Cation dynamics by $^1$H and $^{13}$C MAS NMR in hybrid organic–inorganic (CH$_3$CH$_2$NH$_3$)$_2$CuCl$_4$

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To understand the dynamics of the cation in layered perovskite-type (CH$_3$CH$_2$NH$_3$)$_2$CuCl$_4$, the temperature-dependent chemical shifts and spin–lattice relaxation times $T_1\rho$ in the rotating frame have been measured using $^1$H magic angle spinning nuclear magnetic resonance (MAS NMR) and $^{13}$C cross-polarization (CP)/MAS NMR techniques. Each proton and carbon in the (CH$_3$CH$_2$NH$_3$)$_2^+$ cation is distinguished in MAS NMR spectra. The Bloembergen–Purcell–Pound (BPP) curves for $^1$H $T_1\rho$ in CH$_3$CH$_2$ and NH$_3^+$ and for the $^{13}$C $T_1\rho$ in CH$_3$ and CH$_2$ are revealed to have minima at low temperatures. This implies that the curves represent the CH$_3$ and NH$_3^+$ rotational motions. The amplitude of the cationic motion is enhanced at the C-end, that is, the N-end of the organic cation is fixed to the inorganic layer through N–H···Cl hydrogen bonds, and $T_1\rho$ becomes short with larger-amplitude molecular motions.

Ethylammonium copper chloride (CH$_3$CH$_2$NH$_3$)$_2$CuCl$_4$ is a layered perovskite-type compound that undergoes a complicated sequence of phase transitions. Differential scanning calorimetry (DSC) data indicates several phase transitions, at 236 K ($=T_{C4}$), 330 K ($=T_{C3}$), 357 K ($=T_{C2}$), and 371 K ($=T_{C1}$), as temperature increases. The peaks at 236 K, 330 K, and 371 K are very weak and can perhaps correspond to second-order transformations. The phase transitions in this crystal are mostly connected with changes in the arrangement of the alkylammonium chains. Fig. 1 shows the room-temperature orthorhombic crystal structure of (CH$_3$CH$_2$NH$_3$)$_2$CuCl$_4$.

The hybrids have the orthorhombic crystal structure with the space group $Pbc a$, and the lattice constants are $a = 7.47$ Å, $b = 7.35$ Å, and $c = 21.18$ Å at room temperature. The CuCl$_6$ octahedra are strongly distorted with elongated Cu–Cl bonds orthogonal to each other on adjacent octahedra. The CuCl$_6$ sheets are sandwiched between two layers of alkylammonium. The structure of the organic component consists of a double layer of alkylammonium ions with their charged ends, the nitrogen atoms, oriented to the nearest CuCl$_6$ plane. The complete structure is constituted by corner-sharing CuCl$_6$ octahedra, forming the inorganic layers, and bilayers of organic cations attached to the octahedra by their NH$_3^+$ heads.

The structural geometry and molecular motions of the organic molecules within the layered hybrid structure is important for determining the influence of temperature on the evolution of the structural phase transitions in the perovskite structure. Physical properties in particular depend on the characteristics of metallic anion and the organic cation.

In the present study, the crystal structure and thermal stability for (CH$_3$CH$_2$NH$_3$)$_2$CuCl$_4$ was observed by means of conventional X-ray, thermogravimetric analysis (TGA), and optical polarizing microscopy. In order to clarify the structural geometry and...
dynamics of the cation in the organic–inorganic \((\text{CH}_3\text{CH}_2\text{NH}_3)_2\text{CuCl}_4\), we investigated the chemical shifts and the spin–lattice relaxation time \(T_{1p}\) in the rotating frame using \(^1\text{H}\) magic angle spinning nuclear magnetic resonance (MAS NMR) and \(^{13}\text{C}\) cross-polarization (CP)/MAS NMR. The \(\text{CH}_3\text{CH}_2\) and \(\text{NH}_4\) groups of the \((\text{CH}_3\text{CH}_2\text{NH}_3)_2\text{CuCl}_4\) cation are distinguishable in \(^1\text{H}\) MAS NMR spectra, and the \(\text{CH}_3\) and \(\text{CH}_2\) groups are distinguished by \(^{13}\text{C}\) CP/MAS NMR spectra. We investigated the \(^1\text{H}\) and \(^{13}\text{C}\) dynamics of the cation in the organic–inorganic \((\text{CH}_3\text{CH}_2\text{NH}_3)_2\text{CuCl}_4\),

II. Experimental method

Crystals of \((\text{CH}_3\text{CH}_2\text{NH}_3)_2\text{CuCl}_4\) were obtained by slow evaporation at 25 °C from an aqueous solution of \(\text{C}_3\text{H}_7\text{NH}_2\cdot \text{HCl}\) and \(\text{CuCl}_2\cdot 2\text{H}_2\text{O}\) in the stoichiometric \(2:1\) proportion. The obtained crystals were yellow square plates, typically 5 mm × 5 mm in area and 0.5 mm in thickness.

The structure of the \((\text{CH}_3\text{CH}_2\text{NH}_3)_2\text{CuCl}_4\) crystals was determined at room temperature with an X-ray diffraction system (PANalytical, X’pert pro MPD) with a Cu-Kα \((\lambda = 1.5418\) \(\text{Å}\)) radiation source. Measurements were taken in a \(θ–2θ\) geometry from 10° to 60° at 45 kV and with a tube power of 40 mA and, the TGA curve at a heating rate of 10 °C min\(^{-1}\) was measured under \(\text{N}_2\) atmosphere, and the mass of the powdered sample used in the TGA experiment was 11.41 mg.

The chemical shifts and the \(T_{1p}\) values for \((\text{CH}_3\text{CH}_2\text{NH}_3)_2\text{CuCl}_4\) were determined using a \(\pi/2−τ\) sequence by varying the duration of spin-locking pulses. \(^{13}\text{C}\) \(T_{1p}\) values were measured by varying the duration of the spin-locking pulse applied after the CP preparation period. The width of the \(\pi/2\) pulse used for measuring \(T_{1p}\) for \(^1\text{H}\) and \(^{13}\text{C}\) was 3.7 μs, with the spin-locking field at 67.56 kHz. The chemical shifts and \(T_{1p}\) were measured over a temperature range of 180–430 K.

III. Experimental results

The measured structure at room temperature exhibited orthorhombic symmetry with cell parameters of \(a = 7.480\) \(\text{Å}\), \(b = 7.375\) \(\text{Å}\), \(c = 21.254\) \(\text{Å}\) for \((\text{CH}_3\text{CH}_2\text{NH}_3)_2\text{CuCl}_4\) crystal. This result is consistent with the results reported by Steadman and Willett.\(^{16}\)

The TGA curve of \((\text{CH}_3\text{CH}_2\text{NH}_3)_2\text{CuCl}_4\) is shown in Fig. 2 for measuring thermal stability. The first occurrence of mass loss begins at approximately 430 K \((T_d)\), which is the onset of partial thermal decomposition. The second weight loss of 25.1% near 530 K is due to the removal of the \(\text{CH}_3\text{CH}_2\text{NH}_3\)Cl from the compound, leaving intermediate \(\text{CH}_3\text{CH}_2\text{NH}_3\text{CuCl}_3\) that belongs to another known class of compounds \(\text{ABX}_3\). Near 560 K, \(\text{CuCl}_2\) remains as the residue and when it reaches 580 K, the total weight loss becomes 65.55%. The color of the crystal is dark yellow at room temperature although it has slightly inhomogeneous hue due to surface roughness. As the temperature increases, the color of the crystal varies from dark yellow (300 K, 350 K), brown (400 K), to dark brown (450 K, 500 K), and then they start melting at 530 K as shown in the inset in Fig. 2. The TGA and optical polarizing microscopy results show that the crystal above 430 K allows \(\text{CH}_3\) to partially escape by the breaking the weak \(\text{C}–\text{N}\) bond.

Fig. 1 Orthorhombic structure of a \((\text{CH}_3\text{CH}_2\text{NH}_3)_2\text{CuCl}_4\) crystal at room temperature.

Fig. 2 Thermogravimetric analysis of \((\text{CH}_3\text{CH}_2\text{NH}_3)_2\text{CuCl}_4\) (inset: color changes of a \((\text{CH}_3\text{CH}_2\text{NH}_3)_2\text{CuCl}_4\) crystal according to the temperature): (a) 300 K, (b) 350 K, (c) 400 K, (d) 450 K, (e) 500 K, and (f) 530 K.
temperature is shown in the inset in Fig. 3; the spectrum shows two peaks at chemical shifts of δ = 0.23 and 12.12 ppm, which are assigned to the protons of the CH₃CH₂ and NH₃ groups, respectively. The spinning sidebands for CH₃CH₂ are marked with asterisks and those for NH₃ are marked with open circles. However, the different ¹H signals from CH₂ and CH₃ cannot be resolved, and therefore the combined CH₃CH₂ peak is very broad and has a larger intensity due to the overlap of the CH₂ and CH₃ peaks. The peak with the lower chemical shift is attributed to the protons in CH₃CH₂, and that of the higher chemical shift is attributed to the protons in NH₃. The ¹H chemical shifts for the alkyl and ammonium groups slowly and monotonously vary with temperature, indicating that the surrounding environments of the protons in the alkyl and ammonium groups change continuously, as shown in Fig. 3; here, the chemical shifts for protons in CH₃CH₂ and NH₃ near T_C1, T_C2, and T_C3 are nearly constant with temperature, whereas those for protons in CH₃CH₂ and NH₃ below T_C4 change more abruptly.

The T₁ρ values for the CH₃CH₂ and NH₃ protons in (CH₃CH₂NH₃)₂CuCl₄ were obtained as a function of temperature. The magnetization traces of both the alkyl and ammonium groups slowly and monotonously vary with temperature, whereas those for protons in CH₃CH₂ and NH₃ near T_C₁, T_C₂, and T_C₃ are nearly constant with temperature, indicating that the surrounding environments of the protons in the alkyl and ammonium groups change continuously, as shown in Fig. 3; here, the chemical shifts for protons in CH₃CH₂ and NH₃ near T_C₁, T_C₂, and T_C₃ are nearly constant with temperature, whereas those for protons in CH₃CH₂ and NH₃ below T_C₄ change more abruptly.

The T₁ρ values for the CH₃CH₂ and NH₃ protons in (CH₃CH₂NH₃)₂CuCl₄ were obtained as a function of temperature. The magnetization traces of both the alkyl and ammonium protons may be described by a single exponential function:

\[
\frac{S(t)}{S_0} = \exp(-t/T_{1\rho}),
\]

where S(t) is the magnetization as a function of the spin-locking pulse duration t, and S₀ is the total nuclear magnetization of the proton at thermal equilibrium.¹⁹ The recovery curves for several delay times were measured, and the T₁ρ values were obtained from the slopes by the delay time vs. intensity, at several different temperatures. This analysis method was used to obtain the T₁ρ values for each proton in CH₃CH₂ and NH₃, which are plotted as a function of inverse temperature in Fig. 4. The T₁ρ values for the CH₃CH₂ and NH₃ protons in the (CH₃CH₂NH₃)⁺ cations exhibit similar trends with temperature. The proton T₁ρ data do not show evidence of a change near the phase-transition temperature; the T₁ρ values of protons in the CH₃CH₂ and NH₃ groups of (CH₃CH₂NH₃)₂CuCl₄ are almost continuous near T_C₁, T_C₂, and T_C₃, and these values are of the order of few milliseconds. The T₁ρ values abruptly decreased with temperature in the region approaching T_C₄. The relaxation time for the ¹H nucleus is minimal at 190 K and 200 K for CH₃CH₂ and NH₃, respectively. This feature of T₁ρ indicates that distinct molecular motions are present. The T₁ρ values are related to the corresponding values of the rotational correlation time, τ_C, which is a direct measure of the rate of molecular motion. For the spin–lattice relaxation time in the rotating frame, the experimental value of T₁ can be expressed in terms of the correlation time τ_C for the molecular motion, as suggested by the Bloembergen–Purcell–Pound (BPP) function:¹⁹,²²

\[
T_{1\rho}^{-1} = (N/20)(\gamma_H\gamma_C\mu_H/r_{H-C})^2\left[4\tau_C(1 + \omega_H^2\tau_C^2) + \tau_C^3[1 + (\omega_C^2\tau_C^2)]\right] + 6\tau_C[1 + (\omega_H + \omega_C)^2\tau_C^2] + 6\tau_C[1 + (\omega_H^2\tau_C^2)].
\]

Here, γ_H and γ_C are the gyromagnetic ratios for the ¹H and ¹³C nuclei, respectively; N is the number of directly bound protons; r_{H-C} is the H–C internuclear distance; h is the reduced Planck constant; ω_H and ω_C are the Larmor frequencies of ¹H and ¹³C, respectively; and ω_L is the frequency of the spin-locking field. We analyzed our data assuming that T₁ρ would show a minimum when ω_Lτ_C = 1, and that the BPP relation between T₁ρ and the characteristic frequency ω_L could be applied. We sensitively controlled the minima in the T₁ρ temperature variations and the slopes around the minima. From these results, the value of (γ_Hγ_Cμ_H/r_{H-C})² for the proton in eqn (2) was obtained. We then calculated the temperature dependences of the τ_C values for protons by using the obtained values of (γ_Hγ_Cμ_H/r_{H-C})². The temperature dependence of τ_C follows a simple Arrhenius equation:

\[
\tau_C = \tau_0 \exp(-E_a/RT),
\]

where E_a is the activation energy. This is the Arrhenius equation:

\[
\frac{S(t)}{S_0} = \exp(-t/T_{1\rho}),
\]
where $\tau_0$ is a pre-exponential factor, $T$ is the temperature, $R$ is the gas constant, and $E_a$ is the activation energy. Thus, the slope of the linear portion of a semi-log plot should yield $E_a$. The $E_a$ value for the rotational motion can be obtained from the log $\tau_c$ vs. $1000/T$ curve shown in Fig. 5; we obtained $E_a = 12.19 \pm 1.30 \text{ kJ mol}^{-1}$ and $E_a = 8.33 \pm 0.50 \text{ kJ mol}^{-1}$ for CH$_3$CH$_2$ and NH$_3$, respectively. The rotational motion for alkyl groups is activated, whereas the rotational motion for ammonium groups at the end of the organic cation is less strongly activated.

The structural analysis of the carbons in (CH$_3$CH$_2$NH$_3$)$_2$CuCl$_4$ was performed by $^{13}$C CP/MAS NMR, and the corresponding spectrum is shown in Fig. 6, as a function of temperature; the $^{13}$C CP/MAS NMR spectrum at room temperature shows two signals at chemical shifts of $\delta = 50.77$ ppm and $\delta = 113.50$ ppm with respect to tetramethylsilane (TMS), which can be assigned to CH$_3$ and CH$_2$, respectively. The $^{13}$C chemical shift of CH$_2$ abruptly shifts with temperature, whereas that of CH$_3$ changes only much less with temperature. The full width at half maximum (FWHM) linewidths for the $^{13}$C of CH$_3$ and CH$_2$ in Fig. 7 showed a monotonic decrease with increasing temperature, with no particular anomalies attributable to the phase transitions. The linewidth of the $^{13}$C signal assigned to CH$_3$ is broad compared to that of CH$_2$, and the linewidth narrows significantly with increasing temperature. This narrowing of the $^{13}$C linewidths is attributed to internal motions that the line widths follow the same temperature dependence as some internal motions, hence the motions are responsible for the line widths.

To obtain the $^{13}$C $T_{1p}$ values, the nuclear magnetization was also measured at several temperatures as a function of delay time. The signal intensity of the nuclear magnetization recovery curves for $^{13}$C is described by a single exponential function as in eqn (1) at all temperatures. The $^{13}$C $T_{1p}$ values for CH$_3$ and CH$_2$ in (CH$_3$CH$_2$NH$_3$)$_2$CuCl$_4$ are plotted as a function of inverse temperature in Fig. 8. The temperature dependences of the $^{13}$C MAS NMR $T_{1p}$ values seem to be similar. The $T_{1p}$ values for CH$_3$ and CH$_2$ both
increase with temperature in the same manner; whereas, the $^{13}$C $T_{1p}$ values near the phase-transition temperatures are approximately continuous. The $T_{1p}$ values for CH$_3$ and CH$_2$ at room temperature are 33.85 ms and 109.40 ms, respectively. The amplitude of the cationic motion is enhanced at its CH$_3$ end, and the central CH$_2$ moiety is fixed to the NH$_3$ group in the organic cation. The $T_{1p}$ curve below $T_{C2}$ can be reproduced by BPP theory. The BPP curves for CH$_3$ and CH$_2$, showing minima at low temperatures, is almost the same as those of the CH$_3$CH$_2$ and NH$_3$ shifts of the $^1$H MAS NMR measurements. $E_r$ for the rotational motion of CH$_3$ and CH$_2$ can be obtained from the log $T_{1p}$ vs. 1000/$T$ curve shown in Fig. 5; we obtained $E_r = 21.35 \pm 0.45$ kJ mol$^{-1}$ for CH$_3$ and $E_r = 19.72 \pm 1.76$ kJ mol$^{-1}$ for CH$_2$, respectively, which, considering their error ranges, are the same values.

IV. Conclusion

We discuss the molecular motions for cation of Cu-based hybrid materials, where we replace Pb with nontoxic Cu metal for lead-free perovskite solar cells, and investigate their potential toward solar cell applications based on ionic dynamics of the cation in hybrid organic–inorganic [CH$_3$CH$_2$NH$_3$]$_2$CuCl$_4$ by NMR studies. The cation dynamics and interionic interactions through hydrogen bonds are expected to be closely related with the physical properties due to the potential applications. The cation dynamics in a layered perovskite-type [CH$_3$CH$_2$NH$_3$]$_2$CuCl$_4$ were investigated as a function of temperature by $^1$H MAS NMR and $^{13}$C CP/MAS NMR experiments. The CH$_3$, CH$_2$ and NH$_3$ units in the CH$_3$CH$_2$NH$_3$ cation were distinguished by the $^1$H MAS NMR spectra, and the CH$_3$ and CH$_2$ units in the CH$_3$CH$_2$NH$_3$ cation were also clearly distinguished in the $^{13}$C CP/MAS NMR spectra. To obtain detailed information about the cation dynamics of this crystal, the spin–lattice relaxation time $T_{1p}$ in the rotating frame for both $^1$H and $^{13}$C were measured, revealing that these atoms undergo rotational motions at low temperatures. The BPP curves for the $^1$H $T_{1p}$ in CH$_3$CH$_2$ and NH$_3$, and for the $^{13}$C $T_{1p}$ in CH$_3$ and CH$_2$, were shown to have a minimum at low temperatures; the $T_{1p}$ of $^1$H and $^{13}$C showed a minimum and is governed by the tumbling motion of the CH$_3$CH$_2$H$_3$ and NH$_3$ groups, indicating that the $^1$H and $^{13}$C atoms in the CH$_3$CH$_2$NH$_3$+ groups exhibit high mobility at low temperatures. The molecular motions for $^1$H and $^{13}$C in the CH$_3$CH$_2$NH$_3$+ cation were very free at low temperatures. $T_{1p}$ provides insight into the changes in the cation reorientation rates at low temperature. The $^{13}$C $T_{1p}$ values in CH$_3$ increased with temperature, a trend that has been observed in alkyl chains attached to the (CH$_3$-CH$_2$NH$_3$) cation due to its greater mobility toward its free end. The CH$_3$CH$_2$NH$_3$ cationic motion is enhanced at the opposing end of the cation to the NH$_3$+ group probably because this group is bound to the inorganic layer through the N–H···Cl hydrogen bonds. The $^{13}$C $T_{1p}$ is usually dominated by the fluctuation of the anisotropic chemical shift, and it becomes shorter with larger-amplitude molecular motions. This implies that the amplitude of the cationic motion is enhanced at the C-end, that is, the N-end of the organic cation is fixed at the inorganic layer through N–H···Cl hydrogen bonds. The cationic motion, being associated with the fluctuation of the molecular axis, is expected to be gradually excited with increasing temperature.

Conflicts of interest

There are no conflicts to declare.

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