

Electronic Phenomena of Transition Metal Oxides (Volume II)

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The electronic phenomena of transition metal oxides are not yet an active research area, but they can be exploited for numerous applications aimed at reducing the energy consumption and increasing the functionality of electronic devices. In order to design and develop new solid oxide materials with bespoke properties, a fundamental understanding of the relationship between electronic and crystallographic structure, lattice dynamics, and ionic and electronic transport is needed. Energy conversion, superconductivity, resistive switching, or photovoltaics are only a few examples of applications of transition metal oxides. With the ongoing miniaturization of electronic components, nanoscale properties must be understood in detail, which requires the use of measurement techniques with high spatial resolution. In this context, redox processes and the interplay of electronic and ionic conductivity, point defects, and extended defects must be analyzed to understand the complexity of the chemistry and electrochemistry of transition metal oxides. The second volume of our Special Issue, “Electronic Phenomena of Transition Metal Oxides”, compiles illustrative examples of the various functionalities and applications offered by transition metal oxides in various forms ranging from thin films and nanotubes to bulk materials such as single crystals and ceramics. Seven research articles and two reviews are included in the present volume.

Among the transition metal oxides, binary and ternary titanates such as TiO_2 and SrTiO_3 are particularly important due to their unique electronic properties and versatility. Cieřlik et al. reviewed how reduction and oxidation influence the work function of TiO_2 (110) and SrTiO_3 single crystals (Contribution 1). They employed various complementary surface-sensitive techniques such as X-ray photoelectron spectroscopy, low-energy electron diffraction, scanning tunneling microscopy, and Kelvin probe force microscopy to monitor the transformations of the surface morphology and electronic structure upon exposure to high-temperature treatment. Depending on oxygen activity, the formation or annihilation of oxygen vacancies can be induced, associated with in-plane and out-of-plane diffusion processes in the surface and subsurface regions. This allows the modification of the surface work function in the ranges of 3.4–5.0 eV and 2.9–4.5 eV for TiO_2 and SrTiO_3 , respectively, which show that the electronic properties of the surface can be adjusted for various applications via dedicated pretreatment.

Eglitis et al. reviewed the first principles simulations of $\text{SrTiO}_3/\text{BaTiO}_3$, $\text{SrTiO}_3/\text{PbTiO}_3$, and $\text{SrZrO}_3/\text{PbZrO}_3$ (001) heterostructures, with a particular focus on the effect of non-stoichiometry (Contribution 2). Using ab initio B3PW simulations, they found that charge redistribution only has a minor effect on the electronic structure, whereas stoichiometry changes can significantly shift the band edges. A strong dependence on the AO or BO_2 termination of the topmost layer of the film on the band gap was observed. In comparison with bulk materials, the covalency of the B-O bonds near the heterostructure boundary increases, especially in stoichiometric films.



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The theoretical study by Luo et al. dealt with nanotube systems, which are rolled up from Me-C₈B₄C and Me-C₈N₄C graphene allotropes (Contribution 3). By applying density functional theory at the Perdew–Burke–Ernzerhof (PBE) level, it was found that these single-walled carbon nanotubes can exhibit high mechanical strength and Young's moduli reaching up to 60%. The metallic behavior of B-substituted nanotubes and the semiconducting behavior with band gaps in the range of 3.1 to 3.3 eV for N-substituted nanotubes were predicted when employing hybrid B3LYP functionals, which shows the potential for applications of nanotube systems in the field of photocatalytic water splitting.

The interaction of transition metal oxides with graphene-like surfaces was investigated in a study on molybdenum trioxide by Nadolska et al. (Contribution 4). The stability of MoO_{3-x} monolayers on graphene under mechanical and electrical stimuli was evaluated through conductive atomic force microscopy in combination with electron spectroscopy and Kelvin probe force microscopy. Depending on the size of the monolayer islands, the islands can be moved on the surface or completely detached by applying mechanical forces via the AFM tip. This process can be enhanced and controlled with the additional application of electric stimuli via the electrodegradation of the oxide. In nonstoichiometric oxide layers, highly heterogeneous electrical properties related to the distribution of oxygen vacancies were observed, thus defining the rules for designing graphene-based metal oxide devices.

The influence of defects on the optical properties of a model transition metal oxide, SrTiO₃ was investigated by Lazar et al. (Contribution 5). They found that even in high-quality commercial single crystals, the optical properties are heterogeneous, as revealed by birefringence studies. Below the phase transition at 105 K, a nonlinear temperature dependence of the birefringence and the optical indicatrix orientation was observed. Even above the transition temperature, a slight residual birefringence was present, which was associated with the influence of local mechanical stress induced by dislocations. This relationship was illustrated through investigating SrTiO₃ bi-crystals showing birefringence close to the boundary even up to room temperature.

Sarsekhan et al. studied copper selenite, a promising material for photonics and electronics (Contribution 6). They chemically deposited nanocrystals on a SiO₂/Si template and investigated the structural, optical, and electronic properties. The phase of the deposited CuSeO₃ nanocrystals was orthorhombic but could be tuned to monoclinic and triclinic via subsequent vacuum annealing. Together with the crystallographic phase, the electronic and optical properties changed upon thermal reduction, indicating a subtle influence of the defect concentration on the electronic structure, which would allow the material properties to be tailored for various applications related to optoelectronics and sensors.

A combined experimental and theoretical study on Rb₂KWO₃F₃ elpasolite, a UV-transparent material, was conducted by Atuchin et al. (Contribution 7). They synthesized the material via the solid-state reaction route and investigated the electronic structure using X-ray photoelectron spectroscopy, revealing the presence of a W oxidation state of 6+. Simulations using density functional theory indicate that the valence band maximum is related to O 2p orbitals and the conduction band minimum is related to W 5d orbitals, resulting in a large bandgap of 4.38 eV. Hence, the WO₃F₃ component is mainly responsible for the electronic structure and transparency up to the UV regime, whereas the effects of Rb and K substitution are rather minor.

Kornyakov et al. synthesized a new copper vanadate Cs₂Cu₂[V₄O₁₂]Br₂ via chemical vapor transport and evaluated the structural evolution with temperature (Contribution 8). They found that the material undergoes three structural phase transitions upon heating, which are governed by the orientations of [V₄O₁₂]^{4−} rings connected by (VO)²⁺ to a layer-like structure. This behavior, which is not observed in similar copper–vanadium

compounds, illustrates how the complex atomistic arrangements of transition metal oxides influence their macroscopic properties.

Shi et al. studied the high-temperature superconductor $\text{CuBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{10+\delta}$ (Cu1234) (Contribution 9). Although the material shows promising properties such as high transition temperature, critical current density, and irreversible field at liquid nitrogen temperatures, the material decomposes at higher temperatures. Polycrystalline Cu1234 already decomposes at temperatures of 350 °C at 1 bar O_2 . However, at higher oxygen pressures of 100 or 150 bar, the decomposition temperature increases to 550 and 600 °C, respectively, illustrating how thermal stability can be increased by preventing oxygen loss.

In summary, the second volume of this Special Issue, “Electronic Phenomena of Transition Metal Oxides”, showcases the diverse spectrum of the properties of transition metal oxides. This diversity is associated with a high level of complexity in the structure–property relationships of the crystallographic structure and the distribution of point and extended defects. Hence, a proper material characterization at the nano- and macroscales is needed to build a reliable basis for the design and prediction of transition metal oxides with tailored properties for energy-saving applications.

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