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The electronic structure of KTaO_3 : a combined x-ray spectroscopic investigation

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Abstract

The electronic structure of potassium tantalate (KTaO_3) is studied by various spectroscopic techniques, namely x-ray photoelectron spectroscopy (XPS), x-ray emission spectroscopy (XES), and x-ray absorption spectroscopy (XAS). The experiments are compared with theoretical band structure calculations. Excellent agreement between theory and experiment is achieved. XPS and XES reveal that the valence band is dominated by strongly hybridized Ta 5d and O 2p states. Furthermore, we find that the Ta N_{III} resonant inelastic x-ray spectroscopy (RIXS) spectra consist of three distinct features. For excitation energies close to the Ta 4p absorption threshold an elastic recombination peak and a resonant Raman-like loss feature are present in addition to nonresonant-like x-ray emission. In comparison with band structure calculations we are able to assign the loss feature to charge transfer excitations between occupied Ta 5d and O 2p states and unoccupied Ta 5d states.

1. Introduction

Potassium tantalate (KTaO_3) is a well known model system for ferroelectric materials. KTaO_3 is a perovskite with cubic symmetry at room temperature. Very recently, an n-channel accumulation-type field-effect transistor (FET) has been fabricated by using a KTaO_3 single crystal as an active element [1]. The properties of KTaO_3 have been studied intensely, mostly in combination with other interesting related ferroelectric materials like potassium niobate (KNbO_3) or mixed $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ [2–4] crystals. The electronic structure of KTaO_3 , mostly in combination with KNbO_3 , has been investigated by a sequence of band

structure calculations, such as empirical parameter adjustment studies [5, 6], first-principles self-consistent methods [7, 8], precision all-electron total energy calculations [9–11], and density functional theory [12]. From the experimental point of view, x-ray photoelectron spectroscopy (XPS) provides a powerful tool for the analysis of the spatial distribution of the occupied electron density and chemical bonding, especially in combination with band structure calculations. Previous studies have applied XPS to KTaO_3 [8, 3, 13], and compare the experiments with the calculated total density of states (tDOS). However, since KTaO_3 is an insulator, XPS measurements are affected by charging effects; in addition, the sample preparation is crucial. X-ray emission spectroscopy (XES) is an element-specific technique which allows one to record the partial densities of states (pDOS). In addition, no charging effects arise, and due to the larger escape depth, no sample preparation is required. Resonant inelastic x-ray spectroscopy (RIXS) is a tool for investigating the electronic properties of ferroelectric materials that allows one to study intra-atomic correlation as well as interatomic hybridization effects [14, 15]. In the last few years this spectroscopic technique has been applied to ferroelectric materials, like SrTiO_3 [16] or KNbO_3 [17, 15]. Postnikov *et al* [15] previously published RIXS spectra of KTaO_3 ; however, they were not able to distinguish between x-ray resonant Raman scattering and nonresonant x-ray fluorescence. The measurements presented here show significantly better resolution and signal to noise ratio. We present a detailed x-ray spectroscopic study of KTaO_3 by means of XPS, XES, XAS and RIXS. The experiments are compared with theoretical calculations carried out using the all-electron full-potential linearized augmented plane-wave (FLAPW) method. Our results are compared with earlier results on the related compound KNbO_3 [17, 15].

2. Experimental and theoretical details

High quality KTaO_3 single crystals were grown by the Czochralski method.

The XAS, XES and RIXS-spectra were recorded at the Advanced Light Source (Beamline 8.0.1) using the soft x-ray fluorescence end station of the University of Tennessee at Knoxville [18]. Photons with an energy of 400–580 eV are delivered to the end station via a spherical grating monochromator. The Ta 5d–4p and O 1s spectra were obtained with a 1500 lines mm^{-1} , 10 m radius grating. Ta 4p and O 1s x-ray absorption spectra were recorded in partial fluorescence yield (PFY) mode.

The XPS valence band and outer core levels were recorded using a PHI 5600ci multi-technique spectrometer with monochromatic Al $K\alpha$ ($h\nu = 1486.6$ eV) radiation of 0.3 eV FWHM bandwidth, with the sample at room temperature. The resolution of the analyser is 1.5% of the pass energy, 0.35 eV. All spectra were obtained using a 400 μm diameter analysis area. During the measurements, the pressure in the main chamber was kept below 1×10^{-9} mbar. The sample was fractured *in situ*. The survey spectrum taken directly after fracturing the sample shows only low contamination of hydrocarbon and C 2p states should have no influence on the valence band spectra. Since KTaO_3 is a Mott–Hubbard insulator, the sample had to be neutralized with the help of a charge neutralizer which produces a constant flux of electrons on the sample surface. The spectra were calibrated with respect to the C 1s line of adsorbed carbon ($E_B = 285.0$ eV) [19].

The FLAPW calculations were performed using the WIEN97 code [20].

3. Results and discussion

3.1. XPS and XES

Figure 1 shows the recorded XPS valence band, the Ta N_{III} , O $K\alpha$ nonresonant XES spectra and the corresponding calculated partial densities of states (pDOS) for KTaO_3 . Furthermore,

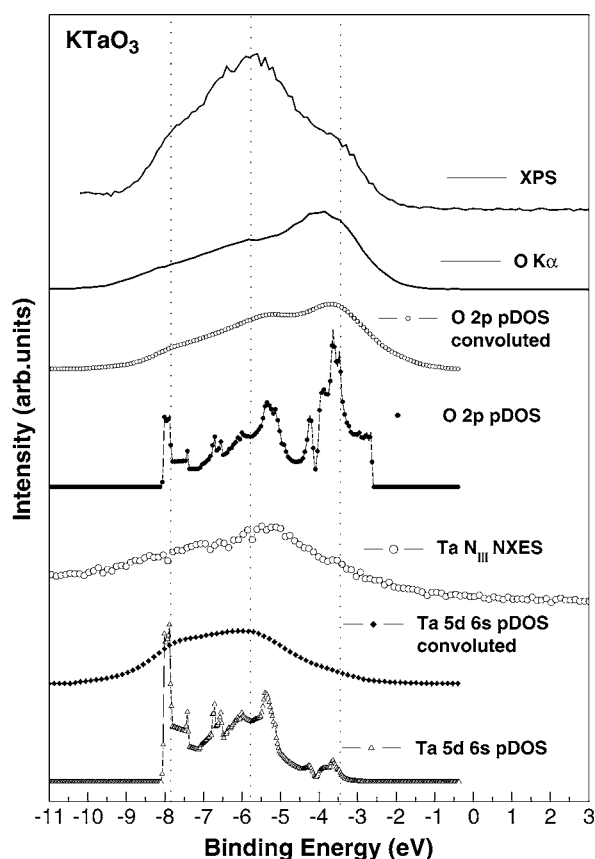


Figure 1. Comparison of the experimental XPS (TDOS) with NXES measurements and the calculated pDOS for Ta and O.

the calculated pDOS, convoluted with the experimental resolution, are plotted in figure 1. The XPS valence band consists of three distinct main features, labelled by vertical lines in figure 1 at -3.7 , -5.5 and -7.8 eV on the binding energy scale. Due to strong Ta 5d–O 2p hybridization, the XPS valence band region consists of overlapping bands; therefore it is helpful to resolve complementary the pDOS of the constituents by XES spectroscopy. The Ta N_{III} and O $K\alpha$ XES spectra have been brought to a binding energy scale using the corresponding XPS core level binding energies. The O $K\alpha$ XES spectrum shows a maximum at -4 eV, mainly comprising the band located at -3.7 eV in the XPS valence band spectrum. This is in agreement with theory, plotted below the corresponding experimental results in figure 1. The features at -5.5 and -7.8 eV in the XPS valence band can be attributed to the maximum at -5.5 eV and the shoulder at -7.8 eV of the Ta N_{III} XES spectrum shown in figure 1. The agreement with theory is again good. Moreover, the shoulders which can be found in the O $K\alpha$ NXES spectrum and also in the calculated spectrum convoluted with experimental resolution presented in figure 1 around -5.5 and -7.8 eV indicate a strong hybridization between the Ta 5d and O 2p states throughout the whole valence band of KTaO_3 .

3.2. XAS and RIXS

Figure 2 shows the XAS spectrum of the Ta 4p-edge of KTaO_3 recorded in PFY mode.

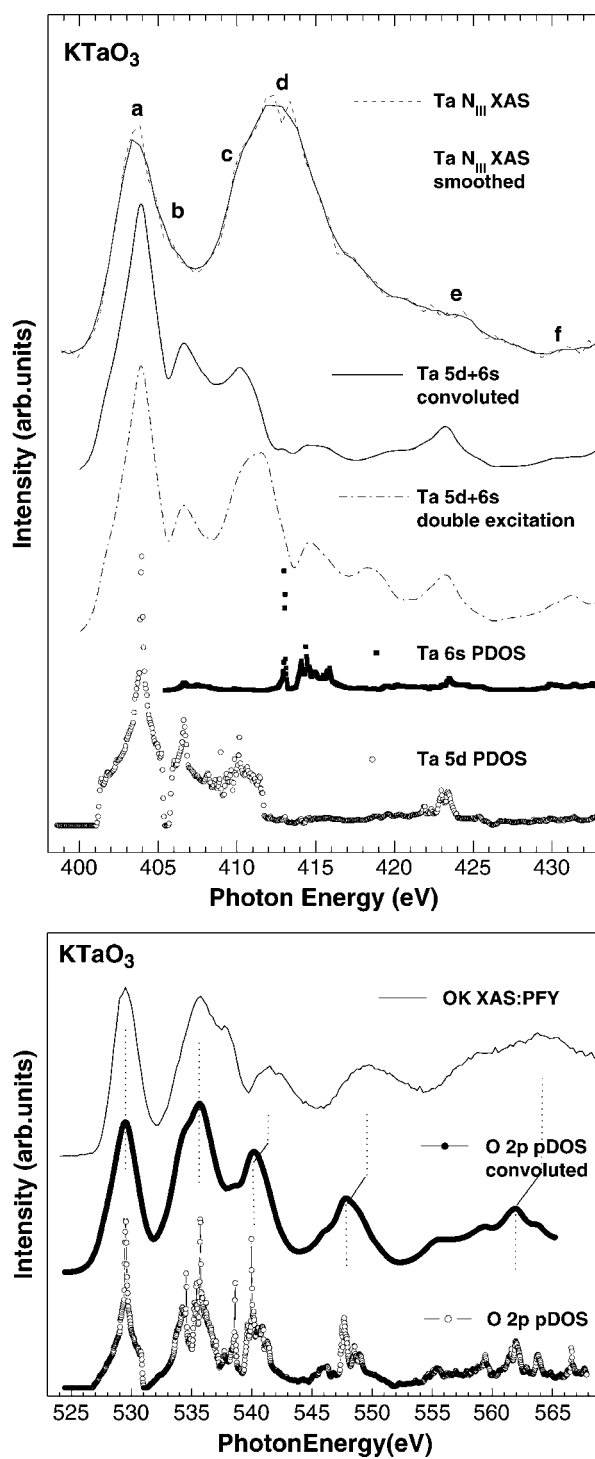


Figure 2. Upper panel: Ta $4p_{3/2} \rightarrow 5d6s$ XAS spectrum of KTaO₃; the calculated Ta 5d and Ta 6s pDOS are also plotted for comparison. Lower panel: O K α XAS spectrum and the corresponding O 2p pDOS. All XAS spectra were recorded in PFY mode.

The XAS spectrum (dashed spectrum) consists of six distinguishable features labelled a–f; the Ta N_{III} absorption edge is at 404 eV (feature a). The agreement between the experimental result and the calculation (second trace in figure 2, upper panel) is good and allows the following assignment of the features: peak a and a rather weak feature b in the Ta $4p \rightarrow 5d$ XAS spectrum are found as being due to empty Ta 5d states as well as feature f. The features c and e have been previously identified as loss structures of the Ta 4f and Ta 4d states from EELS measurements [21]. Moreover, Nb $2p \rightarrow 4d$ XAS measurements on KNbO_3 show similar features [13, 15]. The calculations suggest that the features c and e also comprise empty Ta 5d states. There are differences between experiment and theory regarding feature d of the XAS spectrum, which can be explained by double excitation processes. Incoming photons with an excitation energy of 412.6 eV lead to an ejection of Ta $4p_{3/2}$ electrons. These electrons donate about 8 eV of their energy to O 2p or Ta 5d valence electrons. The dashed-dotted spectrum in figure 2 (third trace, upper panel) corresponds to a calculation which considers such double excitation processes and results in satisfactory agreement between experiment and theory regarding feature d in the Ta N_{III} XAS.

The lower panel of figure 2 shows the O $K\alpha$ XAS of KTaO_3 . Similar XAS spectra for the unoccupied states of oxygen have been reported for the related compound KNbO_3 [13, 22]. The O $K\alpha$ XAS shows local maxima at 529.5, 535.7, 537.8, 541.6, 549.6 and 564.1 eV. Very good agreement with the calculated O 2p pDOS is achieved. The feature at 537.8 eV in the O $K\alpha$ XAS spectrum is not reproduced by the calculation and is possibly due to hybridized O 2p–Ta 5d states, similar to the results obtained for KNbO_3 [13].

Figure 3 displays the Ta N_{III} resonant x-ray emission spectra for selected excitation energies. Because the Ta $4p_{3/2}$ and the Ta $4p_{1/2}$ states are separated by 62 eV due to spin orbit splitting, the emission measurements are free of overlapping effects, in contrast to the Nb $5p_{4f} \rightarrow 3d_{3/2}$ emission of KNbO_3 [17, 15]. The changes appear for excitation energies in the range of 402.8–406.3 eV displaying a three peak structure. Besides normal-like x-ray emission and the elastic recombination peak a Raman-like loss feature is found which reaches its maximum intensity under resonant x-ray emission conditions at an excitation energy of $E_{\text{exc}} = 404.8$ eV. Above $E_{\text{exc}} = 406.3$ eV the loss feature disappears or evolves into normal fluorescence.

KTaO_3 is well known to be an insulator with d^0 electron configuration and is a charge-transfer compound. Hence, the hybridization of Ta 5d and O 2p electrons plays an important role in the valence band formation of the compound, and the 3d wavefunction for such systems is known to be more extended compared to other transition metal compounds. It has been found that under these conditions the resonant emission features can at least qualitatively be interpreted within the band approach [14]. The loss feature is located around 7.5 eV below the elastic recombination peak. Using the calculated DOS we find the difference between the occupied and unoccupied Ta 5d and O 2p states to be around 7 eV. Thus, the loss feature in the Ta N_{III} RIXS spectra can be explained as being due to charge transfer transitions between O 2p–Ta 5d states in the valence band and free Ta 5d states in the conduction band.

4. Conclusions

The electronic properties of the ferroelectric model compound KTaO_3 have been investigated by a comprehensive x-ray spectroscopic study. XPS valence band and the corresponding XES measurements of the Ta N_{III} and the O $K\alpha$ states reveal strong hybridization between Ta 5d and O 2p states in the valence band of KTaO_3 . XAS on the Ta N_{III} edge shows a feature which is attributed to a double excitation process. The O $K\alpha$ XAS spectrum exhibits a feature which is likely due to hybridized O 2p–Ta 5d in the conduction band of KTaO_3 . RIXS measurements

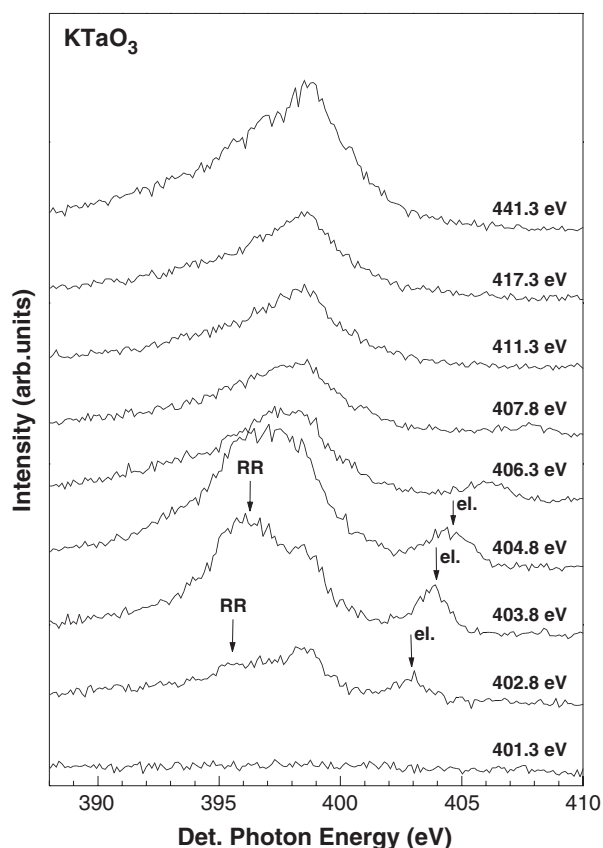


Figure 3. Ta 5d_{6s} → 4p_{3/2} RIXS spectra of KTaO₃. The excitation energy is tuned through the Ta N_{III} threshold. The elastic peak (el) and the resonant Raman loss feature (RR), present at low excitation energies, are also labelled.

performed on the Ta N_{III} edge consist of a strong normal-like emission feature and a Raman-like loss feature which can be associated with transitions between overlapping O 2p–Ta 5d states in the valence band and unoccupied Ta 5d states. An overall very good agreement with the FLAPW band structure calculations is found. In summary, we are able to reveal a complete picture of the electronic structure and the hybridization effects of KTaO₃ by using different experimental techniques and comparing the experiment with band structure calculations.

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