

# Solid State Physical Chemistry

Development of novel functional materials responding to light and electromagnetic waves for solving environmental and energy issues

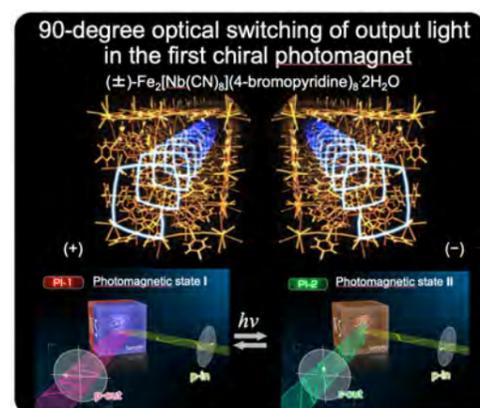
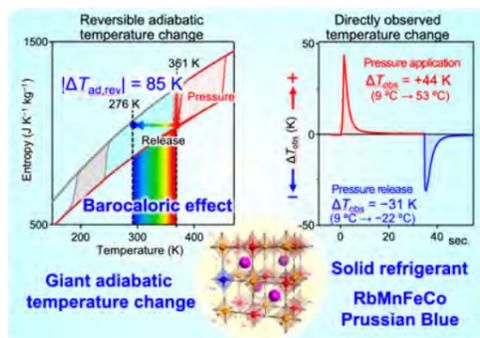
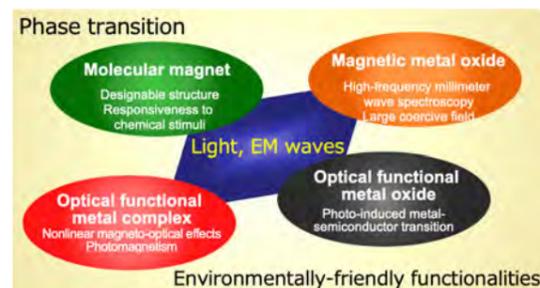
We are working on the development of novel functional materials responding to light and electromagnetic waves and materials for solving environmental and energy issues. Various materials from metal complexes, such as Prussian blue, to metal oxides and metal alloys have been investigated by chemical synthetic approach. Regarding correlation phenomena of magnetism and light/electromagnetic wave, we have been promoting research on magneto-optical and nonlinear optical magnetism. By utilizing nano-scale chemical synthesis, novel functional materials were synthesized from abundant elements such as iron or titanium; epsilon-iron oxide,  $\epsilon\text{-Fe}_2\text{O}_3$ , showing huge coercive field and high-frequency millimeter wave absorption, and lambda-titanium oxide,  $\lambda\text{-Ti}_3\text{O}_5$ , exhibiting photo-induced metal-semiconductor transition at room temperature as well as heat storage properties that proposes a novel concept of preserving heat energy for a prolonged period. We are working on environmentally friendly research with a view to technology applications contributing to big data, IoT, and renewable energy.

## Synthesis of magnetic materials with novel magnetic functionalities based on molecular design

We are studying metal complexes to realize novel magnetic functionalities based on molecular design. Metal complexes are excellent in terms of optimization of the crystal structure by changing organic ligands and designing of metal ions based on magnetic chemistry, which is a big advantage in molecular design. We have synthesized high-spin clusters, and one-, two-, and three-dimensional network metal assemblies. Furthermore, the design of functional magnetic material is possible utilizing the flexibility of the metal complex and the variety of coordination geometries around the metal ion, e.g., magnetic materials responding to physical stimuli such as light, heat, pressure, and to chemical stimuli such as gas adsorption, molecular adsorption, and humidity. We have pioneeringly reported various novel functionalities, for example, a magnet exhibiting two compensation temperatures, a humidity-sensitive magnet, a porous magnet that responds to solvent vapor, and so on. Recently, we have reported a metal complex that exhibits both ferroelectricity and ferromagnetism. Furthermore, we have synthesized a cyanide-bridged metal complex that shows the effect of increasing and decreasing temperature, upon applying and releasing pressure. We have reported that it shows the world's largest reversible adiabatic temperature change among the calorific effects of solid-solid transition refrigerants. The realization of highly efficient solid refrigerants is expected.

## Observation of new magnetic phenomena and functionalities associated with magneto-optical correlation

One of the important features of ferromagnetic metal complexes is in their broad range of color due to visible light absorption, suggesting a possibility of controlling the electronic states and magnetic characteristics by means of visible light. From this point of view, we have synthesized various photomagnetic materials using metal complexes and observed novel phenomena including photoinduced magnetic pole inversion and photoinduced magnetization, in which paramagnetism and ferromagnetism are reversibly photoswitched. Recently, we have observed light-induced spin-crossover ferromagnetism and 90-degree optical switching of the polarization plane of second harmonic light. Furthermore, we could control light using the magnetic materials that we develop. We focus on nonlinear magneto-optical effects and have reported the second example of magnetization-induced second harmonic generation (MSHG) in a bulk ferromagnet, the first example of MSHG in a chiral ferromagnet, and the first observation of magnetization-induced third harmonic generation (MTHG) in a ferromagnet. Furthermore, from recent the studies on phonon observations by terahertz light, we observed low-frequency oscillations of  $\text{Cs}^+$  ions in a Prussian blue framework and also a new developed Cs-detection method using terahertz light.



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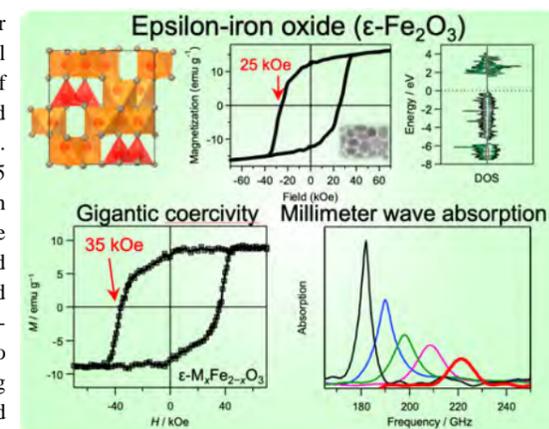
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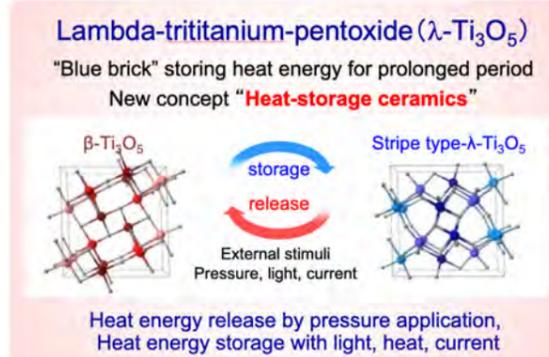
## Study of novel magnetic oxides with electromagnetic environmentally protective function

Magnetic metal oxides, represented by iron oxides, have been used in our lives for their chemical stability and insulation property. We have been studying the synthesis of novel magnetic oxides by chemical approaches and have succeeded to isolate a single phase of  $\epsilon\text{-Fe}_2\text{O}_3$  for the first time.  $\epsilon\text{-Fe}_2\text{O}_3$  shows a large coercive field ( $H_c$ ) over 20 kilo-oersted (kOe) at room temperature, which is the largest  $H_c$  value among magnetic oxides. Recently, we succeeded to enlarge the  $H_c$  value and achieved a gigantic  $H_c$  value of 35 kOe in a metal substituted  $\epsilon\text{-Fe}_2\text{O}_3$ . This  $H_c$  value is comparable to those of rare-earth magnets. Due to such a large magnetic anisotropy,  $\epsilon\text{-Fe}_2\text{O}_3$  can be reduced to a single nano-size of less than 10 nm while maintaining its magnetic order, and we discovered that it is the world's smallest hard ferrite magnet at 7.5 nm. Furthermore, we discovered that metal-substituted  $\epsilon\text{-Fe}_2\text{O}_3$  can effectively and frequency-selectively absorb millimeter waves, which have the highest frequency of all magnetic materials. We are also promoting research into applications of these properties, such as magnetic recording media and millimeter wave absorption materials, and some of these are being developed in the market as the thinnest and lightest high-performance millimeter wave absorbers.



## Synthesis of a metal oxide with room-temperature photoreversible phase transition and proposal of a novel concept "heat storage ceramics"

Titanium oxides containing  $\text{Ti}^{3+}$  are colored black and have electron spins. We have investigated black titanium oxide by nano-scale chemical synthesis, and discovered a new type of metal oxide, lambda type trititanium pentoxide ( $\lambda\text{-Ti}_3\text{O}_5$ ). This material shows photoinduced phase transition from black colored lambda phase (metallic conductor) to brown colored beta phase ( $\beta\text{-Ti}_3\text{O}_5$ ) (semiconductor). Moreover, the reverse phase transition was also observed by photoirradiation. This is the first example of a metal oxide which shows photoreversible phenomenon at room temperature. Since  $\lambda\text{-Ti}_3\text{O}_5$  is very economical and environmentally friendly material and is obtained as nanoparticles,  $\lambda\text{-Ti}_3\text{O}_5$  is expected as a next generation high-density optical storage material. Additionally,  $\lambda\text{-Ti}_3\text{O}_5$  is capable of preserving heat energy for a prolonged period, proposing a novel concept of "heat storage ceramics." This material absorbs and releases a large heat energy of  $230 \text{ kJ L}^{-1}$ , and the preserved heat energy could be released by applying a weak pressure of 60 MPa. Furthermore, the present system could store the heat energy by electric current or light and release the heat energy by various external stimuli repetitively. The present heat storage ceramic is expected as a new material for solar thermal power generation systems or for realizing efficient uses of industrial waste heat generated from furnaces.



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