Communication

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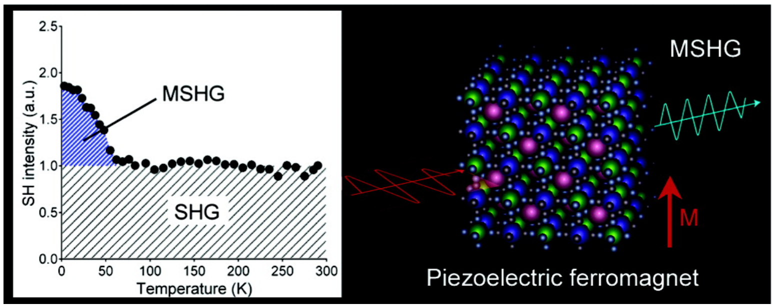

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Nonlinear Magnetooptical Effects Caused by Piezoelectric Ferromagnetism in $F\bar{4}3m$-type Prussian Blue Analogues

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In the past decade, various interesting magnetic properties have been reported with Prussian blue analogues,[1] for example, high Curie temperature (T_C) values[2] and magnetic functionalities, such as humidity response[3] and photomagnetism.[4] In addition, new functions have been recently studied,[5] such as pressure-induced CN flip, zero thermal expansion, and hydrogen storage. Prussian blue analogues have two types of crystal structures, $M_A[M_B(CN)_6]_{2/3}\cdot zH_2O$ (space group $Fm\bar{3}m$) and $AM_A[M_B(CN)_6]$ ($F\bar{4}3m$), where M_A and M_B are transition metal ions, and A is an alkali ion. To maintain charge neutrality, $M_A[M_B(CN)_6]_{2/3}\cdot zH_2O$ has vacancies of $[M_B(CN)_6]$ and the ligand water molecules coordinate to the M_A ion, and zeolitic water molecules exist in the lattice.[6] In $AM_A[M_B(CN)_6]$, the M_A ions coordinate to six cyanonitrogen, and the A ion is located in the interstitial site of the lattice (Figure 1a).[7,8] It is noteworthy that the position of the A ion in this type of crystal produces a $\bar{4}$ rotoinversion operator. Hence, the crystal structure is noncentrosymmetric. In this work, we observed the second harmonic generation (SHG) and magnetization-induced effect in the SHG with $AM_A[M_B(CN)_6]$-type Prussian blue analogues of $CsCo[Cr(CN)_6]\cdot 0.5H_2O$ and $RbMn[Fe(CN)_6]$. In these systems, a large interaction between the nonlinear optical response and the magnetic spins was observed. The present SHG observations indicate that $AM_A[M_B(CN)_6]$-type Prussian blue analogues are piezoelectric ($T > T_C$) and piezoelectric ferromagnet ($T < T_C$). In this paper, we show this new magnetooptical functionality due to the interaction between electronic and magnetic properties of $AM_A[M_B(CN)_6]$-type Prussian blue analogues.

$Cs^{I}Co^{II}[Cr^{III}(CN)_6]\cdot 0.5H_2O$ and $Rb^{I}Mn^{II}[Fe^{III}(CN)_6]$ of the target samples and $Co^{II}[Cr^{III}(CN)_6]_{2/3}\cdot 4.8H_2O$ of the reference sample were prepared by the procedures reported in our previous papers,[8,9] and their elemental analyses were confirmed by an inductively coupled plasma mass spectroscopy and a standard microanalytical method (Supporting Information). The CN stretching frequencies in the IR spectra of $CsCo[Cr(CN)_6]\cdot 0.5H_2O$, $Co[Cr(CN)_6]_{2/3}\cdot 4.8H_2O$, and $RbMn[Fe(CN)_6]$ were 2166, 2168, and 2152 cm^{-1}, respectively. Scanning electron microscope (SEM) images showed that the prepared samples consisted of cubic microcrystals with particle sizes of 140 ± 30 nm ($CsCo[Cr(CN)_6]\cdot 0.5H_2O$), 80 ± 10 nm ($Co[Cr(CN)_6]_{2/3}\cdot 4.8H_2O$) (Supporting Information), and 2.1 ± 1.1 μm ($RbMn[Fe(CN)_6]$).[9b] SHG measurements of powder-form samples were conducted in the reflection mode using the following instruments. Incident light was provided by a Q-switched Nd:YAG laser (HOYA Continuum, Minilite II, wavelength of 1064 nm, pulse duration of 10 ns, repetition rate of 15 Hz). SH light was detected by a photomultiplier tube (Hamamatsu, R329-02) through color filters and a band-pass filter. The angles of incidence and reflection on the sample were 45° (Supporting Information).

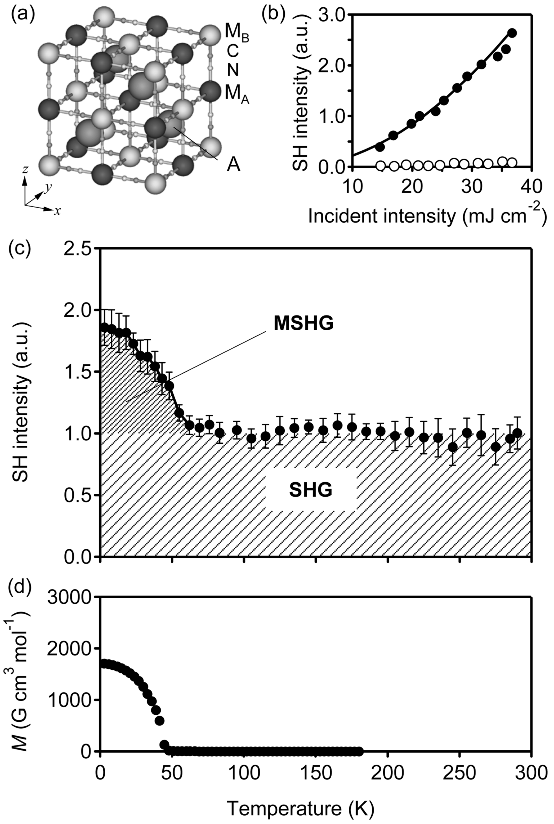

Figure 1. (a) The unit cell of $AM_A[M_B(CN)_6]$ ($F\bar{4}3m$). (b) The SH intensity versus incident light intensity of $CsCo[Cr(CN)_6]\cdot 0.5H_2O$ (●) and $Co[Cr(CN)_6]_{2/3}\cdot 4.8H_2O$ (○) at 295 K (incident light = 1064 nm). The solid line represents the fitting curve using a quadratic function. (c) Temperature dependence of the SH intensity generated from $CsCo[Cr(CN)_6]\cdot 0.5H_2O$ (incident light intensity = 22 mJ cm^{-2}). MSHG, Magnetization-induced SHG. (d) Field-cooled magnetization curve of $CsCo[Cr(CN)_6]\cdot 0.5H_2O$ in a magnetic field of 10 G.

When $Cs^{I}Co^{II}[Cr^{III}(CN)_6]\cdot 0.5H_2O$ was irradiated by 1064 nm light at 295 K, 532 nm light was observed. Since the intensity of the 532 nm light increased with the square of the incident light intensity (Figure 1b), the observed 532 nm light is clearly SH light. The temperature dependence of the SH intensity showed that the SH intensity was nearly constant between 295 and 55 K, but the SH intensity increased below 55 K and the intensity at 5 K was 1.9 times larger than the intensity at 295 K (Figure 1c). This temperature dependence corresponds to the temperature dependence of magnetization of this system (Co^{II}: $S = 3/2$; Cr^{III}: $S = 3/2$), which is a ferromagnet with a Curie temperature of 46 K (Figure 1d). In contrast, $Co^{II}[Cr^{III}(CN)_6]_{2/3}\cdot 4.8H_2O$, the reference sample, did not exhibit SHG over the entire temperature range.

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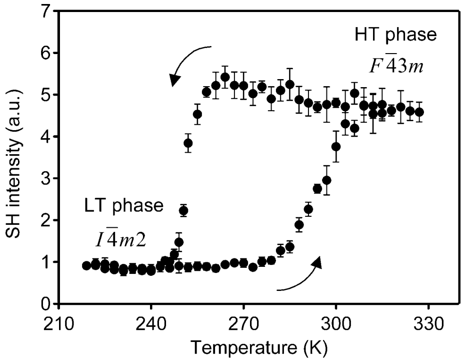

Figure 2. Temperature dependence of SH intensity generated from RbMn[Fe(CN)$_6$] (incident light = 1064 nm, intensity = 11 mJ cm^{-2}).

The SHG observed in $Cs^{I}Co^{II}[Cr^{III}(CN)_6]\cdot 0.5H_2O$ is understood by the following. The second-order optical response is described by $P_i(2\omega) = \chi_{ijk}^{(2)}(-2\omega;\ \omega,\ \omega)E_j(\omega)E_k(\omega)$, where $P_i(2\omega)$ is the second-order nonlinear polarization and $\chi_{ijk}^{(2)}$ is the second-order nonlinear susceptibility tensor. X-ray powder diffraction (XRD) patterns show that the crystal structures of $Cs^{I}Co^{II}[Cr^{III}(CN)_6]\cdot 0.5H_2O$ and $Co^{II}[Cr^{III}(CN)_6]_{2/3}\cdot 4.8H_2O$ are $F\bar{4}3m$ (a = 10.618(2) Å) and $Fm\bar{3}m$ (a = 10.560(1) Å), respectively. The $F\bar{4}3m$-type structure is noncentrosymmetric, and hence, SHG is permitted in $Cs^{I}Co^{II}[Cr^{III}(CN)_6]\cdot 0.5H_2O$. This space group has a crystallographic term ($\chi_{ijk}^{(2)\mathrm{cry}}$) in the second-order nonlinear susceptibility, that is, $\chi_{xyz}^{(2)\mathrm{cry}}$, $\chi_{yzx}^{(2)\mathrm{cry}}$, $\chi_{zxy}^{(2)\mathrm{cry}}$, and $\chi_{xyz}^{(2)\mathrm{cry}} = \chi_{yzx}^{(2)\mathrm{cry}} = \chi_{zxy}^{(2)\mathrm{cry}}$. Furthermore, below T_C, the magnetic ordering creates a magnetic term ($\chi_{ijk}^{(2)\mathrm{mag}}$). This second-order nonlinear susceptibility term is called the magnetization-induced second harmonic generation (MSHG).[10,11] Thus, the enhanced SH intensity below T_C is due to the creation of the $\chi_{ijk}^{(2)\mathrm{mag}}$ term. Since the ferromagnetic phase of $Cs^{I}Co^{II}[Cr^{III}(CN)_6]\cdot 0.5H_2O$ is in the $I\bar{4}\underline{m}\underline{2}$ magnetic space group,[12] the nonzero tensor elements in $\chi_{ijk}^{(2)}$ are described by the contribution of the $\chi_{ijk}^{(2)\mathrm{cry}}$ and $\chi_{ijk}^{(2)\mathrm{mag}}$, that is, $\chi_{xyz}^{(2)\mathrm{cry}} + \chi_{xyz}^{(2)\mathrm{mag}}$, $\chi_{yzx}^{(2)\mathrm{cry}} + \chi_{yzx}^{(2)\mathrm{mag}}$, $\chi_{zxy}^{(2)\mathrm{cry}} + \chi_{zxy}^{(2)\mathrm{mag}}$ (Supporting Information). In contrast, $Co^{II}[Cr^{III}(CN)_6]_{2/3}\cdot 4.8H_2O$ is a $Fm\bar{3}m$-type crystal and is centrosymmetric. Thus, all tensor elements of $\chi_{ijk}^{(2)}$ are zero and SHG is forbidden.

Next, we measured the SHG of RbMn[Fe(CN)$_6$], which shows a charge-transfer phase transition between the high-temperature (HT) phase and low-temperature (LT) phase. The electronic states of the former and the latter are $Mn^{II}(t_{2g}^{3}e_{g}^{2};\ S = 5/2)-NC-Fe^{III}(t_{2g}^{5};\ S = 1/2)$ and $Mn^{III}(e_{g}^{2}b_{2g}^{1}a_{1g}^{1};\ S = 2)-NC-Fe^{II}(b_{2g}^{2}e_{g}^{4};\ S = 0)$, respectively.[9] At 295 K, the SH intensity of the HT phase increased with the square of the incident light intensity (Supporting Information). In the temperature dependence of the SH intensity, a thermal hysteresis loop was observed (Figure 2). The SH intensity of the HT phase is 5 times stronger than that of the LT phase in the inside of the thermal hysteresis loop. The space groups of the HT and LT phases are $F\bar{4}3m$ and $I\bar{4}m2$, respectively.[9,13] These space groups have nonzero elements of $\chi_{xyz}^{(2)\mathrm{cry}}$, $\chi_{yzx}^{(2)\mathrm{cry}}$, and $\chi_{zxy}^{(2)\mathrm{cry}}$, which cause both phases to show SHG. The variation in the SH intensity with the phase transition is due to the change in the magnitudes of tensor elements between the HT and LT phases.

In this work, SHG and MSHG were observed in $AM_A[M_B(CN)_6]$-type ($F\bar{4}3m$) Prussian blue analogues. These observations are remarkable results in the fields of magnetooptics and magnetic materials since reports of bulk MSHG have been limited.[10a,d,11,14] Simultaneously, $F\bar{4}3m$-type Prussian blue analogue-based magnets are proven to be piezoelectric ferromagnets, that is, condensed matter with both piezoelectric and ferromagnetism. Since a variety of $F\bar{4}3m$-type Prussian blue analogues can be prepared, these analogues will open a new avenue in the study of piezoelectric ferromagnets and nonlinear magnetooptics.

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Supporting Information Available: The syntheses and elemental analyses, the SEM images, the MSHG tensor elements, the setup of SHG measurement, the SH intensity versus incident light intensity of the HT phase of RbMn[Fe(CN)$_6$], and the MSHG generated from the LT phase of RbMn[Fe(CN)$_6$] are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) The present MSHG is essentially different from the MSHG observed in electrochemically synthesized $(Fe_xCr_{1-x})[Cr(CN)_6]_{2/3}\cdot 5H_2O$ films of ref 11. The latter is due to an electrochemically distorted crystal structure ($C2$ space group).

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