Optical-switching of second harmonic light in chiral photomagnet

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To control the physical properties and functionalities of materials via optical stimulation is an attractive issue. Spin-crossover phenomenon has been extensively studied because it realizes temperature-, pressure-, or photo-switching of the physical properties and functionalities. In particular, photo-switching from the low-spin (LS) state to the high-spin (HS) state, which is known as light-induced excited spin-state trapping (LIESST), is effective for optical control. Up to date, we have reported various unique photomagnetic materials using cyano-bridged bimetallic assemblies.1,2 For example, we have reported an iron-octacyanoniobate metal complex, Fe2[Nb(CN)8]·(4-pyridinealdoxime)·2H2O and a photo-induced ferromagnetism originated by LIESST effect for the first time.3 In this work, we synthesize a new 3-dimensional chiral cyano-bridged bimetallic assembly of iron-octacyanoniobate, (±)-Fe2[Nb(CN)8](4-bromopyridine)8·2H2O (I),4 and firstly observed spin-crossover-induced second harmonic generation (SHG), light-reversible spin-crossover long-range magnetic ordering, and optical-reversible switching of the magnetization-induced second harmonic generation (MSHG) effect.

Cyano-bridged FeNb bimetallic assembly of I has a chiral structure in the I4122 space group (Fig.1). The temperature (T) dependence of the molar magnetic susceptibility (χM) shows a thermal phase transition between the high-temperature (HT) phase and the low-temperature (LT) phase. The transition temperatures from the HT to LT (T1/2↓) and from the LT to HT (T1/2↑) are 112 K and 124 K, respectively. The UV-vis absorption spectra exhibits optical absorptions at 430 nm and 560 nm, which are assigned to 1A1 → 1T2 and 1A1 → 1T1 transitions on the FeII LS site, respectively. Therefore, the transition from the HT to LT in the χM–T plot is due to spin-crossover from FeIIHS (S = 2) to FeII LS (S = 0).

Photomagnetic effect of I was investigated. Irradiating the LT phase with 473-nm light at 2 K produces large spontaneous magnetization. (Hereafter, called PI-1.) The saturation magnetization (Ms) at 5 T is 7.6 μB, close to the expected Ms value of 7.8 μB due to ferrimagnetic coupling between NbIV (S = 1/2) and the photo-produced FeII HS (S = 2). UV-vis spectrum and Mössbauer spectrum indicated that the observed bulk magnetization is due to the light-induced spin-crossover from FeII LS to FeII HS, i.e., LIESST effect. Next, we investigated the optical-switching effect on MSHG. Prior to irradiation, SHG for the LT phase of the paramagnetic state was measured. The SH intensity versus analyzer rotation angle (θ) plot shows that θmax is 0° at ±H0, which is similar to the θ dependence of the SH intensity observed at 80 K. In the PI-1 phase, which is produced by LIESST effect with 473-nm light irradiation, θmax at ±H0 is +88 ± 3° (Fig. 2). In contrast, at −H0, θmax is −86 ± 4°. In the PI-2 phase, produced by Reverse-LIESST effect with 785-nm light irradiation, the θmax values are returned to +3 ± 1° and −3 ± 1° at ±H0 and −H0, respectively. In the present system, LIESST and Reverse-LIESST effects control the polarization plane of the output SH light. The photo-reversibility was confirmed by alternative irradiation of 473-nm light and 785-nm light, which showed photo-reversible change in the SH intensity at θ = 0°.

Reference

Fig. 1 Crystal structure of I.