

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

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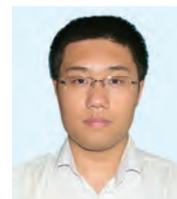
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Scope of Research

Transition metal oxides display a wide variety of interesting and useful functional properties, including electronic conduction, superconductivity, ferroelectricity, and ferromagnetism. In fact, some of these oxides have been 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. With advanced oxide-synthesis techniques such as high-pressure synthesis and epitaxial thin film growth, we are currently exploring such functional oxides.

KEYWORDS

Solid State Chemistry

Functional Transition Metal Oxides

Epitaxial Thin Film Growth

High Pressure Synthesis

Perovskite Structured Oxides



Selected Publications

Chen, W. T.; Saito, T.; Hayashi, N.; Takano, M.; Shimakawa, Y., Ligand-hole Localization in Oxides with Unusual Valence Fe, *Sci. Rep.*, **2**, 449/1-6 (2012).

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Azuma, M.; Chen, W. T.; Seki, H.; Czpski, M.; Olga, S.; Oka, K.; Mizumaki, M.; Watanuki, T.; Ishimatsu, N.; Kawamura, N.; Ishiwata, S.; Tucker, M. G.; Shimakawa, Y.; Attfield, J. P., Colossal Negative Thermal Expansion in BiNiO₃ Induced by Intermetallic Charge Transfer, *Nat. Comm.*, **2**, 347 (2011).

Inoue, S.; Kawai, M.; Ichikawa, N.; Kageyama, H.; Paulus, W.; Shimakawa, Y., Anisotropic Oxygen Diffusion at Low Temperature in Perovskite-Structure Iron Oxides, *Nat. Chem.*, **2**, 213-217 (2010).

Long, Y. W.; Hayashi, N.; Saito, T.; Azuma, M.; Muranaka, S.; Shimakawa, Y., Temperature-induced A-B Intersite Charge Transfer in an A-site-ordered LaCu₃Fe₂O₁₂ Perovskite, *Nature*, **458**, 60-63 (2009).

Kan, D.; Terashima, T.; Kanda, R.; Masuno, A.; Tanaka, K.; Chu, S.; Kan, H.; Ishizumi, A.; Kanemitsu, Y.; Shimakawa, Y.; Takano, M., Blue-light Emission at Room Temperature from Ar⁺-irradiated SrTiO₃, *Nat. Mater.*, **4**, 816-819 (2005).

Valence Change of A'-site Mn by A-site Doping in $\text{La}_{1-x}\text{Na}_x\text{Mn}_3\text{Ti}_4\text{O}_{12}$

Recently, we have successfully synthesized a novel A-site-ordered perovskite $\text{LaMn}_3\text{Ti}_4\text{O}_{12}$. Our analysis of the X-ray diffraction, X-ray absorption spectrum, and magnetization of this compound suggested that the compound has a nominal composition of $\text{La}^{3+}\text{Mn}^{1.66+}_3\text{Ti}^{4+}_4\text{O}_{12}^{2-}$, with an unusually low valence Mn ion at the A'-site. Mn with a valence lower than +2 is very rare for oxides.

To precisely evaluate the cation-valence state in $\text{AMn}_3\text{Ti}_4\text{O}_{12}$, it is quite important to determine not only the overall stoichiometry but also the precise site occupancies of each ion. However, Ti/Mn mixing is not easy to explore from the structure refinements using normal (non-resonant) X-ray or neutron diffraction techniques because Ti and Mn have similar X-ray scattering factors and neutron scattering amplitudes. To overcome this, we adopted a resonant X-ray diffraction (RXRD) technique, which enables elements with close atomic numbers like Ti and Mn to be distinguished by making use of contrast between their anomalous scattering factors f' and f'' .

In this study, we focus on a $\text{La}_{1-x}\text{Na}_x\text{Mn}_3\text{Ti}_4\text{O}_{12}$ system, in which Na^+ substitution for La^{3+} at the A-site effectively causes the hole doping and would affect the A'-site Mn valence. $\text{La}_{1-x}\text{Na}_x\text{Mn}_3\text{Ti}_4\text{O}_{12}$ ($x = 0, 0.5, 1$) were synthesized under high-pressure and high-temperature conditions, and their crystal structures and magnetic properties were investigated. Ti/Mn occupancies at the B site were also examined by using resonant X-ray diffraction, and the results confirm that they are stoichiometric with high Ti/Mn site selectivity. The Na^+ substitution changes the valence state of the A'-site Mn but not of the B-site Ti, and thus the compositions of the synthesized samples are expressed as $\text{La}_{1-x}\text{Na}_x\text{Mn}^{((5+2x)/3)+}_3\text{Ti}^{4+}_4\text{O}_{12}$ (Figure 1). The magnetic properties change from spin-glass-like to anti-ferromagnetic to spin-glass-like behavior according to the valence states of A'-site Mn.

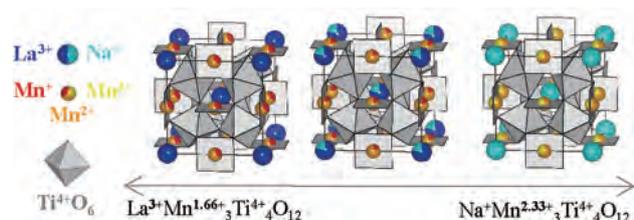


Figure 1. Crystal structure and valence change of A'-site Mn of $\text{La}_{1-x}\text{Na}_x\text{Mn}_3\text{Ti}_4\text{O}_{12}$.

Anisotropic In-Plane Lattice Strain Relaxation in Brownmillerite $\text{SrFeO}_{2.5}$ Epitaxial Thin Films

Oxygen-deficient Fe-based perovskites exhibit various structural and physical properties depending on the amount as well as the arrangement of the oxygen vacancies. Importantly these materials with various oxygen vacancies are synthesized by either oxidation or reduction reactions of the brownmillerite $\text{SrFeO}_{2.5}$. Recently, it was also demonstrated that such reactions of the epitaxial thin films and artificial superlattices of the brownmillerite provided information about the oxygen-ion diffusion. Thus, it is important to learn the structural properties of the epitaxial thin films of the brownmillerite.

In this study we performed detailed structural characterizations and found the anisotropic in-plane lattice relaxation behavior of brownmillerite $\text{SrFeO}_{2.5}$ epitaxial thin films grown on (110) DyScO_3 substrates. The in-plane lattices in the films less than 50 nm thick are fixed by the substrate lattice, whereas partial in-plane lattice relaxation along the [010] direction occurs in a 50 nm thick film. When the thickness reaches 98 nm, the film eventually exhibits lattice relaxation in both the [010] and the [10-1] in-plane directions.

The high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) observations for the partially relaxed film (Figure 2) revealed that in the bottom region, a dislocation, at which additional Fe atoms are seen, leads to formations of the stacking faults. In the surface region of the film, the complicated lattice defects propagated from the bottom result in the partial in-plane lattice relaxation associated with the disordered arrangements of the FeO_4 tetrahedra and the FeO_6 octahedra in the surface region. The preferential generation of the dislocations in the (10-1) plane can be explained by taking into account the anisotropic thermal expansion of $\text{SrFeO}_{2.5}$, which results in the increase in the lattice mismatch between the film and the substrate only along the [010] direction in the cooling process after the film deposition.

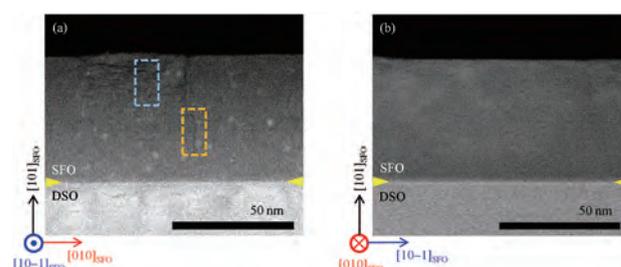


Figure 2. Anisotropic in-plane lattice strain relaxation revealed by HAADF-STEM observations. The images were taken along the (a) $[10-1]_{\text{SFO}}$ (left) and (b) $[010]_{\text{SFO}}$ (right) directions.