Contribution ID: **102**

Type: **oral presentation**

New functionalities originating from phase transition phenomena in cyano-bridged bimetal assemblies and metal oxides

Monday, July 6, 2015 4:10 PM (40 minutes)

Development of functional materials has been extensively studied in the field of solid-state chemistry. Up to date, we have developed various unique photomagnetic mateirals using cyano-bridged bimetallic assemblies [1-4]. Furthermore, we have reported a new crystal structure of titanium oxide, lambda-titanium oxide (λ-Ti3O5), which exhibits a photo-reversible metallic (Pauli paramagnetic) phase to semiconductor (non-magnetic) phase transition at room temperature [5]. In addition to these photo-functional materials, we have developed a pure phase of epsilon-iron oxide nanomaterials, which exhibit a high frequency millimeter wave absorption [6]. Here, I introduce novel photomagnetic functionalities on iron-octacyanoniobates, light-induced spin-crossover magnetic phenomenon in Fe2Nb(CN)88·2H2O [3], and photoreversible light-induced spin-crossover phenomenon, spin-crossover-induced second harmonic generation (SHG), and photoswitching of magnetization-induced SHG (MSHG) in Fe2Nb(CN)88·2H2O [1]. In addition, novel thermodynamic functionality of lambda-titanium oxide is introduced [7].
Light-induced spin-crossover magnetic phenomenon: The long-range magnetic ordering of the FeII(HS)(S= 2) site network in a metal–organic framework caused by a light-induced excited spin-state trapping (LIESST) effect. The iron-octacyanoniobate, Fe2Nb(CN)88·2H2O, exhibits a spin-crossover magnetic properties, in which a strong superexchange interaction between photo-produced FeII(HS) and neighbouring NbIV(S= 1/2) atoms operates through CN bridges. The photomagnetic phase showed magnetic transition at 20 K and a coercive magnetic field of 240 Oe.
90-degree optical switching of output SH light in a chiral photomagnet: A novel magnetooptical phenomenon, 90-degree optical switching of output SH light is first observed in a chiral photomagnet. We developed a new chiral structured magnet, where Fe ions and Nb ions are three dimensionally bridged by CN ligands. By alternatively irradiating with 473-nm blue light and 785-nm light, the spontaneous magnetization of the material can be reversibly switched. Using this chiral photomagnet, we investigated SHG nonlinear optical effects. As a result, at a nonmagnetic state before light irradiation, input light with a horizontal polarization plane was converted to an output light with a vertical polarization plane. However, when the sample was transformed into a magnetic state (photomagnetic state I) by irradiating with 473-nm light, an output light with a horizontal polarization plane was observed. Furthermore, when irradiated with 785-nm light to photogenerate a magnetic state with weak magnetization (photomagnetic state II), the polarization plane of the output light was returned to vertical. In this way, we succeeded in 90-degree switching of the polarization plane of the output SH light by changing the state of the magnet with 473-nm and 785-nm lights. There have not been any other reports of chiral photomagnets, and this is the first successful example. With the development of such a novel material, chirality and magnetic properties were coupled to exhibit 90-degree switching of the polarization plane of the output light.

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Session Classification: Opening lecture