International Research Center for Elements Science – Advanced Solid State Chemistry –

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XU, Yuanhui (Ph D) School of Environmental and Chemical Engineering, Yanshan University, China, P.R., 12 December 2019–4 December 2020

Scope of Research

Transition metal oxides have a wide variety of interesting and useful functional properties, including electronic conduction, superconductivity, ferroelectricity, and ferromagnetism. In fact, some of these oxides are used in current electronic devices. Our research mainly focuses on perovskite-structured transition metal oxides with novel functional properties due to complex couplings between their lattices, charges and spins. We are currently exploring such functional oxides with advanced oxide-synthesis techniques such as high-pressure synthesis and epitaxial thin film growth.

KEYWORDS

Solid State Chemistry
Functional Transition Metal Oxides
Epitaxial Thin Film Growth
High Pressure Synthesis

Selected Publications

Tan, Z.; Denis Romero, F.; Saito, T.; Goto, M.; Amano Patino, M. E.; Koedtruad, A.; Kosugi, Y.; Chen, W.-T.; Chuang, Y.-C.; Sheu, H.-S.; Attfield, J. P.; Shimakawa, Y., Charge Disproportionation and Interchange Transitions in Twelve-Layer $BaFeO_3$, *Phys. Rev. B*, **102,** 054404 (2020).

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Goto, M.; de Irujo-Labalde, X. M.; Saito, T.; Garcia-Martin, S.; Shimakawa, Y., Successive and Site-Selective Oxygen Release from B-Site-Layer-Ordered Double Perovskite Ca_2FeMnO_6 with Unusually High Valence Fe^{4+}, *Inorg. Chem.*, **59,** 2024 (2020).

Kan, D.; Kobayashi, K.; Shimakawa, Y., Electric Field Induced Modulation of Transverse Resistivity Anomalies in Ultrathin $SrRuO_3$ Epitaxial Films, *Phys. Rev. B*, **101,** 144405 (2020).

Denis Romero, F.; Amano Patino, M. E.; Haruta, M.; Kurata, H.; Attfield, J. P.; Shimakawa, Y., Conversion of a Defect Pyrochlore into a Double Perovskite via High-Pressure, High-Temperature Reduction of Te^{6+}, *Inorg. Chem.*, **59,** 343-349 (2020).

Charge Disproportionation and Interchange Transitions in Twelve-Layer $BaFeO_3$

Among compounds containing the high valent Fe ions, $BaFeO_3$ is of particular interest because several polymorphic phases with differently connected $Fe^{4+}O_6$ octahedra are known (Figure 1). The simple cubic perovskite $BaFeO_3$, which is synthesized by low-temperature topochemical oxidation of $BaFeO_{2.5}$, consists of cubic close-packed layers (*c*) in a stacking sequence …*ccc* …(3*C*), as shown in Figure 1a. When $BaFeO_3$ is synthesized at high temperature and ambient pressure, the six-layer hexagonal [6H, Figure 1b] polymorph is obtained. This consists of corner-sharing and face-sharing octahedra with the stacking sequence of …*cchcch*… (*h* = hexagonal close-packed layer). A rhombohedral 12-layer compound (12R) with the stacking sequence …*cchhcchhcchh*… [Figure 1c] was also reported in oxygen-deficient $BaFeO_{3-\delta}$ (δ~0.1) obtained by high-pressure and high-temperature oxidation of brownmillerite $BaFeO_{2.5}$. The structure can also be considered as one where additional *h* layers are introduced into the 6H $BaFeO_3$ arrangement.

Here we investigated the structural and magnetic properties of fully oxygen stoichiometric $BaFeO_3$ containing unusually high valence Fe^{4+}, leading to the discovery of a remarkable sequence of electronic and magnetic transitions on cooling; $2Fe^{4+} \rightarrow Fe^{3+} + Fe^{5+}$ charge disproportionation and ordering over two sites accompanied by a structural distortion at 500 K; charge disproportionation of the remaining Fe^{4+} with magnetic order at 280 K; and an unprecedented charge interchange where Fe^{3+} and Fe^{5+} states are exchanged between two sites with spin orientation change at 50 K. Such successive charge disproportionation and interchange transitions with all charges fully ordered in each phase may result from the presence of both corner-sharing and face-sharing octahedra. The 12-layer $BaFeO_3$ demonstrates possibilities within the rich variety of transitions in charge-lattice-spin coupled systems.

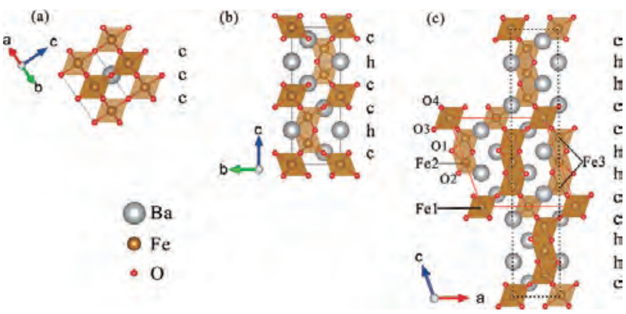

Figure 1. Crystal structures of (a) 3*C*, (b) 6*H*, and (c) 12-layer $BaFeO_3$.

Electric Field Induced Modulation of Transverse Resistivity Anomalies in $SrRuO_3$ Epitaxial Films

Perovskite strontium ruthenate $SrRuO_3$ (SRO) is an itinerant ferromagnet whose anomalous Hall effect (AHE) is dominantly contributed by the Berry curvature. Recently, ultrathin films of SRO were reported to exhibit anomalies in transverse (Hall) resistivity r_{xy} that were seen as hump structures (referred to as hump resistivity, ρ_{hump}) in the magnetic-field dependence of r_{xy}. The anomalies cannot be explained by the conventional framework of AHE and are often attributed to the emergence of the topological Hall effect (THE) due to formations of topologically nontrivial magnetic textures such as skyrmions. However, such topological magnetic textures have not been experimentally observed for SRO films and the origin of the anomalies (or ρ_{hump}) has been under debate. In fact, alternatives to the topological interpretation of the anomalies have been proposed. As shown in Figure 2, inhomogeneity in coercive field (*H*c) and r_{AHE} (coexistence of positive and negative r_{AHE}) has been shown to explain the emergence of hump structures in the r_{xy}-H curves (or ρ_{hump}).

Here we show that the ρ_{hump} in the SRO channel layers in the field-effect transistor structures are modulated by applied gate voltages V_G. The applications of positive and negative V_G, respectively, increase and decrease ρ_{hump}. In addition, the V_G-induced changes in ρ_{hump} are essentially the same as those of the saturated ρ_{AHE}. These observations indicate that the transverse resistivity anomalies emerge because of the coexistence of the anomalous Hall resistivity with distinct mechanisms, *i.e.*, intrinsic and extrinsic ρ_{AHE}. Topological interpretation for ρ_{hump} such as formations of topologically nontrivial magnetic structures is not necessary. Furthermore, the V_G-induced changes in ρ_{hump} are dominated by the intrinsic ρAHE while the extrinsic ρ_{AHE} remains unchanged under the V_G applications. Our results reveal that electric field induced changes in the anomalous Hall effect depend on its mechanism.

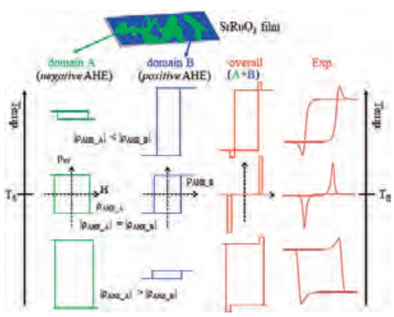

Figure 2. Schematics of the alternative model for transverse resistivity anomalies (hump resistivity, ρ_{hump}) in $SrRuO_3$.