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

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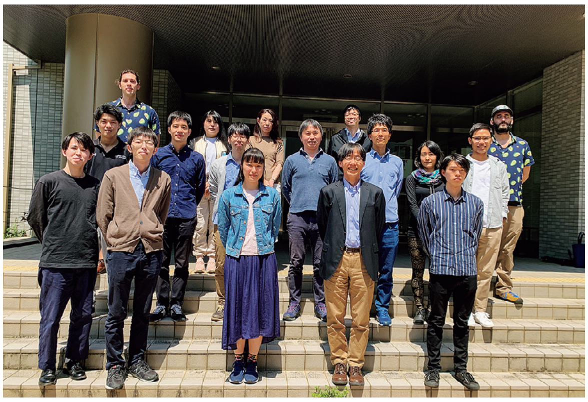
Scope of Research

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
High Pressure Synthesis
Heterointerface
Functional Metal Oxides
Epitaxial Thin Film Growth

Recent Selected Publications

Goto, M.; Oguchi, T.; Shimakawa, Y., Geometrical Spin Frustration and Monoclinic-Distortion-Induced Spin Canting in the Double Perovskites Ln_2LiFeO_6 (Ln = La, Nd, Sm, and Eu) with Unusually High Valence Fe^{5+}, *J. Amer. Chem. Soc.*,**143,** 19207 (2021).

Kosugi, Y.; Goto, M.; Tan, Z.; Kan, D.; Isobe, M.; Yoshii, K.; Mizumaki, M.; Fujita, A.; Takagi, H.; Shimakawa, Y., Giant Multiple Caloric Effects in Charge Transition Ferrimagnet, *Sci. Rep.*, **11,** 12682 (2021).

Kan, D.; Suzuki, I.; Shimakawa, Y., Tuning Magnetic Anisotropy by Continuous Composition-Gradients in a Transition Metal Oxide, *J. Appl. Phys.*, **129,** 183902 (2021).

Injac, S. D. A.; Xu, Y.; Romero, F. D.; Shimakawa, Y., Pauli-Paramagnetic and Metallic Properties of High Pressure Polymorphs of $BaRhO_3$ Oxides Containing Rh_2O_9, *Dimers Dalton Trans.*, **50,** 4673 (2021).

Tan, Z.; Koedtruad, A.; Goto, M.; Iihoshi, M.; Shimakawa, Y., Layered Hexagonal Perovskite Oxides 21R $Ba_7Fe_5Ge_2O_{20}$ and 12H $Ba_6Fe_3Ge_3O_{17}$, *Inorg. Chem.*, **60,** 1257 (2021).

Colossal Barocaloric Effect by Large Latent Heat Produced by First-Order Intersite-Charge-Transfer Transition

Solid thermomaterials are attracting much attention because they can be used to make innovative energy systems. An especially important application of thermomaterials is refrigeration technology. Materials showing large latent heat can be regarded as solid caloriceffect materials, where entropy changes significantly in response to external fields, and they can be used to provide more efficient refrigeration than conventional refrigeration systems. They also eliminate the need for hydrofluorocarbon refrigerants, which are widely used in vapor-compression refrigeration but are linked to global warming. Candidate materials showing solid state caloric effects have been extensively explored. Typical solid-state caloric effects induced by magnetic fields, electric fields, and pressure are, respectively, called magnetocaloric, electrocaloric, and barocaloric effects. The magnetocaloric effects in solids, where a magnetic entropy difference between ferro- and para-magnetic spin alignments is produced by an external magnetic field, have been intensively studied for decades. Very recently, plastic crystals were reported to show colossal barocaloric effects. The exploration of new caloric materials is therefore accelerating.

We found in this study that the A-site-ordered quadruple perovskite-structure oxide $NdCu_3Fe_4O_{12}$ shows a colossal latent heat of 25.5 kJ/kg (157 J/cc), which corresponds to a large entropy change of 84.2 J/K·kg, produced by an intersite charge-transfer (CT) transition occurring near room temperature (Figure 1). The transition is first-order and is accompanied by an unusual magnetic ordering, not caused by simple magnetic interactions between spins, and a large negative-thermalexpansion-like volume change. We also demonstrated that the large latent heat is utilized through a barocaloric effect. The observed entropy change of 65.1 J/K·kg at 5.1 kbar is much larger than those reported in known giant barocaloric materials and is comparable to the largest changes reported in inorganic solid materials. The results point to $NdCu_3Fe_4O_{12}$ as a candidate material for use in thermal energy storage and refrigeration through the barocaloric effect.

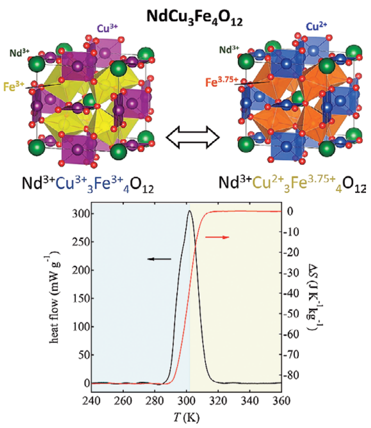


Figure 1. Crystal structure and valence states in high and low temperature phases of $NdCu_3Fe_4O_{12}$. DSC curve and Corresponding entropy change ΔS near room temperature measured during cooling.

Perpendicular Magnetic Tunnel Junctions Based on Half-Metallic $NiCo_2O_4$

Magnetic tunnel junctions (MTJs) with perpendicular magnetic anisotropy (PMA) have been regarded as an imperative component for next-generation high-density non-volatile memory devices. The tunnel magnetoresistance (TMR) ratio in MTJs is closely tied with spin polarization of conduction carriers in magnetic electrodes. Actually, MTJs composed of half-metals whose conduction carriers are fully spin-polarized (100 % spin polarization) have been reported to show large TMR ratios. Therefore, exploring magnetic materials that have high spin polarization as well as sufficient perpendicular magnetic anisotropy (PMA) is crucial for further developing perpendicular MTJs.

The inverse-spinel $NiCo_2O_4$ (NCO), in which the T_d-site is populated by Co, and the O_h-site is occupied by Ni and Co evenly, is a ferrimagnetic metal with a transition temperature above 400K and saturated magnetization of 1.5–2 m_B per formula unit (f.u.) [Figure 2]. Compressively strained epitaxial films of NCO (grown on $MgAl_2O_4$ substrates) have also been revealed to possess PMA, whose anisotropy energy is as large as 0.2 MJ/m^3 at room temperature. Theoretical calculations indicated that the density of states at the E_F consists of only the minority-spin sub-band, leading to the half-metallic band structure with the spin polarization of -100 %. These observations imply that NCO is a candidate material that has both high spin polarization and sufficient perpendicular magnetic anisotropy, highlighting its potential application for spintronic devices.

Here, we show that all-oxide perpendicular MTJs, consisting of NCO as magnetic electrodes and the spinel oxide $MgAl_2O_4$ (MAO) as a tunnel barrier layer, have TMR ratios as large as 230 % under out-of-plane magnetic fields [Figure 2]. This result indicates that the spin polarization in perpendicularly magnetized NCO is as high as -73 %. Our experimental results demonstrate the potential of NCO as a half-metal with perpendicular magnetic anisotropy.

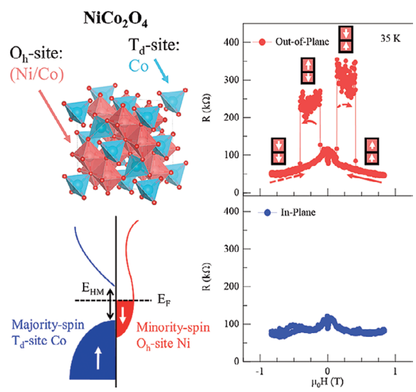


Figure 2. Crystal structure and schematic band diagram around the E_F of the inverse spinel oxide $NiCo_2O_4$. Out-of-plane and in-plane magnetic field dependence of the $NiCo_2O_4/MgAl_2O_4/NiCo_2O_4$ junction resistance.