials in small concentrations. The photorefractive properties (e.g. diffraction efficiency, two-beam coupling gain, sensitivity) depend strongly on the concentration and valence state of the impurities; e.g. the influence of small concentrations of iron on the optical properties has been investigated in detail [3]. Tailoring of crystals for applications requires detailed knowledge about the processes in the crystal, and therefore information about the incorporation site of ions is especially required. A common method for investigating this kind of material is that of electron spin resonance (ESR) [4]. As ESR can only be applied for atoms with unpaired electrons, x-ray photoelectron diffraction can give additional information, especially for atoms that occur in different valence states. We present the results of our investigations on cleaved pure and niobium-containing KTaO$_3$ surfaces obtained for various angles. The polar and azimuthal variation of the intensity of electrons emitted from the atoms at different lattice sites will be used as a 'fingerprint' for the location of impurity atoms as long as they are occupying regular lattice sites. By this method we will check whether tantalum ions are replaced by niobium ions, as is expected [5, 6]

The intensity of x-ray photoelectron spectroscopy signals from ordered surfaces is influenced by the atoms surrounding the emitter. This has been known since the work of Siegbahn and co-workers, and is described as x-ray photoelectron diffraction (XPD) [7, 8]. The outgoing photoelectrons are diffracted by the effective atomic potentials [9]. Using typical energies above a few hundred eV, the scattering at the neighbour atoms leads to an intensity enhancement in the direction of the scatterer. This is called 'forward focusing',

because the scattering atoms act like focusing lenses for the passing photoelectrons [10]. As a result the XPD spectra are influenced by the local geometry of the emitter. The patterns of variation are characteristic of the emitting site [11] and can be used to distinguish between differently coordinated sites [12]. Besides this, forward focusing can have a significant influence on the quantification of XPS data [13]. There has been a rapid expansion in recent years in the application of XPD in structure determination, especially for surface adsorption sites. It is only possible here to cite a few representative examples [14–21] from several hundred papers.
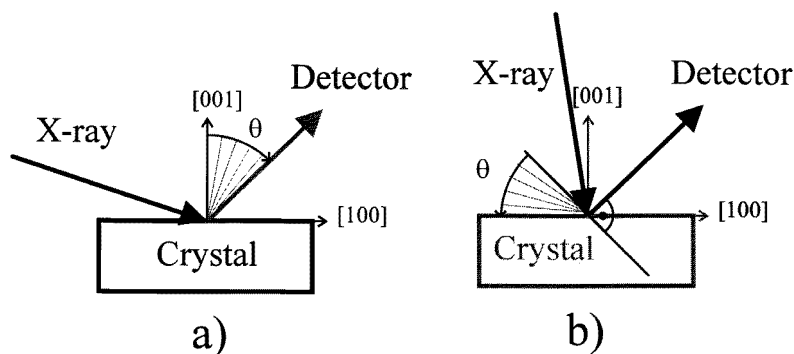

Figure 1. The experimental geometry for the XPD measurements for pure and niobium-doped $KTaO_3$. The variation of the polar angles is: (a) by rotating the detector for a VG ADES 400; (b) by rotating the sample for a PHI 5600ci.

2. Experimental details

The measurements were obtained using a VG ADES-400 angle-resolving spectrometer and a Phi 5600ci ESCA spectrometer. Both spectrometers were equipped with a dual x-ray anode (Mg and Al Kα). The base pressure used was about 10^{-10} mbar. The analyser of the ADES-400 can be rotated within two perpendicular planes; the acceptance angles are $1.25°$ in the polar direction as determined by the entrance slit of the analyser. The spectra presented were obtained by keeping the azimuthal angle constant at $0°$ and changing only the polar angle as shown in figure 1. The angle between the incident x-ray beam and the surface normal of the sample was $72°$ for all experiments. The angle variation of the spectra obtained with the Phi 5600ci was achieved by rotating the sample. This spectrometer is equipped with a multi-channel analyser; thus it was used for the measurements on the doped samples. The angle between the x-ray beam and the analyser is fixed at $54°$. The spectra were obtained with an acceptance angle of $2°$. Single-crystalline surfaces of the samples were prepared by *in situ* cleaving (UHV conditions) [22, 23]. The size of the samples was about 4×4 mm^2.

All of the measurements were carried out on cleaved (001) surfaces of single crystals. The data presented here were obtained using Al Kα radiation ($\hbar\omega = 1486.7$ eV—VG ADES-400) and Mg Kα radiation ($\hbar\omega = 1253.6$ eV—Phi 5600ci). All of the spectra for the pure sample presented in figure 2 were obtained using the VG spectrometer due to the better angular resolution, whereas the Phi ESCA was used for the doped sample because of the higher photoelectron intensity (figure 3).
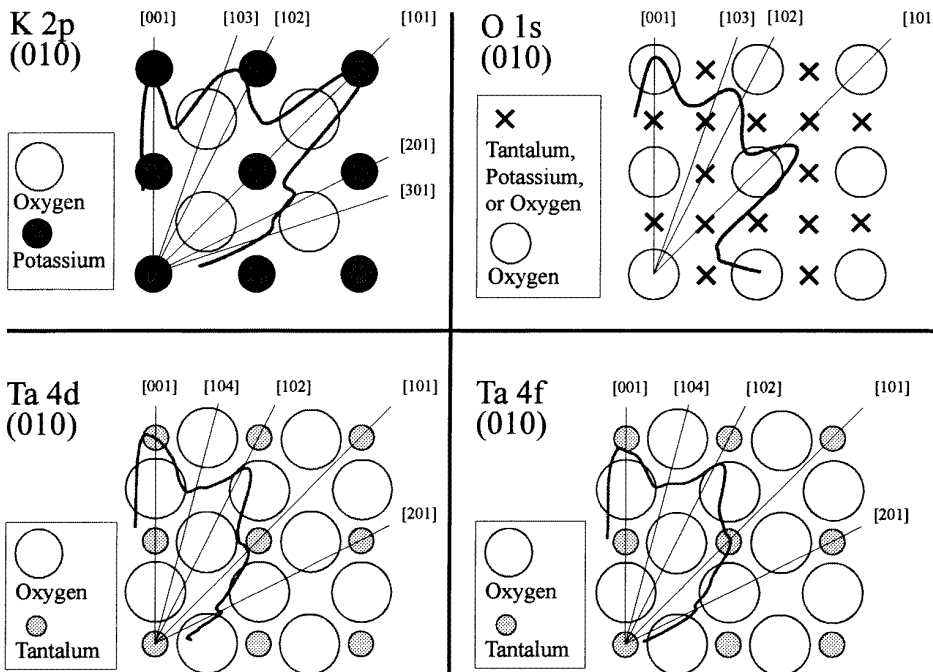
Figure 2. Radial plots of the XPD spectra for K 2p, Ta 4d, Ta 4f and O 1s for pure $KTaO_3$. The crosses for O 1s indicate either tantalum, potassium or oxygen depending on the crystal plane.

Each point in the XPD spectrum was obtained from a complete XP spectrum. The intensity was determined from the peak after subtracting the inelastic background with an algorithm developed by Tougaard [24]. The resulting XPD spectra were smoothed using cubic splines (see figure 3).

3. Results and discussion

The spectra of the pure sample were obtained by measuring the most intense XPS lines (K 2p, Ta 4f and O 1s). For comparison and verification of the angular distribution, the Ta 4d peak was measured too. The XP spectra were measured for polar angles from $-20°$ to $80°$. In figure 2 the XPD spectra are drawn as a polar plot; this curve is plotted underneath a partial structure plot of $KTaO_3$, which has ideal perovskite structure with the space group $Pm3m$. The lines shown in the diagram refer to the low-indexed crystal directions. In these directions the smallest distances between the atoms can be found. A possible relaxation of the surface could not be detected in the spectra. The applied method (XPD) is a rather surface-sensitive technique, and thus changes in the surface structure should become visible.

The x-ray-emitted electrons are now diffracted by the surrounding atoms of the emitter. The most important effect which can be observed is a forward scattering into the direction of the neighbouring atoms. This means that the diffracting atoms act like a focusing lens to the electrons. For that reason a maximum of the intensity of the emitted electrons can be expected in the low-indexed directions. This effect is dominant only for high kinetic

energies (about 1 keV). The two spectra of tantalum with kinetic electron energies of 1461.7 eV (Ta 4f) and 1260.7 eV (Ta 4d) have the same shape; therefore forward focusing can be considered as the most important effect when interpreting these spectra. For these tantalum spectra, both 4d and 4f maxima can be observed in the direction of the nearest tantalum atoms ([101]) and the oxygen atoms ([001], [104], [102] and [201]). As expected, the smaller the distance between the emitter and the next scatterer, the more distinct the maxima. Hence, the highest intensities can be found in the [001] and the [102] directions, where scattering atoms are located very close to the emitter. But even more distant atoms contribute to the diffraction maxima, e.g. oxygen in the [104] direction; besides, these maxima are less distinct because oxygen is a very weak scatterer. The intensity decreases for larger angles, but the modulation is still visible.
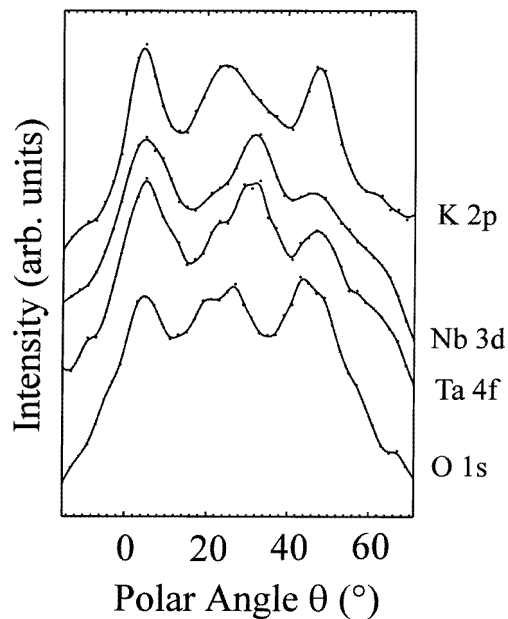

Figure 3. A comparison of Nb 3d with K 2p, Ta 4f and O 1s XPD spectra for niobium-doped KTaO$_3$.

For the K 2p signal, even more maxima can be observed. The highest intensity due to the diffraction at the next oxygen atoms can be found in the [103], [101] and [301] directions. The maxima in the direction of the nearest potassium atoms are located in the directions [001], [102] and [201]. The XPD spectra of potassium and tantalum show maxima in the directions [001] and [101]. Significant differences in the spectra are observed in the directions between [001] and [101] at polar angles between 10° and 35°. Electrons emitted from the potassium site are strongly scattered into the [103] direction, whereas electrons from the tantalum site show a significant maximum in intensity in the [102] direction. The shape of the XPD spectra is evidently determined by the position of the emitting atom in the lattice; therefore these spectra can be used as a 'fingerprint' for the localization of the emitters, as long as they are occupying regular lattice sites.

The O 1s signal results from oxygen in three different crystal positions. Therefore the interpretation of the XPD spectrum of oxygen is more difficult than that of the spectra of potassium and tantalum. The emitted electrons are diffracted by the neighbouring oxygen

atoms, and further at potassium, niobium or oxygen, depending on the corresponding crystal planes. This is shown in figure 2. Significant maxima can only be found in the main directions [001], [103]/[102] and [101], as electrons emitted from oxygens of all three different planes contribute to them.

Additional investigations were performed on niobium-doped $KTaO_3$ samples in order to determine the position of the niobium atoms within the $KTaO_3$ lattice. Again only the most intense XPS lines (Ta 4f, Nb 3d, K 2p and O 1s) were measured as functions of polar angle.

In the periodic table both niobium and tantalum can be found in group VA whereas potassium belongs to group IA. Taking this into consideration it could have been anticipated that niobium will be found at the same lattice position as tantalum, because of the similarity of their chemical properties. This is already known from Raman scattering [5] and ion channelling studies [6]. Here it will serve as a proof for the applicability of XPD for the determination of the positions of impurity atoms in crystal lattices. In figure 3 the variation in intensity is shown as a function of angle for K 2p, Nb 3d, Ta 4f and O 1s for the niobium-doped sample. The angular variations for the doped sample appear to be slightly different due to the different experimental preconditions, but no fundamental differences from the case of the undoped sample (figure 2) were found in the shapes of the spectra (figure 3). Even for the low concentrations of niobium atoms, maxima in the XPD spectra of Nb 3d can be clearly identified. They appear in the [001], [104], [102] and [201] directions and can be compared nicely with those of tantalum. The spectra of potassium and oxygen are quite different. In particular, the intensity of the maxima in the [101] direction is quite different for potassium on the one hand and niobium and tantalum on the other hand. From the nearly identical shapes of the XPD spectra of niobium and tantalum it can be concluded that the atomic surroundings of the two emitters appear to be identical. This leads to the conclusion that the niobium atoms are located at the same—or at least very similar—positions as the tantalum atoms. Thus the chemical formula can be written as $KTa_{1-x}Nb_xO_3$, $x = 0.08$. The atomic concentration x of niobium was determined by XPS.

4. Conclusions

X-ray photoelectron diffraction has proved to be a valuable method for the determination of the positions of impurity atoms in lattices. This has been demonstrated for niobium atoms in a $KTaO_3$ crystal. In agreement with previous results, it was shown that niobium occupies the same positions as tantalum. This resulted from the comparison of the angular distribution of the photoelectrons; these plots can be used as very specific fingerprints of the local environment of the emitting atoms. It is expected that this method will be improved considerably in the near future by the use of monochromatized light sources and a smaller acceptance of the analyser in connection with calculations of the angle-dependent photoelectron spectra. Thus it appears to be possible to determine also off-centre positions of impurity atoms applying *R*-factor analyses, as is proposed, by *ab initio* shell-model simulations [25].

Acknowledgment

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