

Direct determination of the charge transition level of dopants in oxides by x-ray photoelectron spectroscopy

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Charge transition levels of dopants directly influence material properties, but experimental numbers are difficult to obtain. It will be demonstrated how x-ray photoelectron spectroscopy can be applied to directly determine charge transition levels of dopants in oxides. Oxidizing and reducing treatments induce changes of the Fermi level at the surface, accompanied by changes of the oxidation state of the dopant. The approach is exemplified for 0.2 mol % V-doped BaTiO₃ bulk ceramics, revealing a V^{5+/3+} charge transition at a Fermi level ≈ 0.15 eV above the conduction-band minimum. Consequently, V is present as V⁵⁺ and acting as a donor in BaTiO₃ for most experimental conditions.

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I. INTRODUCTION

Charge transition levels (CTLs) of defects and dopants, which correspond to the Fermi level at which a defect or dopant changes its charge state (valence), are key quantities which determine material properties. In the case of BaTiO₃, doping is employed to control electrical properties of multilayer ceramic capacitors (MLCCs) [1], heating elements and sensors of positive temperature coefficient resistors [2], and optical properties in photorefractive materials [3]. Transition metals with variable oxidation states are widely used as dopants. The valence of such transition-metal dopants changes whenever the Fermi level, determined by overall charge neutrality, is crossing a specific charge transition level in the band gap. The charge transition levels directly affect optical and electrical properties [3,4], but also the oxygen vacancy concentration, i.e., how easy it is to oxidize or reduce the compound [5,6]. Knowledge of the charge transition levels is thus a key to understand the effect of doping.

Oxidation states and charge transition levels of impurity ions in oxides can be determined by a variety of techniques such as temperature-dependent conductivity and Hall effect, deep-level transient spectroscopy (DLTS), electron paramagnetic resonance (EPR), Mössbauer spectroscopy, photo- and cathodoluminescence spectroscopy, or thermogravimetric studies [5,7–18]. The most direct way to determine charge transition levels of dopants is by thermogravimetry, measuring the weight of a sample in dependence on oxygen activity [18].

Still, this is not a direct measurement, as it requires describing the data with a quantitative defect model. EPR can identify selected oxidation states only, and the determination of charge transition levels requires combination with temperature-dependent conductivity measurements and assumptions regarding the nature of the carriers involved in conduction. Photo- and cathodoluminescence are spatially resolved techniques providing accurate optical transitions, but the assignment of transitions to specific defect species is also not possible directly. The same is true for all characterization techniques mentioned above. Assigning activation or transition energies to certain defect species can become more complex or even impossible when more than a single dopant is present, which is very often the case in technological materials.

This contribution introduces a complementary and versatile experimental approach based on x-ray photoelectron spectroscopy (XPS) to determine charge transition levels of dopants in oxides directly, i.e., free of any parameters and not depending on a model fitted to experimental data. The approach is based on a manipulation of the Fermi level at the surface of an oxide, which can, for example, be achieved by changing the oxygen vacancy concentration in a near-surface region through oxidizing and reducing sample treatments. The CTL is then identified from the Fermi level recorded for that specific sample condition for which the dopant is present in two different oxidation states. Charge transition levels have already been determined in our group by means of XPS previously. In these studies, either conducting materials such as Sn-doped In₂O₃ (ITO) [19], thin films of insulating materials such as CeO₂ or BiFeO₃ deposited onto conducting Pt or (La,Sr)MnO_{3- δ} substrates [20,21], or insulating samples [La-doped Pb(Zr,Sn,Ti)O₃] with thin conducting top electrodes (ITO) [22] have been used to avoid charging during XPS measurement. In any of the reported measurements, the concentration of the species exhibiting the charge transition has been several atomic percent or more. In such cases, there is an influence of defect interactions. The present approach is

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overcoming the previous limitations by employing a (thick) bulk ceramic oxide without conducting substrate or top electrode and a low dopant concentration. Such conditions are typical for polycrystalline ceramics used in technology, allowing for a much broader application of the procedure.

The XPS approach for the determination of charge transition levels is exemplified for 0.2 mol % V-doped BaTiO₃ bulk ceramics. Vanadium is used as a codopant of BaTiO₃ to improve device behavior of MLCCs [23,24]. As discussed by Böttcher and co-workers [12], a difficulty in analyzing the properties of V in BaTiO₃ is the low solubility of well below 1%, associated with the formation of secondary phases for high V content. From EPR studies of strongly reduced samples, the presence of V²⁺ has been suggested [5,25]. This was later confirmed by Böttcher and co-workers [12], who also reported 4+ and 5+ oxidation states in as-sintered samples. Two different density-functional-theory (DFT) calculations of V-doped BaTiO₃ are available. Kaneda and co-workers revealed that V is preferentially substituting for Ti and that it can occur as V³⁺, V⁴⁺, or V⁵⁺ [24]. The V^{4+/3+}- and V^{5+/4+}- transitions are very close in energy, resulting in a narrow range of the stability of V⁴⁺. Both charge transition levels are within 0.5 eV from the conduction-band minimum. Kanagawa and co-workers employed hybrid HSE06 functional calculations to rhombohedral BaTiO₃, which is the stable polymorph at 0 K. The energies of the V^{5+/4+} and V^{4+/3+} transitions are obtained at ≈ 2.25 eV and ≈ 2.6 eV above the valence-band maximum, respectively. In addition, a V^{3+/2+} transition is reported at ≈ 3.2 eV above the valence-band maximum. All three transition levels lie within the band gap of 3.69 eV for rhombohedral BaTiO₃ [26].

II. EXPERIMENTAL

The bulk ceramic BaTiO₃ sample used in the experiment is prepared by the conventional solid-oxide route starting with a high-quality hydrothermal BaTiO₃ powder (Prod: BT-01 Sakai Chemical Trading Co., Ba/Ti = 0.999%, 99.99% purity) using a recipe partially developed earlier [27]. TiO₂ and V₂O₅ are added to obtain a Ba:(Ti + V) ratio of 0.997, assuming that V is occupying the B site of the ABO₃ perovskite lattice [24,28]. A chemical analysis of identically prepared samples has revealed a V concentration of 0.2 mol % which is twice the nominally added V content. X-ray diffraction at room temperature revealed a single-phase tetragonal structure. We observe secondary phases by x-ray diffraction only for higher nominal V content, which is consistent with electron-microscopy analysis reported in literature [29]. Further details of sample preparation are given in the Supplemental Material [30].

XPS spectra of V-doped BaTiO₃ samples were recorded with a 45° takeoff angle using a Physical Electronics PHI 5700 spectrometer equipped with a monochromatic Al K α source as part of the Darmstadt Integrated System for Materials Research (DAISY-MAT [31]). Binding energies are calibrated using sputter-cleaned Ag, revealing a Gaussian broadening of the Fermi edge by <0.4 eV. The BaTiO₃ sample is reduced in an Ar/5% H₂ mixture at 900 °C for 10 h. Thereby, oxygen vacancies are introduced, inducing a sufficient electronic conductivity to avoid charging during photoemission [32].

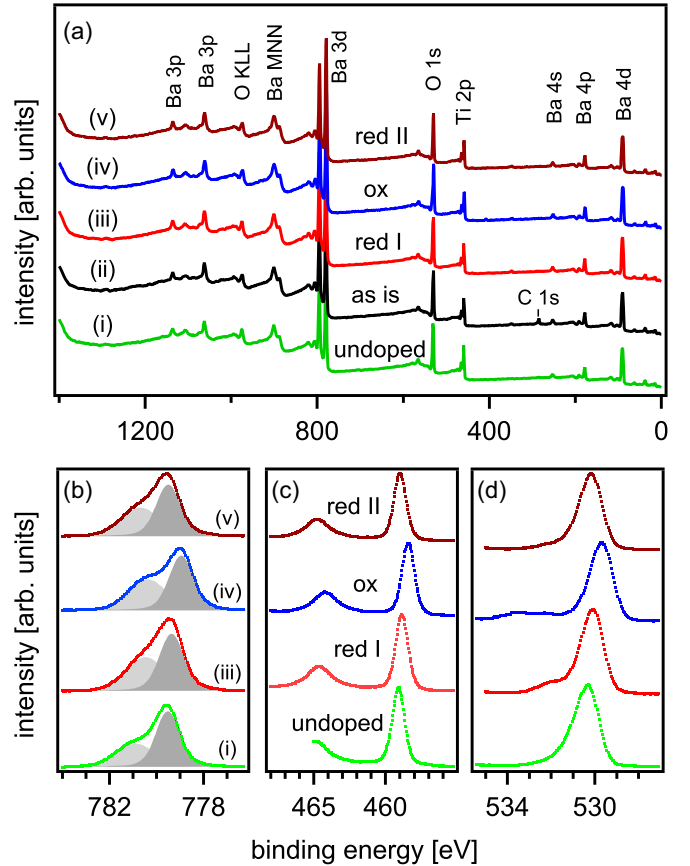


FIG. 1. X-ray photoelectron survey spectra (a), Ba 3d_{5/2} (b), Ti 2p (c), and O 1s (d) core-level spectra of an undoped (i) and of a 0.2 % V-doped BaTiO₃ sample (ii-v): Reduced and surface cleaned undoped BaTiO₃ (i); 0.2 % V-doped BaTiO₃ sample after reduction in Ar/H₂ (ii), after surface cleaning by annealing in vacuum at 500 °C (iii), after reoxidation of the surface using an oxygen plasma source (iv), and after a second vacuum annealing at 500 °C (v). The gray shaded regions in (b) correspond to a deconvolution of the Ba 3d_{5/2} component into the surface (light gray) and the bulk component (dark gray).

III. RESULTS AND DISCUSSION

An XP survey spectra of the as-reduced sample is displayed in Fig. 1(a). A noticeable amount of carbon is observed, which originates from air exposure of the sample. The carbon can be removed by a procedure involving annealing in a vacuum chamber connected to the spectrometer first at 400 °C in 0.5 Pa O₂ for 1 hour and subsequently at 500 °C in vacuum for 2 hours in order to remove any oxygen incorporated during the first annealing step. This procedure ensures a clean surface and maintains the electrical conductivity of the sample to avoid charging during XPS analysis. The undoped BaTiO₃ reference sample included in Fig. 1 has undergone the same reduction and *in situ* cleaning treatment, resulting in a C-free surface and no charging during XPS measurements.

Panels (b)–(d) in Fig. 1 display Ba 3d_{5/2}, Ti 2p, and O 1s core-level spectra of the 0.2 mol % V-doped BaTiO₃ after surface cleaning (iii), after a subsequent reoxidation of the sample using an oxygen plasma generated by a tectra MKII plasma source operated in atomic mode (iv), and after a

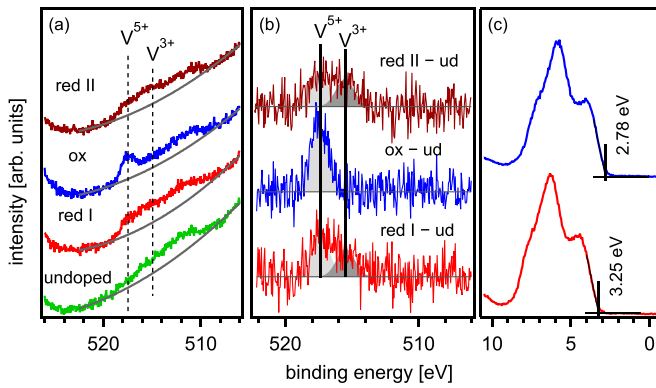


FIG. 2. (a) As-recorded XP spectra in the V $2p$ spectral region for undoped BaTiO₃ (green), and a 0.2% V-doped BaTiO₃ sample after reduction and surface cleaning (red), after surface reoxidation (blue), and after a second annealing in vacuum (brown). The solid black lines correspond to the subtracted background. (b) Background-subtracted difference spectra with spectra deconvolution of the V $2p_{3/2}$ component. (c) Valence-band spectra of the reduced and the reoxidized sample. The numbers correspond to the extracted position of the valence-band maxima.

second annealing in vacuum at 500 °C. The reoxidation is performed at room temperature to restrict the oxidation to the near-surface region and thereby maintain the electrical conductivity of the bulk of the sample. All spectra show the characteristic features of BaTiO₃, including the typical splitting of the Ba emission into two doublets with a low-binding-energy bulk and a high-binding-energy surface component [33]. While the origin of the surface component remains unclear, the presence of a different surface phase is excluded from (i) the absence of other components in the O $1s$ spectra, (ii) the proper Ba:Ti ratio, and (iii) the core-level to valence-band maximum binding-energy differences, which compare well with other samples. In contrast to previous experiments, in which polycrystalline-undoped and Mn-doped BaTiO₃ pellets have been reduced at 1100 °C [32], the surface of the reduced sample is also not enriched in Ba in the present case. The milder reducing conditions in the present experiments are corroborated by the Ti $2p$ emission, which does not exhibit the characteristic Ti³⁺ related to the low-binding-energy shoulder as in the previous work [32].

Due to low V content in the sample of only 0.2 mol % [34], the spectral region of the V $2p$ emission is recorded with a lower resolution (pass energy increased by a factor of 2) and a sampling time of ≈ 12 h in order to increase the signal-to-noise ratio. The spectra of the V $2p$ region are displayed in Fig. 2(a). The increasing intensity toward lower binding energy is related to background emission of the Ti $2p$ peak (see also survey spectra in Fig. 1). The reduced and cleaned sample (red spectrum) exhibits two steplike features at binding energies of ≈ 511 eV and ≈ 518 eV, respectively. The feature at ≈ 511 eV is also observed in a nominally undoped BaTiO₃ ceramic sample (green spectrum), making it unlikely to be caused by metallic V. Moreover, the coexistence of metallic V and V⁵⁺ (see below) in the same phase is thermodynamically not possible. The area of the V $2p$ emission of the reoxidized sample corresponds to a V concentration of

0.2%, in good agreement with the V concentration determined from chemical bulk analysis, giving further credit to not assign the background emission to vanadium. After reoxidation of the surface with the oxygen plasma, the steplike feature at ≈ 518 eV develops into a symmetric peak with a binding energy of 517.4 ± 0.1 eV. The binding energy corresponds well with vanadium in the 5+ oxidation state [35,36]. The V $2p$ emission of the reduced sample exhibits also a second lower oxidation state, as discussed in more detail below.

A better representation of the changes of the V oxidation state is obtained by subtracting a second-order polynomial background as indicated in Fig. 2(a) by black solid lines. The background-subtracted spectrum of the undoped BaTiO₃ is then subtracted from those of the background-subtracted spectra of the V-doped sample. The differences are displayed in Fig. 2(b). A single V $2p_{3/2}$ emission is observed for the reoxidized surface, while the spectrum of the reduced surface can be deconvoluted into two contributions with a binding-energy difference of 1.9 eV. The low-binding-energy V component reappears after the second reduction step, demonstrating reversibility of the spectral changes.

The lower-oxidation-state component observed in the reduced samples may correspond either to V⁴⁺ or to V³⁺. The V $2p_{3/2}$ emission of metallic V has a binding energy of 512 – 513 eV [35,36], suggesting a binding-energy difference of ≈ 1 eV per oxidation state. This agrees with XPS measurements of different stages of Na intercalation into V₂O₅ [37]. Given the binding-energy difference of the two V $2p$ components in Fig. 2(b) of 1.9 eV, it is suggested that the low-binding-energy component observed in the reduced samples is assigned to V³⁺. Consequently, the reduction of V proceeds directly from V⁵⁺ to V³⁺. A small contribution of V⁴⁺ species cannot be excluded, however. A direct transition from V⁵⁺ to V³⁺ is approximately in line with the DFT calculation of Kaneda and co-workers [24].

Eventually, the charge transition level is determined from the Fermi-level position, which can be extracted from the linear extrapolation of the leading edge of the valence-band emission as for SrTiO₃ [38]. It is mentioned that the valence-band maximum shifts in parallel with the Ba $3d$ and Ba $4d$ bulk components, the Ti $2p$, and the O $1s$ core levels. This indicates that the variation of the electrostatic potential within the information depth of the measurement (2–3 times the inelastic mean free path of the photoelectrons of ≈ 2 nm) is small, in agreement with a recent analysis of BaTiO₃/RuO₂ Schottky barrier heights, which are not affected by doping [32]. This is to be expected, as the extension of space-charge regions in BaTiO₃ is comparatively high due to the high dielectric permittivity. For materials having lower permittivity, such as SrTiO₃, the extension of the space region is comparable to the information depth and affects the spectral shapes and binding energies [39–41]. For the reduced sample, the valence-band maximum is determined to be 3.25 eV below the Fermi level, as indicated in Fig. 2(c). This energy corresponds to the V^{5+/3+} charge transition level, as the reduced sample exhibits approximately equal amounts of V⁵⁺ and V³⁺. Taking the band gap of BaTiO₃ at room temperature as 3.1 eV [42], the V^{5+/3+} CTL is located 0.15 eV above the conduction-band minimum. For Fermi levels below this CTL, V will be in 5+ oxidation state and constitutes a donor species

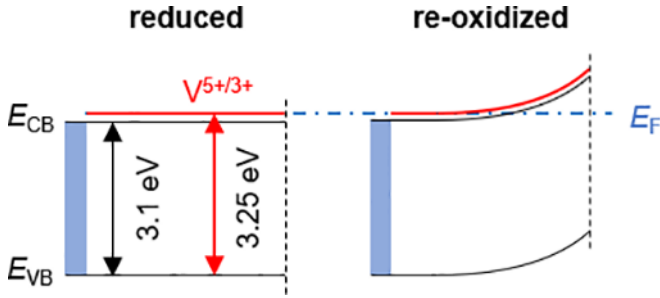


FIG. 3. Energy-band diagrams of reduced and reoxidized V-doped BaTiO₃. The V^{5+/3+} charge transition level (red line) is slightly above the conduction-band minimum energy, E_{CB} (black line).

for such conditions. For Fermi levels above this value, V will be in the 3+ oxidation state and acts as an electron trap. This will only be the case in the presence of a high concentration of oxygen vacancies under highly reducing conditions. The result agrees with the presence of V²⁺ species under highly reducing conditions observed by EPR measurements [5,12,25], as even higher Fermi levels than those obtained in the present experiment are possible, and EPR is sensitive to rather low concentrations. The donorlike behavior of V under most experimental conditions also does not contradict the insulating and *p*-type nature of electrical conduction of the studied samples before reduction. This is induced by the A-site deficiency, which results in a concentration of Ba vacancies, double acceptors, which is higher than the concentration of V donors and thereby dominates the Fermi level and electrical properties. The situation encountered for the reduced and oxidized states of the surface are summarized in Fig. 3.

The experiment reveals noticeable differences compared to recent DFT calculations of the V_{Ti} defect in BaTiO₃ [26]. The calculations employed the hybrid HSE06 functional in rhombohedral BaTiO₃, which is the stable polymorph at 0 K. The energies of the V^{5+/4+} and V^{4+/3+} transitions are obtained at ≈ 2.25 eV and ≈ 2.6 eV above the valence-band maximum, respectively. In addition, a V^{3+/2+} transition is reported at ≈ 3.2 eV above the valence-band maximum. All three transition levels lie well within the given band gap of 3.69 eV for rhombohedral BaTiO₃ [26]. A previous calculation does not reveal a V^{3+/2+} transition but also no better agreement of the calculated CTLs with those determined in this work. It is recalled that the charge transition level is determined directly by the present approach, lacking the uncertainty of assignment to a specific origin inherent to other techniques but being compatible with previous EPR studies. Therefore, it provides an ideal benchmark for DFT calculations to reveal the origin of the deviation between experiment and simulation.

IV. SUMMARY AND CONCLUSIONS

In summary, an approach to quantitatively determine the charge transition level of dopants in oxides by means of x-ray photoelectron spectroscopy has been described. By oxidizing and reducing treatments, oxygen vacancies are inserted and removed from the near-surface region. Thereby, the Fermi level at the surface is modified, which is accompanied by changes of the oxidation state of the dopant. The charge transition level is then identified from the Fermi-level position determined for the sample condition, for which a mixture of oxidation states is observed. The approach allows for a direct, parameter-free, and model-independent determination of charge transition levels of dopants in oxides. The direct determination is enabled by the potential of XPS to simultaneously record oxidation states and the Fermi level.

As a first application of the approach, the charge transition level of vanadium in BaTiO₃ polycrystals has been investigated, revealing that V is, under most experimental conditions, acting as a donor in this compound, with a direct transition from V⁵⁺ to V³⁺ at a Fermi level ≈ 0.15 eV above the conduction-band minimum. The direct determinations of charge transition levels provides benchmarks for comparison with theoretical calculations and also contributes to a better understanding of material properties by enabling more quantitative defect models. With extended sampling times of the spectra, it has even been possible to extract the charge transition level for a doping concentration of only 0.2%, opening a new avenue for studying the dependence of CTLs on defect concentration. The approach is expected to be very versatile, as it allows us to determine CTLs in dependence on defect concentration and measurement temperature. It can also be applied if other defects and dopants are present, as the determination of the Fermi level and the oxidation state is not affected by the presence of other species, as long as the relevant emission lines do not overlap. Together, the different features of the presented approach make it particularly useful for technological materials where multiple dopants are often involved.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [43].

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