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

http://msk2.kuicr.kyoto-u.ac.jp/~shimak-lab/indexE.html

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Visitors

IWANOWSKA, Monika	University of Rennes 1, France, 16 February–21 July 2008
GRANDSIRE, Anne-Flore	University of Montpellier, France, 20 June–20 August 2008
Prof PAULUS, Werner	University of Rennes 1, France, 1 April 2008
Prof YUSUF, S, M	Bhabha Atomic Research Centre, India, 13 June 2008
Dr ARGYRIOU, Dimitri	Helmholtz Zentrum Berlin, Germany, 22 August 2008
Dr dos SANTOS, Antonio Moreira	Oak Ridge National Laboratry, USA, 22 August 2008
Prof WOODWARD, Patrick M	Ohio State University, USA, 27 August 2008
Prof CHOU, Fang-Cheng	National Taiwan University, Taiwan, 1–5 September 2008

Scope of Research

Transition-metal oxides show lots of interesting and useful properties. They include ferroelectrics, ferromagnets, conductors, batteries, and so on. These materials are widely used in current electronic devices. The wide variety of their crystal structures gives rise to various electronic structures, which lead to interesting and useful physical and chemical properties. We are focusing on the fundamental physics and chemistry of these "functional oxides" and seeking new materials with new functions. We are conducting systematic studies of material synthesis based on phase equilibrium information. Precise crystal structures are analyzed by X-ray and neutron diffractions. Electronic and magnetic structures are discussed based on the results of electronic structure calculations and physical property measurements.

Research Activities (Year 2008)

Publications

Yamada I, Takata K, Hayashi N, Shinohara S, Azuma M, Mori S, Muranaka S, Shimakawa Y, Takano M: A Perovskite Containing Quadrivalent Iron as a Charge-disproportionated Ferrimagnet, *Angew. Chem. Int. Ed.*, **47**, 7032-7035 (2008).

Shimakawa Y: A-site Ordered Perovskites with Intriguing Physical Properties, *Inorg. Chem. Mat. Forum*, **47**, 8562-8570 (2008).

Oka K, Yamada I, Azuma M, Sato K, Takeshita S, Koda A, Kadono R, Takano M, Shimakawa Y: Magnetic Ground State of Perovskite $PbVO_3$ with Large Tetragonal Distortion, *Inorg. Chem.*, **47**, 7355-7359 (2008).

Inoue S, Kawai M, Shimakawa Y, Mizumaki M, Kawamura N, Watanabe T, Tsujimoto Y, Kageyama H, Yoshimura K: Single-crystal Epitaxial Thin Films of $SrFeO_2$ with FeO_2 "infinite layers", *App. Phys. Lett.*, **92**, [161911-1]-[161911-3] (2008).

Single-crystal Thin Films of Infinite-layer Structure $SrFeO_2$ with Square-planer Coordination of Fe^{2+} Ions

There are a number of oxides with transition-metal ions such as Fe, Co, and Ni. Ionic states of the transition metals can vary in the oxides. For strontium (Sr) and iron (Fe) containing perovskite-structure oxides, the oxygen content and Fe ionic state were considered to change between $SrFeO_3$ and $SrFeO_{2.5}$. Last year a new compound, infinite-layer structure $SrFeO_2$, was reported in Nature to be synthesized by using a low temperature reduction with CaH_2.

Immediately after this report, we succeeded in preparing "single-crystal thin films of infinite-layer structure $SrFeO_2$". A $SrFeO_{2.5}$ precursor thin film was first deposited by a pulsed-laser-deposition method and the film was then reduced at low temperature with CaH_2. The resultant sample was confirmed to be a single-crystal infinite layer $SrFeO_2$ from X-ray diffraction and absorption experiments.

Figure 1. Crystal Structure of $SrFeO_{2.5}$ and $SrFeO_2$.

With the epitaxially grown thin-film samples, we can investigate mobile behaviors of oxygen ions. The results on high oxygen mobility will be useful for fuel-cell applications. The study on single-crystal thin-film samples will also reveal anisotropic crystal and electronic structures of the compound. New physical properties of the infinite-layer structure may appear by using epitaxial strain from the substrate lattice. The present success of preparing the single-crystal thin film $SrFeO_2$ has great impacts on not only research fields of fundamental solid state physic and chemistry but also application fields of new material synthesis with new functions.

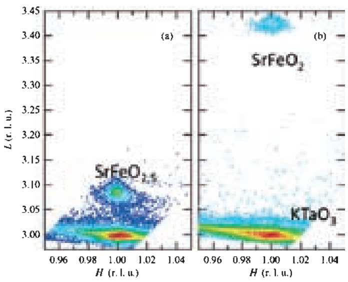

Figure 2. X-ray diffraction of $SrFeO_{2.5}$ and $SrFeO_2$.

$PbTiO_3$ and $BiCoO_3$ with Large Polar Distortions

$PbTiO_3$-based ferroelectric and piezoelectric materials are widely used in memory devices, actuators, and transducers. The search for new ferroelectric and piezoelectric perovskites had been limited to the systems with d^0 ions such as Ti^{4+}, Nb^{5+}, and Ta^{5+} in the B-sites of a perovskite ABO_3. We have investigated perovskites stabilized at high pressures with other transition metals in the B-site and lead or bismuth in the A-site. As results, $PbVO_3$ and $BiCoO_3$ are found to be isostructural with $PbTiO_3$. These have tetragonal distortions (c/a = 1.229 for $PbVO_3$ and 1.267 for $BiCoO_3$) much larger than that of $PbTiO_3$ (c/a = 1.062). The magnetic properties of $PbVO_3$ were the key to understand the origin of this large polar distortion. The temperature dependence of the measured magnetization of multidomain single-crystal samples showed a broad maximum centered around 180 K, indicating a two-dimensional antiferromagnetism with frustration. The two-dimensional magnetism is due to the ordering of d_{xy} orbitals, which is thought to also be related to the large tetragonal distortion of $PbVO_3$.

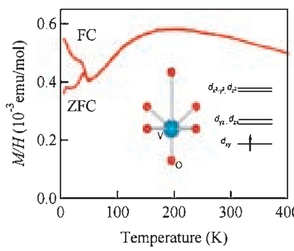

Figure 3. Temperature dependence of magnetic susceptibility of $PbVO_3$ crystal and a schematic drawing of orbital ordering due to a large tetragonal distortion.

Presentations

Complex Ordered Perovskites with Intriguing Physical Properties: Shimakawa Y, Zing Conferences on Solid State Chemistry, Cancun, Mexico, 11 March 2008.

Complex Ordered Perovskites with Intriguing Physical properties: Shimakawa Y, MRS 2008 Satellite Meeting on Advanced Technologies for Advanced Characterizations of Advanced Materials, Beijing, China, 16 June 2008.

Charge and Orbital Orderings in Some New Oxides: Azuma M, UC Santa Barbara Workshop on Frontiers in Complex Oxides, Santa Barbara, USA, 6–12 July 2008.

$PbVO_3$ and $BiCoO_3$ with Large Tetragonal Distortions: Azuma M, 7th Korea-Japan Conference on Ferroelectricity, Jeju, Korea, 6–9 August 2008.

Grants

Shimakawa Y, Strategic State-of-the-art Solid State Chemistry for New Functional Materials: Exploring for New Multi-functional Materials, Creative Scientific Research, 1 April 2007–31 March 2012.

Azuma M, Search for Anomalous Magnetic, Electric and Dielectric Phenomena in Transition Metal Oxides with Active s-electrons, Grant-in-Aid for Scientific Research (B), 1 April 2007–31 March 2010.