

Ln-[Fe(CN)₅NO] crystals showing photo-switchable polarization of second harmonic light

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Photoswitching of second-harmonic generation (SHG) has been intensively studied for the application of optical devices.¹ Recently, our laboratory has reported photo switching of SH intensity in [Dy(phen)₂(NO₃)(H₂O)] [Fe(CN)₅(NO)] · 3H₂O (**DyFe**).² In this study, we report the SHG properties of [Ln(phen)₂(NO₃)(H₂O)] [Fe(CN)₅NO] · nH₂O (**LnFe**) (Ln = Pr, Nd, Gd, Tb, Ho) and photo switchable polarization of SH light in **TbFe**.

Syntheses of **LnFe** crystals were performed by mixing an aqueous solution of Ln(NO₃)₃ and Na₂[Fe(CN)₅NO], and a methanolic solution of 1,10-phenanthroline. According to single crystal X-ray analyses, they were isostructural with space group *Pna*2₁. From the powder SHG measurements and crystal SHG measurements, elements of second-order susceptibility tensors were estimated. Among **LnFe**, **TbFe** has relatively larger χ_{zzz} and χ_{yyz} values and is suitable for observing interaction between tensor elements. Crystal SHG measurements under photo irradiation at 100 K revealed that χ_{zyy} , χ_{zzz} , and χ_{yyz} after 473 nm light irradiation are 1.7, 1.2, 0.6 times as large as those before the irradiation, respectively. They restored their original values with irradiation of 804 nm light. Due to this variety of photo effects on these elements, the polarization of output SH signal was switched by irradiation of 473 nm and 804 nm light by 18 ± 4 degrees when the polarization of incident laser was 14.7 degrees to the *z*-axis.

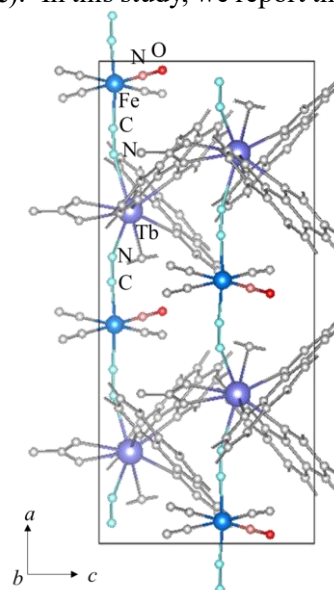


Figure 1. Crystal structure of **TbFe** viewed from the *b*-axis.

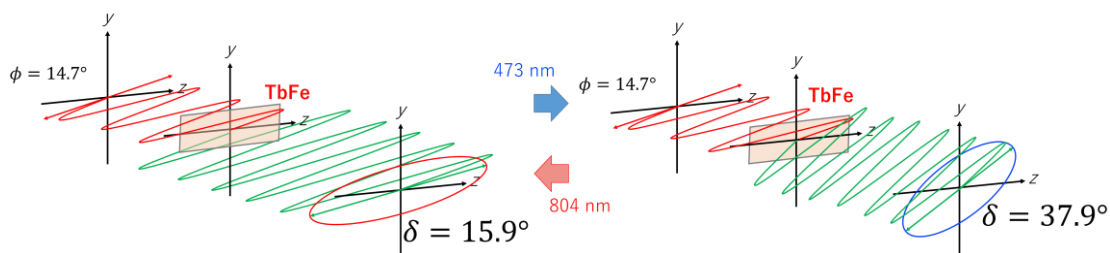


Figure 2. Schematic image of photo switchable polarization of SH light from **TbFe**.

1) S. Ohkoshi, S. Takano, K. Imoto, M. Yoshikiyo, A. Namai, H. Tokoro, *Nature Photonics* **2014**, 8, 65.

2) M. Komine, K. Imoto, A. Namai, M. Yoshikiyo, S. Ohkoshi, *Inorg. Chem.* **2021**, 60, 2097.