Synthesis and the Magnetism of the Metal Halide-based Organic/Inorganic Layered Perovskite

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Metal halide-based layered perovskites, $(\text{RNH}_3)_2\text{MCl}_4$, self-organized organic/inorganic multilayer structure were synthesized, where R is a simple alkylammonium molecule with a long chain length, $(\text{CH}_3(\text{CH}_2)_{17})$ or a 1-methyl-naphthalene ($\text{C}_{10}\text{H}_9\text{CH}_2$), M is 3d transition metal elements. Its layered perovskite structure was checked by a FT-IR method. The perovskites of $\text{CH}_3(\text{CH}_2)_{17}\text{NH}_3$ with Cu and Cr showed ferromagnetism ($T_C = 10$ K and 42 K, respectively), and Mn and Fe antiferromagnetism ($T_N = 41$ K and 95 K, respectively). These results roughly corresponded to the results for methyl and ethyl ammonium complexes reported. The naphthalene complex with Cu also showed ferromagnetism, however, the Curie temperature became low. It was considered that the relative large chromophore might disturb the Jahn-Teller distortion of CuCl_6 octahedra. 1-methyl-naphthylamine- hydrochloride was luminous with the wavelength of 350 nm under ultraviolet light irradiation, but its Cu complex was quenched.

Key words: layered perovskite, alkylchain, naphthalene, organic/inorganic multilayer, complex, photoinduced magnetism, light irradiation

1. Introduction

There are widespread group of salts having the general formula $(\text{RNH}_3)_2\text{MX}_4$, where M is a divalent cation, X a halide ion and R one of a wide range of organic moieties ¹⁾⁻⁶⁾. The R groups with NH_3^{3+} maintaining Van der Waals contact with one another can be incorporated to the constraining area of the $(\text{MX}_4)_n^{2n-}$ layer. Within that constraint, a wide variety is possible as exemplified in fig.1. The layer perovskite halide salts merit attention from three points of view; using the inorganic layer as templates to hold organic moieties, structural phase transitions ⁷⁾ and excellent models for two-dimensional cooperative magnetism. From the point of view of magnetism, simple alkylammonium molecules with a short chain length have been employed as an organic layer in the layered perovskite, where they play only the role of a barrier layer. If functionalized ammonium molecules such as chromophore-linked ones ⁸⁾ are employed, a variety of novel organic/inorganic magnetic materials assembled at a molecule scale would be designed and a large enhancement of the interaction between these layers could be arisen.

We synthesized the layered perovskite of a simple alkylammonium molecule with a long chain length, $(\text{CH}_3(\text{CH}_2)_{17}\text{NH}_3)_2\text{MCl}_4$ in place of a large volume of chromophores. Estimates of the superexchange interaction between adjacent layers have been lead to be $J = 10^{-3} \sim 10^{-20}$

J for $n=1 \sim 10$, where J is the exchange interaction within the layer and n the number of a methylene unit ⁴⁾. In this case, the interlayer coupling might be mainly of dipolar origin. Also, we tried to synthesize the layered perovskite with 1-methyl-naphthalene ($\text{C}_{10}\text{H}_9\text{CH}_2$). Present paper describes the results of the magnetic and optical measurements of these perovskites.

2. Experimental Details

We synthesized the layered perovskites $(\text{RNH}_3)_2\text{MCl}_4$, where a two-dimensional layer of corner-sharing MCl_6 octahedra (M : Cr, Mn, Fe, Co, Ni, Cu and Zn) and a organic ammonium molecule RNH_3 (R : $\text{CH}_3(\text{CH}_2)_{17}$ and $\text{C}_{10}\text{H}_9\text{CH}_2$) was alternately piled up. Fig.1 shows the schematic illustration of layered perovskites. Small crystals of these materials were prepared by the reaction of organic ammonium chlorides with stoichiometric amounts of MCl_2 in boiling ethanol ⁹⁾.

The infrared spectra were recorded on a Shimadzu FTIR-8200PC spectrometer equipped with a DLATGS detector with a resolution of 4 cm^{-1} by an ATR method. The number of interferogram accumulations was 20. The UV-visible and fluorescence spectra (190-800 nm) were

Fig.1 Schematic illustration of layered perovskites $(\text{RNH}_3)_2\text{MCl}_4$, where a two-dimensional layer of corner-sharing MCl_6 octahedra and a organic ammonium molecule RNH_3 .

acquired on a Hitachi U-3000 and a F-4500 spectrophotometer, respectively. The magnetization was measured by a SQUID magnetometer in a magnetic field up to 55 kOe from 2.0 K to 300 K. The background signal from the substrate was carefully subtracted.

3. Results and Discussions

3.1 Structure

The FT-IR was used to decide molecular structures of the layered perovskites. Fig.2 shows the FT-IR spectra for the samples with $R=\text{CH}_3(\text{CH}_2)_{17}$ and $M=\text{Cr}$, Mn , Fe , Co , Ni and Cu . The spectrum for octadecylamine-hydrochloride ($\text{CH}_3(\text{CH}_2)_{17}\text{NH}_3\cdot\text{HCl}$), which is the precursor material of the complex, is also shown in this figure. The peaks for the spectrum of octadecylamine-hydrochloride at 2954, 2925, 2853, 1610 and 1465 cm^{-1} are assigned to the $\text{C-H}(\text{CH}_3)$ stretching [$\nu(\text{CH}_3)$], $\text{C-H}(\text{CH}_2)$ asymmetric stretching [$\nu_{as}(\text{CH}_2)$], $\text{C-H}(\text{CH}_2)$ symmetric stretching [$\nu_s(\text{CH}_2)$], $\text{N-H}(\text{NH}_3)$ stretching [$\nu(\text{NH}_3)$] and CH_2 scissoring [$\delta(\text{CH}_2)$], respectively ^{7),10)}. On the other hand, the spectra for the complex with $M=\text{Cr}$, Mn , Fe , Co , Cu show the additional broad peak around 3100 cm^{-1} , which is originated in the hydrogen bonding between an ammonium cation and a halide anion, and the shift of the peak of $\nu(\text{NH}_3)$ from 1610 to 1580 cm^{-1} . These indicate the presence of layered perovskite structure with MCl_6 octahedra and octadecylamine. On the other hand, the spectrum of the complex with Ni does not show any difference from the precursor material, which indicates that the complex with Ni is not able to be synthesized in this method. The perovskites of 1-methyl-naphthalene with MCl_6 octahedra were also confirmed in the same manner.

3.2 Magnetism

Fig.3 shows the magnetization curves at 4.5 K for the $(\text{RNH}_3)_2\text{MCl}_4$, $R=\text{CH}_3(\text{CH}_2)_{17}$ and $M=\text{Cr}$, Mn , Fe , Co and Cu . The complexes with Cr and Cu become

Fig.2 FT-IR spectra for the samples with $R=\text{CH}_3(\text{CH}_2)_{17}$ and $M=\text{Cr}$, Mn , Fe , Co , Ni and Cu . The spectrum for octadecylamine-hydrochloride is also shown.

ferromagnet. The Bohr magneton number per one metal atom at the saturation state is 3.7 and $1.1\mu_B/\text{atom}$, whose values are corresponding to that of the Cr^{2+} and Cu^{2+} ions, respectively. Furthermore, a hysteresis in the magnetization curve was observed for the Cr complex. The coercive force reached 1.2 kOe at 2 K . While, the complexes with Mn and Fe show antiferromagnetism and the complex with Co paramagnetism. The Curie temperature T_C and Néel temperature T_N decided by the temperature dependence of the susceptibility measured at 50 Oe are listed in table.1. T_C was 10 K and 42 K for $M=\text{Cu}$ and Cr , and T_N was 41 K and 95 K for $M=\text{Mn}$ and Fe , respectively. The asymptotic Curie temperature for $M=\text{Co}$ was nearly zero. The values for the complexes with short alkylchain length reported are also listed in this table ²⁾⁻⁶⁾. T_C and T_N obtained are nearly the same with those of the complexes with the other alkylchain length. This result indicates that the interlayer exchange coupling of these complex is not be a dominant factor for the phase transition. However, three dimensional cooperative effect could not be neglected only for the Cr complex because of its relative large coercive force.

The perovskite of methyl-naphthalene with Cu also showed ferromagnetism. However, the Curie temperature was 5 K , which value is lower than that of the octadecylamine complex. Namely, the organic layer can have an influence on the magnetic layer. The ferromagnetic exchange in these compounds are considered to arise from orbital ordering brought about by an antiferrodistortive displacement of the halide ions within the basal plane, which is in turn the result of Jahn-Teller distortion of the CuCl_6 octahedra ¹⁾. Namely, the single unpaired electron at each Cu^{2+} site occupies an x^2-y^2 orbital, such orbitals being rendered orthogonal to one another by the cooperative Jahn-Teller distortion. In case of the octadecylamine complex, the molecule has an enough small crosssection area into the constraining space of the $(\text{MX}_4)_n^{2n-}$ layer. On the other hand, the naphthylamine is a relative large chromophore, so that it might disturb the Jahn-Teller distortion of CuCl_6 octahedra and decrease the curie temperature.

Fig.3 Magnetization curves for the $(\text{RNH}_3)_2\text{MCl}_4$, $R=\text{CH}_3(\text{CH}_2)_{17}$ and $M=\text{Cr}$, Mn , Fe , Co and Cu at 4.5 K .

Table.1 The Curie temperature T_C and Néel temperature T_N for the $(\text{RNH}_3)_2\text{MCl}_4$, $\text{R}=\text{CH}_3(\text{CH}_2)_{17}$ and $\text{M}=\text{Cr}$, Mn, Fe, Co and Cu.

3-d metal	Cr	Mn	Fe	Co	Ni	Cu
electronic state	d^4	d^5	d^6	d^7	d^8	d^9
magnetic moment (μ_B)	3.7	0.3	0.1	2.8	-	1.1
T_C (K)	42 50 ²⁾					10 8.9 ³⁾
T_N (K)		41 39 ⁴⁾	95 94 ⁵⁾			

3.3 Light irradiation effect

Fig.4 shows the UV-visible absorption and fluorescence emission spectra of the *l*-methyl-naphthylamine-hydrochloride ($\text{C}_{10}\text{H}_9\text{CH}_2\text{NH}_3\cdot\text{HCl}$) and its layered perovskite with Cu. The wavelength of the excitation light for fluorescence emission measurement is 230 nm. The absorption peaks at 230 and 290 nm are detected for the *l*-methyl-naphthylamine-hydrochloride. These are the typical naphthalene absorption $E_1(\pi \rightarrow \pi^*)$ and $E_2(\pi \rightarrow \pi^*)$, respectively. On the other hand, the additional peak is observed at 370 nm for the absorption spectra for its Cu complex. We also measured the absorption spectra for $(\text{CH}_3(\text{CH}_2)_{17}\text{NH}_3)_2\text{CuCl}_4$ and two peaks were assigned to $3\sigma \rightarrow d_{x^2-y^2}$ and $4\pi \rightarrow d_{x^2-y^2}$ at 280 and 360 nm, respectively. Namely, the absorption spectrum for naphthyl-ammonium-Cu complex is considered that the absorption originated from CuCl_6 octahedra should be superimposed on the naphthalene spectrum. The emission spectra for *l*-methyl-naphthylamine-hydrochloride shows a intense peak at 350 nm. Remarkably, the peak position locates around that of the absorption originated in CuCl_6 octahedra. In this case, the energy transfer from the organic molecule to the metal would occur. As the result, the emission from its Cu complex is quenched.

Fig.4 UV-visible absorption and fluorescence emission spectra of the *l*-methyl-naphthylamine-hydrochloride ($\text{C}_{10}\text{H}_9\text{CH}_2\text{NH}_3\cdot\text{HCl}$) and its layered perovskite with Cu.

We intended to observe a photoinduced spin change in the layered perovskites. Naphthylamine-hydrochloride-Cu complex is considered to have a possibility that the spin might change during a light irradiation because of the energy transfer. A Hg-Xe lamp was used as the light source and the filtered ultraviolet light was guided by optical fiber into the SQUID magnetometer for irradiation of the sample. Unfortunately, the magnetization of this complex did not show any change between on and off irradiation. One possible reason is that the energy transfer could not be efficient due to the different position of the peak between the emission of naphthalene and absorption of the CuCl_6 octahedra. More detailed experiments for the complexes with various organic molecules and metal halides may be required.

4. Conclusions

Metal halide-based layered perovskites, $(\text{RNH}_3)_2\text{MCl}_4$, self-organized organic/inorganic multilayer structure were synthesized, where R is a simple alkylammonium molecule with a long chain length, $(\text{CH}_3(\text{CH}_2)_{17})$ or a *l*-methyl-naphthalene ($\text{C}_{10}\text{H}_9\text{CH}_2$), M is 3d transition metal elements. Its layered perovskite structure was checked by a FT-IR method. The perovskites of $\text{CH}_3(\text{CH}_2)_{17}\text{NH}_3$ with Cu and Cr showed ferromagnetism ($T_C = 10$ K and 42 K, respectively), and Mn and Fe antiferromagnetism ($T_N = 41$ K and 95 K, respectively). These results roughly corresponded to the results for methyl and ethyl ammonium complexes reported. The naphthlene complex with Cu also showed ferromagnetism, however, the Curie temperature became low. Namely, the relative large chromophore might disturb the Jahn-Teller distortion of CuCl_6 octahedra. The magnetization of this complex did not show any change between on and off irradiation. However, there is a possibility of observing a photoinduced spin change with more detailed experiments for the various layered perovskites.

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