

# Division of Synthetic Chemistry

## - Advanced Inorganic Synthesis -

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



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### Visitors

Prof TAKEUCHI, Ichiro University of Maryland, USA, 26 June 2007  
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## 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 2007)

### Publications

Sakai M, Masuno A, Kan D, Hashisaka M, Takata K, Azuma M, Takano M, Shimakawa Y: Multiferroic Thin Film of  $\text{Bi}_2\text{NiMnO}_6$  with Ordered Double-Perovskite Structure, *Appl. Phys. Lett.*, **90**, [072903-1]-[072903-3] (2007).

Shiraki H, Saito T, Yamada T, Tsujimoto M, Azuma M, Kurata H, Isoda S, Takano M, Shimakawa Y: Ferromagnetic Cuprates  $\text{CaCu}_3\text{Ge}_4\text{O}_{12}$  and  $\text{CaCu}_3\text{Sn}_4\text{O}_{12}$  with A-Site Ordered Perovskite Structure, *Phys. Rev. B*, **76**, [140403-1]-[140403-4] (2007).

Azuma M, Carlsson S, Rodgers J, Tucker M G, Tsujimoto M, Ishiwata S, Isoda S, Shimakawa Y, Takano M, Atfield J P: Pressure-Induced Intermetallic Valence Transition in  $\text{BiNiO}_3$ , *J. Am. Chem. Soc.*, **129**, 14433-14436 (2007).

### Presentations

Complex Ordered Perovskites with Intriguing Physical Properties: Shimakawa Y, Gordon Research Conferences on Solid State Chemistry II, Oxford, UK, 2–7 September 2007.

High Pressure Synthesis of Functional Transition Metal Oxides: Azuma M, ICMR Workshop on Functional Oxide Materials, Santa Barbara, USA, 20–23 August 2007.

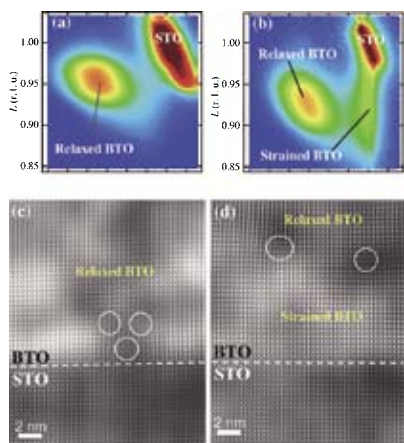
New Multi-Ferriic Compound  $\text{Bi}_2\text{NiMnO}_6$ : Shimakawa Y, 7th Pacific Rim Conference on Ceramic and Glass Technology, Shanghai, China, 11–14 November 2007.

### 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.

## Deposition Rate Control on Defect Structure of Epitaxial Oxide Thin Films

Defect engineering for the epitaxial thin films have recently attracted much attention because strain fields and dislocations affect physical properties of the thin films. We prepared perovskite-type ferroelectric BaTiO<sub>3</sub> thin films grown on a SrTiO<sub>3</sub> (001) substrate by PLD, and found that their defect structures strongly depend on the growth rate. The defect structures, which include structural strain and dislocations were examined by synchrotron radiation x-ray diffraction and cross-sectional HAADF-STEM observations. In a film grown at a low deposition rate (0.01 nm/s), misfit dislocations are found near the interface and a fully relaxed BaTiO<sub>3</sub> thin film grows epitaxially on the substrate. On the other hand, a film grown at a high deposition rate (0.04 nm/s) consists of strained and relaxed BaTiO<sub>3</sub> lattices. The results imply that the structures and strain states in the epitaxial thin films can be controlled by the growth rate.

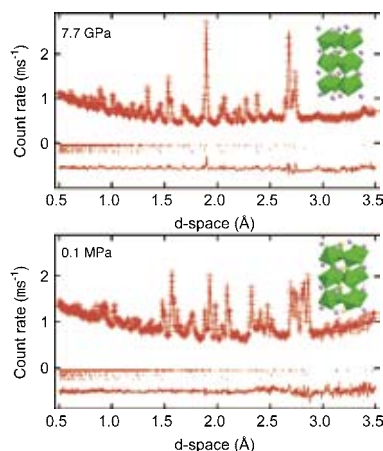


**Figure 1.** Synchrotron x-ray diffraction reciprocal space maps around the (301) Bragg reflection and cross-sectional HAADF-STEM images around the BTO/STO heterointerfaces for the BaTiO<sub>3</sub>/SrTiO<sub>3</sub>(001) epitaxial thin films grown at a low deposition rate (0.01 nm/s) ((a) and (c)) and high deposition rate (0.04 nm/s) ((b) and (d)).

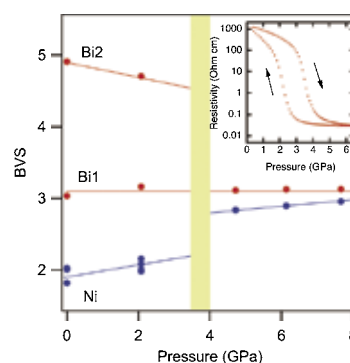
## Pressure-Induced Intermetallic Valence Transition in BiNiO<sub>3</sub>

Charge ordering in oxides, drives many important phenomena such as the Verwey transition of Fe<sub>3</sub>O<sub>4</sub>. The melting of charge order often leads to exotic conducting phenomena near the insulator to metal boundary, such as colossal magnetoresistance in manganites. BiNiO<sub>3</sub> has the

unusual charge distribution Bi<sup>3+</sup><sub>0.5</sub>Bi<sup>5+</sup><sub>0.5</sub>Ni<sup>2+</sup>O<sub>3</sub> with ordering of Bi<sup>3+</sup> and Bi<sup>5+</sup> charges on the A sites of a highly distorted perovskite structure. High pressure neutron diffraction measurements and Bond valence sum calculations show that the pressure-induced melting of the charge disproportionated state leads to a simultaneous charge transfer from Ni to Bi, so that the high pressure phase is metallic Bi<sup>3+</sup>Ni<sup>3+</sup>O<sub>3</sub>. This unprecedented charge transfer between A and B site cations coupled to electronic instabilities at both sites leads to a variety of ground states, and it is predicted that a Ni-charge disproportionated state should also be observable.



**Figure 2.** Time-of-flight powder neutron diffraction data for BiNiO<sub>3</sub> at variable pressures. (a) Rietveld fits of the triclinic structure to ambient pressure (0.1 MPa) data, and of the high pressure orthorhombic structure to 7.7 GPa data.



**Figure 3.** Bi and Ni bond valence sums (BVS) determined from the refined structures of BiNiO<sub>3</sub> at various pressures. The low pressure structure contains two distinct Bi sites, labeled Bi1 and Bi2 (red circles), corresponding respectively to Bi<sup>3+</sup> and Bi<sup>5+</sup>, and four Ni sites (blue circles) all containing Ni<sup>2+</sup>. The high pressure structure contains single Bi and Ni sites, both with valences of 3+. The inset shows the resistivity of BiNiO<sub>3</sub> as a function of pressure exhibiting an insulator to metal transition at around 4 GPa.

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.

### Award

Azuma M, Shimakawa Y and Takano M, Thomson Scientific Research Front Award 2007, Thomson Scientific, 19 September 2007.