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Three-Dimensional Manganese Octacyanoniobate-Based Pyroelectric Ferrimagnet

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A novel pyroelectric ferrimagnet, $[\{Mn^{II}(pyrazine)(H_2O)_2\}\{Mn^{II}(H_2O)_2\}\{Nb^{IV}(CN)_8\}]\cdot 4H_2O$, is synthesized. The crystal consists of an Nb^{IV}–CN–Mn^{II} linked three-dimensional network, which has an electric polarization along the *b* axis. This compound exhibits ferrimagnetism with a Curie temperature of 48 K due to the antiparallel ordering of magnetic spins on Nb^{IV} ($S = 1/2$) and those on Mn^{II} ($S = 5/2$).

Cyano-bridged metal assemblies have been aggressively studied as functionalized magnetic materials.[1] Hexacyanometalate-based magnets are known to exhibit a high magnetic ordering temperature,[2] temperature-induced phase transition,[3] and external stimuli-induced magnetization.[4] In the last decade, octacyanometalate-based magnets have also been receiving much attention.[5] Octacyanometalates $[M(CN)_8]^{n-}$ (M = Mo, W, Nb, etc.) are a versatile class of building blocks that can adopt different spatial configurations depending on the surrounding ligands. Octacyanometalate-based coordination polymer can take various coordination geometries in the crystal structure from zero-dimensional (0-D) to 3-D.[6–9] In order to achieve a long-range magnetic ordering, octacyanometalates having magnetic spins, e.g., $[Mo^{V}(CN)_8]^{3-}$, $[W^{V}(CN)_8]^{3-}$, and $[Nb^{IV}(CN)_8]^{4-}$, are suitable. Some research groups have reported $[Nb^{IV}(CN)_8]^{4-}$-based bimetallic assemblies exhibiting long-range magnetic ordering.[9] Recently, as a new magnetic function, a material that has both spontaneous magnetization and spontaneous electric polarization draws one's attention. In this study, we have prepared a novel type of 3-D cyano-bridged Mn^{II}–Nb^{IV} assembly, $[\{Mn^{II}(H_2O)_2\}\{Mn^{II}(pyrazine)(H_2O)_2\}\{Nb^{IV}(CN)_8\}]\cdot 4H_2O$. This compound showed ferrimagnetism with $T_C = 48$ K and a spontaneous electric polarization, i.e., a pyroelectric ferrimagnet. In this paper, the crystal structure and magnetic properties of this compound are described.

$K_4[Nb(CN)_8]\cdot 2H_2O$ was prepared according to a literature method.[10] Aqueous solutions of $K_4[Nb(CN)_8]\cdot 2H_2O$ (98.7 mg, 0.2 mmol) were slowly diffused into aqueous solutions containing both $MnCl_2\cdot 4H_2O$ (79.2 mg, 0.4 mmol) and pyrazine (160.1 mg, 2 mmol). After a week, reddish brown crystals were obtained. Elemental analyses confirmed that the composition of the compound was $Mn^{II}{}_2[Nb^{IV}(CN)_8]\cdot(pyrazine)\cdot 8H_2O$. Anal. Calcd: Mn, 17.30; Nb, 14.63; C, 22.69; H, 3.17; N, 22.05%. Found: Mn, 17.53; Nb, 14.48; C, 22.43; H, 3.19; N, 21.91%.

In the IR spectra, CN stretching peaks were observed at 2160, 2154, 2148, 2141, 2133, 2129, and 2123 cm^{-1}. In diffuse reflectance spectra (Figure S1), optical absorption was observed at 430 and 460 nm, which were attributed to the d–d transition of Nb^{IV}.[10]

X-ray single-crystal analysis shows that the crystal was monoclinic with a $P2_1$ space group ($a = 7.3785(3)$ Å, $b = 14.4288(7)$ Å, $c = 11.7625(5)$ Å, $\beta = 98.999(2)°$, $Z = 2$). Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-685477. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).[11] Figure 1 shows the asymmetric unit of the compound. The asymmetric unit consisted of $[Nb(CN)_8]^{4-}$, $[Mn1(H_2O)_2]^{2+}$, and $[Mn2(pyrazine)(H_2O)_2]^{2+}$. The coordination geometry around Nb and Mn sites were eight-coordinate square antiprism and six-coordinate pseudo-octahedron, respectively. Four of the CN groups in $[Nb(CN)_8]^{4-}$ were bridged to Mn1, and two of the CN groups were bridged to Mn2. The other two CN groups were free. Nb–C bond distances ranged from 2.27–2.23 Å, and the Nb–C–N bonds were nearly linear with angles ranging between 176–179°. Mn1 was coordinated by four cyanonitrogens at equatorial positions and two oxygen atoms of the water ligand at axial positions. The Mn1–N distances ranged from 2.19–2.21 Å and Mn1–N–C bond angles ranged from 149–177°. Mn2 was coordinated by two nitrogen atoms of $[Nb(CN)_8]^{4-}$, two nitrogen atoms of pyrazine, and two oxygen atoms of the ligand water. The $Mn2–N_{CN}$ and $Mn2–N_{pyrazine}$ bond distances

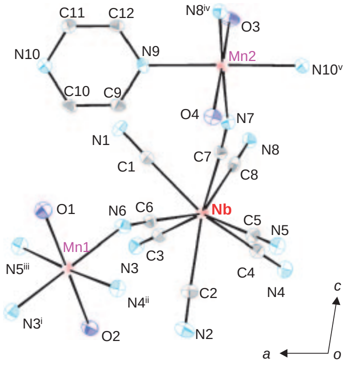

Figure 1. A structural diagram showing the coordination environments around Mn^{II} and Nb^{IV}. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms and non-coordinated water molecules are omitted for clarity [Symmetry codes: (i) $x+1$, y, z; (ii) $-x$, $y-1/2$, $-z+1$; (iii) $-x+1$, $y-1/2$, $-z+1$; (iv) $-x$, $y+1/2$, $-z+2$; (v) $x-1$, y, z].

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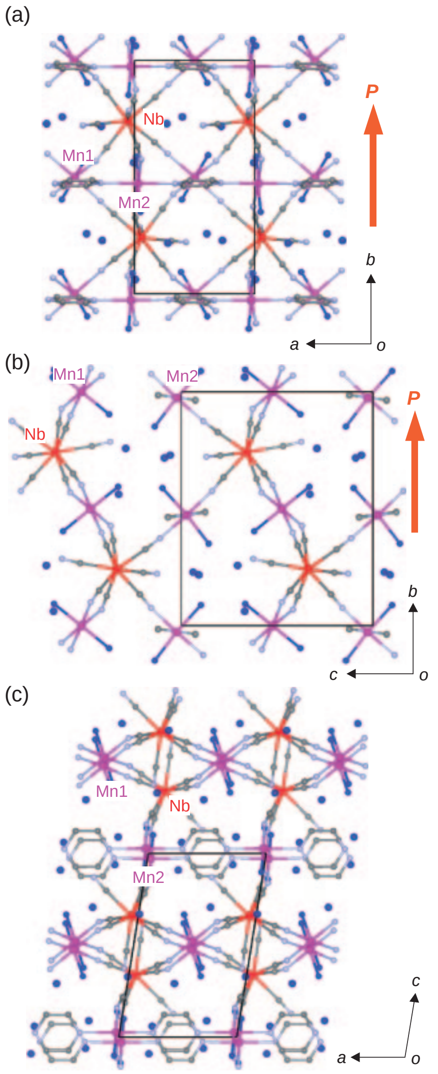

Figure 2. Views of the crystal structure. Red, purple, gray, light blue, and blue balls represent Nb, Mn, C, N, and O, respectively. (a) The projection of 2-D layer in the *ab* plane. (b) The projection in the *bc* plane. (c) The projection in the *ac* plane.

ranged from 2.14–2.16 and 2.28–2.30 Å, respectively. Mn2–N_{CN}–C_{CN} bond angles ranged from 162–165°. The cyano-bridged Mn1–Nb layer in the crystallographic *ab* plane (Figure 2a) was linked by Mn2 through a CN bridge in the crystallographic *c* direction (Figure 2b), and Mn2 was also bridged by pyrazine in the *a* direction (Figure 2c). Four water molecules existed between the layers as zeolitic waters. This compound is a pyroelectric material of a noncentrosymmetric space group ($P2_1$). The electric polarization is along the *b* axis, since there is a 2-fold screw axis along this axis.

The magnetizations versus temperature plots for a single crystal are shown in Figure 3a. In the field-cooled magnetization (FCM) curve at external magnetic field of 10 G (G = 10^{-4} T), spontaneous magnetization appeared at $T_C = 48$ K. In the FCM curve, the magnetization value along crystallographic *a* axis was four times larger than magnetization values along the *b* or *c* axis. The results of DC and AC magnetic measurements for crushed single crystals are shown in Figures S2 and S3, respectively. The magnetization versus external magnetic field plots at 2 K showed that the magnetization along the *a* axis rapidly increased and the saturated value (M_S) was 9.1 μ_B (Figure 3b). The increase of the magnetization along the *b* or *c* axis gradually increased, indicating that the magnetic easy axis was along the *a* axis. The observed M_S value of 9.1 μ_B is in good agreement with the expected value of 9.0 μ_B, assuming that this compound is a ferrimagnet, in which an antiferromagnetic interaction operates between the Nb^{IV} ($S = 1/2$) and Mn^{II} ($S = 5/2$). The magnetic hysteresis loop showed that the coercive field (H_C) of crushed sample was 3 G at 2 K.

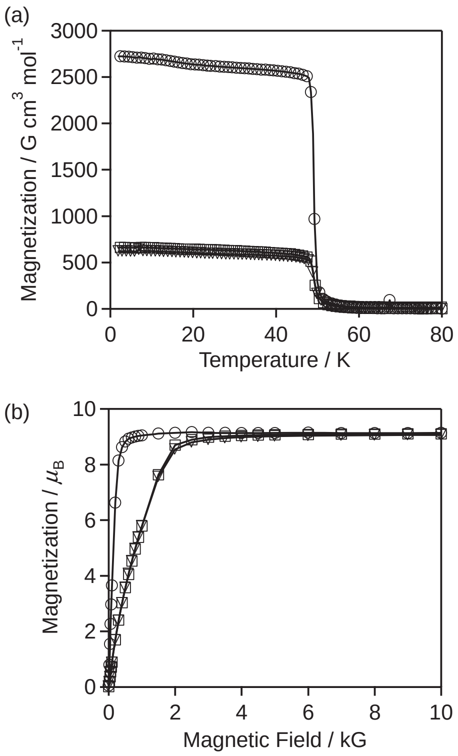

Figure 3. (a) The magnetization vs. temperature plots along *a* axis (○), *b* or *c* axis (▽), and *c* or *b* axis (□) in an external magnetic field of 10 G. (b) Magnetization vs. external magnetic field plots at 2 K along *a* axis (○), *b* or *c* axis (▽), and *c* or *b* axis (□).

In order to elucidate the pyroelectricity, the SHG measurement of a powder sample was conducted in the reflection mode. When the compound was irradiated by 1064-nm light by a Q-switched Nd:YAG laser at 293 K, 532-nm light was observed. Since the intensity of the 532-nm light increased with the square of the incident light intensity (Figure 4), the observed 532-nm light is clearly SH light. The SHG susceptibility at the fundamental light of 1064 nm was 2×10^{-11} esu.

In conclusion, we prepared a octacyanoniobate-based bimetal assembly, $[\{Mn(pyrazine)(H_2O)_2\}\{Mn(H_2O)_2\}\{Nb(CN)_8\}]\cdot 4H_2O$, which showed ferrimagnetism with $T_C = 48$ K, and SHG due to its noncentrosymmetric crystal structure ($P2_1$ space group). Until now, four other octacyanoniobate-based compounds showing ferrimagnetic ordering have been reported ($[Mn(H_2O)_2]_2[Nb(CN)_8]\cdot 4H_2O$; $T_C = 50$ K,[9a] $\{Mn_2(pyrazine)_2(H_2O)_4[Nb(CN)_8]\}\cdot pyrazine\cdot 3H_2O$; $T_C = 27$ K,[9b]

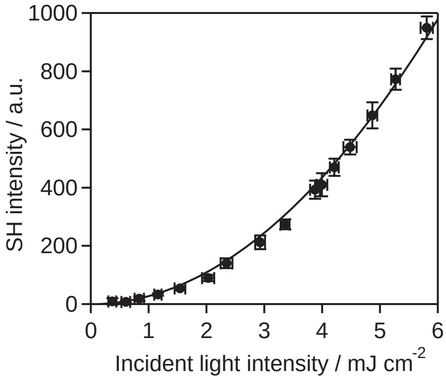

Figure 4. SH intensity vs. incident light intensity at 293 K (incident light = 1064 nm). The solid line represents the fitted curve using a quadratic function.

$\{Mn_2(\text{pyrazine-}N,N'\text{-dioxide})(H_2O)_4[Nb(CN)_8]\}\cdot 5H_2O$; $T_C = 37$ K,[9b] $\{Mn_2(2,2'\text{-bipyrimidine})(H_2O)_2[Nb(CN)_8]\}$; $T_C = 50$ K[9b]). Although the ligand used in $\{Mn_2(\text{pyrazine})_2(H_2O)_4[Nb(CN)_8]\}\cdot\text{pyrazine}\cdot 3H_2O$ is the same as that of our compound, the number of bridging CN group is different (five in their compound but six in our compound). Only our compound shows both magnetic ordering and pyroelectricity.

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Supporting Information

Diffuse-reflectance spectrum, magnetization versus temperature plots for crushed single crystals, AC magnetization of this compound. This material is available free of charge on the web at: http://www.csj.jp/journals/bcsj/.

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11 Crystal data for $[\{Mn^{II}(H_2O)_2\}\{Mn^{II}(\text{pyrazine})(H_2O)_2\}\{Nb^{IV}(CN)_8\}]\cdot 4H_2O$: $C_{12}H_{20}N_{10}O_8Mn_2Nb$, $M_r = 635.13$, monoclinic, space group $P2_1$, $a = 7.3785(3)$, $b = 14.4288(7)$, $c = 11.7625(5)$ Å, $\beta = 98.9990(18)^\circ$, $V = 1236.86(9)$ Å^3, $d_{\text{calcd}} = 1.705$ g cm^{-3}, $T = 90(1)$ K, $Z = 2$, $\mu(\text{Mo K}\alpha) = 15.160$ cm^{-1}, 5686 independent ($R_{\text{int}} = 0.031$) with 19701 observed data, $R1 = 0.0321$, and $wR2 = 0.0871$, goodness of fit = 1.005. A yellow-red-brown crystal having approximate dimension of $0.37 \times 0.17 \times 0.10$ mm^3 was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo Kα radiation. The data were collected at a temperature of 90 ± 1 K. The structure was solved by direct methods using SIR97,[12] expanded using Fourier techniques, and refined by full-matrix least-squares techniques by CRYSTALS. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of pyrazine were refined using riding model. The hydrogen atoms of water molecule were not included during refinement. All calculations were performed using Crystal Structure crystallographic software package.

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