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Editorial

Electronic Phenomena of Transition Metal Oxides

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Transition metal oxides with ABO_3 or BO_2 structures have become one of the major research fields in solid state science, as they exhibit an impressive variety of unusual and exotic phenomena with potential for their exploitation in real-world applications. The interest in these materials was especially triggered by the search for high-temperature superconductors, the demand for insulators with high dielectric constants being the backbone of modern information technology, with the discovery of the resistive switching effect underpinning the field of neuromorphic computing. All of these applications rely on the variability of the oxide's electronic structure, which is mainly determined by the transition metal ion having the ability to adopt different valence states, depending on the chemical surroundings. Hence, the properties of the oxide can be manipulated by modifying its stoichiometry, which can be achieved by applying gradients of electric or chemical potential. As in the case of transition metal oxides, these modifications are often only confined to extended defects, and exhibit an intrinsic heterogeneity that enables the miniaturization of devices down to the nanoscale.

The manifold electronic properties of perovskites with strong correlations between the lattice, electrons, and spins were reviewed by Moshnyaga and Samwer [1]. They asserted that interfaces between different manganite perovskites exhibit a variety of two-dimensional polaronic emergent phases due to the breaking of the crystal symmetry at the boundary between the different perovskite layers. Using advanced thin film growth techniques, heterostructures with novel features related to electronic effects, such as Jahn−Teller correlations, polarons, and high-temperature ferromagnetism can be designed. Even in the transition metal oxides that have been studied for hundreds of years, new discoveries are still being made. This was demonstrated by Angst et al. [2] in relation to the prototype magnetic material Fe_3O_4 (magnetite). They investigated the charge-ordered low-temperature state of high-quality magnetite single crystals by means of electrical measurements and diffractometry, and proved that charge ordering, which is responsible for the well-known metal-insulator Verwey transition, also induces intrinsic ferroelectricity. Hattori et al. [3] investigated the metal-insulator transition of VO_2, which takes place at an experimentally easily accessible temperature range of 65–77 °C. In order to elucidate the phase separation process that accompanies the transition, they constructed a nanostructure for the analysis of the behavior of a single domain, which enabled them to address the kinetics of the phase transition and its dependence on the temperature change, and to develop a domain-dependent model for the metal-insulator transition.

The nature of antiferroelectricity in the classical lead-based perovskites $PbZrO_3$ and $Pb(Zr_{0.7}Ti_{0.3})O_3$ was revisited by Kajewski [4], who pointed out that the defect structure of both the lead and zirconium sublattice is of extreme importance for the antiferroelectric properties. Experimentally, it was shown that unexpected phase transitions could be induced upon doping with Nb and Bi, respectively, interfering with the complex interplay between the crystallographic structure and polarization by breaking the symmetry.

Several contributions to the Special Issue deal with the ab initio simulation of transition metal oxides. Eglitis et al. [5], for instance, conducted simulations of the (001) surface of

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ReO_3, representing a typical covalent metal, and compared it to the different zirconates. They found a systematic trend in the surface structure of all of the analyzed materials, with an inward relaxation of the upper layer, an outward relaxation of the second layer, and also an inward relaxation of the third layer. The band gap of the surfaces with BO_2 termination, with either B being Re or Zr, was found to be smaller than that of the bulk. In contrast, the bond population of Zr-O was larger on the surface than compared to the bulk, whereas for the Re-O bond, the opposite behavior was simulated.

The majority of contributions to this Special Issue focus on the model transition metal oxide $SrTiO_3$ crystallizing in the perovskite structure. In this material, the electronic conductivity is closely related to extended defects such as dislocations and grain boundaries, as these act as seeds for the formation of metallic filaments upon reduction. In our own contribution, we illustrated this effect on a $SrTiO_3$ $\sum 5$ grain boundary by means of local-conductivity atomic force microscopy (LC-AFM) and fluorescence lifetime imaging microscopy (FLIM) [6]. It was shown that the local conductivity at the boundary was much higher than that of the crystal matrix, demonstrating the preferential formation of conducting filaments in dislocation-rich regions. Furthermore, the electronic structure close to the boundary exhibited distinct differences, as indicated by the lower fluorescence lifetime. This illustrated that the structural inhomogeneities in perovskites can distinctively determine the electronic transport properties. Yi et al. [7] reached the same conclusion using an electron beam-induced current (EBIC) and cathodoluminescence (CL) measurements, which revealed that dislocations are recombination centers for excited charge carriers. Moreover, dislocations were found to play a crucial role in resistive switching, wherein well-aligned dislocations appear to support the formation of filaments, in contrast to tangled ones.

From a theoretical point of view, Al-Zubi et al. [8] addressed the electronic states associated with oxygen vacancies in $SrTiO_3$ and how they can be investigated by means of scanning probe methods. The distinctive influence of the local arrangement of the vacancies on the electronic states formed in the band gap was calculated, which could explain several spectroscopic features that have been observed when investigating resistive switching phenomena on the nanoscale. Bussmann-Holder et al. [9] state that the presence of filaments in $SrTiO_3$ also has implications for superconductivity. They determined that a softening of the transverse optical mode of the lattice vibrations occurs with increasing charge carrier density, promoting the formation of polar domains on the nanoscale. As these domains coexist with filamentary conductivity up to a critical charge carrier concentration, local superconducting effects are expected. Additionally, in $SrTiO_3$ single crystals doped with the acceptor Fe, Wojtyniak et al. [10] discovered a nonuniform electronic conductivity, but in this case it related to the dopant segregation effects. Upon thermal treatment at temperatures above 700 °C, the formation of Fe-rich filaments reaching from the surface into the bulk, as well as new crystallographic phases on the surface, were identified, illustrating the variability of the material and its promise for neuromorphic applications.

In summary, this Special Issue provides far-reaching insight into the current state of research on the electronic properties of transition metal oxides, describing their crystallographic structure, electronic structure, chemical composition, and lattice dynamics. The different contributions illustrate the fascinating complexity of electronic transport in solid oxides. It is apparent that there remain many discoveries to be made in materials that have already been known for a long time.

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References

1. Moshnyaga, V.; Samwer, K. Polaronic Emergent Phases in Manganite-based Heterostructures. *Crystals* **2019**, *9*, 489. [CrossRef]
2. Angst, M.; Adiga, S.; Gorfman, S.; Ziolkowski, M.; Strempfer, J.; Grams, C.; Pietsch, M.; Hemberger, J. Intrinsic Ferroelectricity in Charge-Ordered Magnetite. *Crystals* **2019**, *9*, 546. [CrossRef]
3. Hattori, A.N.; Osaka, A.I.; Hattori, K.; Naitoh, Y.; Shima, H.; Akinaga, H.; Tanaka, H. Investigation of Statistical Metal-Insulator Transition Properties of Electronic Domains in Spatially Confined VO_2 Nanostructure. *Crystals* **2020**, *10*, 631. [CrossRef]
4. Kajewski, D. Defects and Lattice Instability in Doped Lead-Based Perovskite Antiferroelectrics: Revisited. *Crystals* **2020**, *10*, 501. [CrossRef]
5. Eglitis, R.I.; Purans, J.; Gabrusenoks, J.; Popov, A.I.; Jia, R. Comparative Ab Initio Calculations of ReO_3, $SrZrO_3$, $BaZrO_3$, $PbZrO_3$ and $CaZrO_3$ (001) Surfaces. *Crystals* **2020**, *10*, 745. [CrossRef]
6. Rodenbücher, C.; Wrana, D.; Gensch, T.; Krok, F.; Korte, C.; Szot, K. The Electronic Properties of Extended Defects in $SrTiO_3$—A Case Study of a Real Bicrystal Boundary. *Crystals* **2020**, *10*, 665. [CrossRef]
7. Yi, W.; Chen, J.; Sekiguchi, T. Electron-Beam-Induced Current and Cathodoluminescence Study of Dislocations in $SrTiO_3$. *Crystals* **2020**, *10*, 736. [CrossRef]
8. Al-Zubi, A.; Bihlmayer, G.; Blügel, S. Electronic Structure of Oxygen-Deficient $SrTiO_3$ and Sr_2TiO_4. *Crystals* **2019**, *9*, 580. [CrossRef]
9. Bussmann-Holder, A.; Keller, H.; Simon, A.; Bihlmayer, G.; Roleder, K.; Szot, K. Unconventional Co-Existence of Insulating Nano-Regions and Conducting Filaments in Reduced $SrTiO_3$: Mode Softening, Local Piezoelectricity, and Metallicity. *Crystals* **2020**, *10*, 437. [CrossRef]
10. Wojtyniak, M.; Balin, K.; Szade, J.; Szot, K. Inhomogeneity and Segregation Effect in the Surface Layer of Fe-Doped $SrTiO_3$ Single Crystals. *Crystals* **2020**, *10*, 33. [CrossRef]