Article

Characterization on Lead-Free Hybrid Perovskite [NH₃(CH₂)₅NH₃]CuCl₄: Thermodynamic Properties and Molecular Dynamics

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Abstract: It is essential to develop novel zero- and two-dimensional hybrid perovskites to facilitate the development of eco-friendly solar cells. In this study, we investigated the structure and dynamics of [NH₃(CH₂)₅NH₃]CuCl₄ via various characterization techniques. Nuclear magnetic resonance (NMR) results indicated that the crystallographic environments of ¹H in NH₃ and ¹³C on C₃, located close to NH₃ at both ends of the cation, were changed, indicating a large structural change of CuCl₄ connected to N–H⋯Cl. The thermal properties and structural dynamics of the [NH₃(CH₂)ₙNH₃] cation in [NH₃(CH₂)ₙNH₃]CuCl₄ (n = 2, 3, 4, and 5) crystals were compared using thermogravimetric analysis (TGA) and NMR results for the methylene chain. The ¹H and ¹³C spin-lattice relaxation times (T₁ρ) exhibited similar trends upon the variation of the methylene chain length, with n = 2 exhibiting shorter T₁ρ values than n = 3, 4, and 5. The difference in T₁ρ values was related to the length of the cation, and the shorter chain length (n = 2) exhibited a shorter T₁ρ owing to the one closest to the paramagnetic Cu²⁺ ions.

Keywords: organic-inorganic hybrid; perovskite; ferroelasticity; nuclear magnetic resonance; thermodynamic properties

1. Introduction

Recently, research on solar cells based on organic-inorganic hybrid materials has progressed very rapidly [1–4]. Initially, CH₃NH₃PbX₃ (X = Cl, Br, I)-based thin-film photovoltaic devices were used as solar cells. Despite the development of CH₃NH₃PbX₃ as a hybrid solar cell, it readily decomposes in humid air, and Pb toxicity is a major concern [5–7]. Therefore, its replacement with environment-friendly hybrid perovskite solar cells is vital.

Further, novel groups of perovskite materials, such as [(CH₃)₂NH₂]Zn(HCOO)₃, consisting of an organic cation and a metal ion, have been discussed [8–14]. They exhibited potential for application in memory manipulation devices and next-generation memory storage technology. In addition, it is necessary to study the structure and dynamics of new materials with zero- and two-dimensional (2D) hybrid perovskites, such as eco-friendly [NH₃(CH₂)ₙNH₃]MX₄. The organic-inorganic hybrid [NH₃(CH₂)ₙNH₃]MX₄ (n = 2, 3, 4, ⋯) crystal structures consist of the corner shared octahedral (MX₄)²⁻ alternated with organic layers and is 2-dimensional, while for M = Co or Zn, the structures are tetrahedral (MX₄)²⁻ sandwiched between layers of organic cations and 0-dimensional. The ammonium ions at the organic-cation terminals form N–H⋯X...
hydrogen bonds with halide ions of the metallic inorganic layer [34–36]. For long chains, in complexes where \( n \) is 5 or more, structural changes due to conformational changes of the chains are important [37]. Among them, an interesting group of hybrid materials is perovskite-type layered \([\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\text{CuCl}_4\). Its crystal structure consists of 2D inorganic \( \text{CuCl}_4 \) layers and 1,5-diaminopentane cations. The \([\text{NH}_3(\text{CH}_2)_5\text{NH}_3]\) organic chains exhibit the longest c-axis. \([\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{CuCl}_4\) crystallizes in the monoclinic space group \( P2_1/c \), with unit-cell parameters of \( a = 7.747 \, \text{Å}, b = 7.203 \, \text{Å}, c = 21.512 \, \text{Å}, Z = 4, \) and \( \beta = 98.48^\circ \) [38].

Filolleau et al. [39] and Kanel et al. [40] reported the magnetic, optical properties, and electron paramagnetic resonance studies of \([\text{NH}_3(\text{CH}_2)_5\text{NH}_3]\text{CuCl}_4\) crystals. Recently, the thermal properties and structural molecular dynamics of \([\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{CuCl}_4\) \((n = 2, 3, 4, \) and 5) have been reported [41–43]. However, a detailed report on the \([\text{NH}_3(\text{CH}_2)_5\text{NH}_3]\text{CuCl}_4\) crystal is yet to be published. A lot of research has been done on the electric and conductive properties of this type of compound [44–47].

In this study, the crystal structure, thermodynamics, and ferroelasticity of \([\text{NH}_3(\text{CH}_2)_5\text{NH}_3]\text{CuCl}_4\) were studied to investigate the \( \text{CuCl}_4 \) anion, which is responsible for the thermal and mechanical properties. Additionally, to obtain information on the coordination geometry and molecular dynamics of the \([\text{NH}_3(\text{CH}_2)_3\text{NH}_3]\) cation, nuclear magnetic resonance (NMR) chemical shifts and spin-lattice relaxation times (\( T_1 \)) for \(^1\text{H} \) and \(^{13}\text{C} \) were measured using the magic angle spinning (MAS) method. The variations in physicochemical properties of this crystal according to the temperature change were explained by considering the cation and the \( \text{CuCl}_4 \) anion. The influence of the CH \( _2 \)-group length in the \([\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\) cation of \([\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{CuCl}_4\) \((n = 2, 3, 4, \) and 5) has also been discussed with reference to a previous report. These results, which consider the methylene chain length, could be useful for facilitating diverse environment-friendly applications in the future.

2. Results

2.1. Crystal Structure

The X-ray diffraction (XRD) powder patterns of the \([\text{NH}_3(\text{CH}_2)_5\text{NH}_3]\text{CuCl}_4\) crystal were obtained at different temperatures during heating, and the results are shown in Figure 1. The XRD patterns from 300 K to 440 K were identical, and the XRD patterns at temperatures above 440 K were due to the melting of the crystal. Additionally, the crystal structure is monoclinic, and the lattice constants, analyzed from the single-crystal XRD results, were \( a = 7.7385 \, \text{Å}, b = 7.2010 \, \text{Å}, c = 21.5308 \, \text{Å}, \) \( \beta = 98.493^\circ, \) and \( Z = 4, \) with the space group \( P2_1/c \). This result is consistent with a previous report [38].

![Figure 1. XRD powder patterns of the \([\text{NH}_3(\text{CH}_2)_5\text{NH}_3]\text{CuCl}_4\) crystal at different temperatures.](image-url)
2.2. Thermal Property and Ferroelastic Twin Domain

To understand the thermodynamic properties, thermogravimetric analysis (TGA) and differential thermal analysis (DTA) results measured at a heating rate of 10 K/min are shown in Figure 2. The first occurrence of molecular weight loss, indicating the initiation of partial thermal decomposition, occurred at approximately 514 K. As the temperature increased, the molecular weight of the \([\text{NH}_3\text{(CH}_2\text{)}_5\text{NH}_3\text{]}\text{CuCl}_4\) crystal decreased. TGA results of a similar compound were reported by another group previously \([24,27,48]\). The 12\% and 24\% losses, calculated from the total molecular weight, were caused by the decomposition of HCl and 2HCl, respectively. The temperatures of HCl and 2HCl loss obtained by TGA were 531 and 583 K, respectively, with a weight loss of 80\% at ~900 K. The molecular weight sharply decreased between 520 and 650 K, with a corresponding weight loss of 70\% at ~650 K. Subsequently, the crystals were analyzed using optical polarizing microscopy experiments with increasing temperature to investigate their thermal stability. The crystals were yellow at room temperature, as shown in the inset of Figure 2. As the temperature increased, the crystals changed from yellow to light brown and finally to dark brown, above 490 K, consistent with that shown in the XRD powder patterns of Figure 1. The possibility to change color was due to decomposition by loss of HCl and also due to the geometrical change of CuCl₄. Near 540 K, the single-crystal surfaces exhibited slight melting. This temperature was similar to the temperature of HCl loss in the TGA experiment. Additionally, no endothermic peak corresponding to a phase transition above 200 K was observed in the differential scanning calorimetry (DSC) curve.

![Figure 2. TGA and DTA curves of \([\text{NH}_3\text{(CH}_2\text{)}_5\text{NH}_3\text{]}\text{CuCl}_4\) (inset: changes in the crystal at the following temperatures: (a) 300 K, (b) 330 K, (c) 390 K, (d) 430 K, (e) 490 K, and (f) 540 K).](image)

A single crystal with ferroelastic properties has two or more orientation states, even in the absence of mechanical stress, and changes from one orientation state to another under mechanical stress \([49,50]\). The domain patterns observed under a polarized optical microscope are shown in Figure 3. One of the most common microstructures is related to twinning, with dominant twin planes oriented nearly perpendicular to each other. Ferroelastic domain patterns, represented by parallel lines, were observed at room temperature (Figure 3a). Although the crystal color changed with an increase in temperature, the twin domain patterns remained unchanged. Finally, the domain pattern turned dark brown...
near 440 K, as shown in Figure 3f, making it difficult to observe. The difficulty in observing the domain pattern above 440 K was due to the phenomenon in which single crystals begin to melt.

![Optical polarizing microscopy images](image)

**Figure 3.** Optical polarizing microscopy images of [NH3(CH2)5NH3]CuCl4 at (a) 300 K, (b) 340 K, (c) 360 K, (d) 390 K, (e) 420 K, and (f) 440 K. Parallel lines represent ferroelastic twin domain walls.

2.3. 1H NMR Chemical Shifts

The temperature dependence of the 1H MAS NMR spectra of the [NH3(CH2)5NH3]CuCl4 crystal was analyzed, and the 1H chemical shifts are shown in Figure 4. In the [NH3(CH2)5NH3] cation, the number of protons related to NH3 and CH2 was 6 and 10, respectively, and the intensity and linewidth of the 1H resonance peak were also related to the number of protons. The 1H signal in NH3 was observed at low temperatures, whereas the 1H signal in CH2 was difficult to observe, owing to its wide linewidth. Above 240 K, the NMR spectrum featured two resonance lines of NH3 and CH2. At 300 K, the 1H chemical shifts in NH3 and CH2 were 12.11 and 2.89 ppm, respectively. 1H signals for NH3 and CH2 overlap each other. Thus, their line widths could not be accurately distinguished in accordance with the temperature change; however, the line width of NH3 was narrower than that of CH2. The spinning sidebands for NH3 and CH2 are marked with open circles and crosses, respectively. The 1H chemical shifts of CH2, indicated by dotted lines in Figure 4, were almost independent of temperature.

The 1H chemical shift for NH3, from 180–220 K, was in the negative direction but shifted slightly in the negative direction at temperatures above that. Therefore, the structural environment of 1H in NH3 changed with the variation of temperature, while the environment of 1H in CH2 changed negligibly.
2.4. 13C NMR Chemical Shifts

13C chemical shifts for the in-situ MAS NMR spectra with increasing temperature are shown in Figure 5. The tetramethylsilane (TMS) reference signal was recorded at 38.3 ppm at 300 K and considered to be the 13C chemical-shift standard. In the [NH3(CH2)5NH3] cation, the CH2 close to NH3 was labeled C3. The CH2 at the center of the cation was labeled C1, and the CH2 between C3 and C1 was labeled C2, as shown in the inset of Figure 5. At 300 K, the 13C chemical shifts were recorded at 27.19, 50.94, 62.95, and 118.46 ppm for C1, C2, C2′, and C3, respectively. The 13C chemical shifts for C1, C2, and C3, with temperature changes, are shown in Figure 5. The chemical shifts of C3 shifted rapidly in the negative direction with temperature change, while C1 shifted in a slightly positive direction. However, there were two different signals (C2 and C2′) for C2. Here, the chemical shift of C2 shifted in a negative direction, while that of C2′ shifted in a slightly positive direction, with a temperature change. The shifting of C2 and C2′ chemical shifts in different directions could be because of the position of C1 at the center of the cation and that of C2 between C1 and C3. In addition, at higher temperatures, the line widths for C1, C2, and C3, as shown in the inset of Figure 5, narrowed significantly owing to high internal mobility [51]. All 13C chemical shifts changed with the increase in temperature, with the C3 chemical shift exhibiting a rapid change.
2.5. $^1$H and $^{13}$C Spin-Lattice Relaxation Times

The intensities of the $^1$H MAS NMR and $^{13}$C MAS NMR spectra were measured by changing delay times at each temperature. The spectral intensity versus the delay time plot followed a mono-exponential function. The recovery traces of magnetization were characterized by the spin-lattice relaxation time, $T_{1\rho}$, as $[52–54]$:

$$P_{\text{H(C)}}(\tau) = P_{\text{H(C)}}(0)\exp(-\tau/T_{1\rho})$$

(1)

where $P_{\text{H(C)}}(\tau)$ and $P_{\text{H(C)}}(0)$ are signal intensities for the proton (carbon) at time $\tau$ and $\tau = 0$, respectively. From the slope of the logarithm of intensity versus the delay time plot, the $^1$H $T_{1\rho}$ values were determined for NH$_3$ and CH$_2$ at several temperatures. The intensity of each signal differed with the delay time. The results of $^1$H $T_{1\rho}$ obtained here and the $^1$H $T_{1\rho}$ of $n = 2, 3, $ and $4$ previously reported are shown in Figure 6 as a function of the inverse temperature. The $^1$H $T_{1\rho}$ values were almost temperature independent and were in the order of 10 ms. However, the $^1$H $T_{1\rho}$ values of NH$_3$, represented with black squares, were shorter than those of CH$_2$, marked with black open squares. Here, the $T_{1\rho}$ values were compared according to the cation length from $n = 2$–5. The $^1$H $T_{1\rho}$ values exhibited similar trends for different methylene chain lengths, with $n = 2$ exhibiting slightly shorter values than $n = 3, 4,$ and $5$. 

Figure 5. MAS $^{13}$C NMR spectra of [NH$_3$(CH$_2$)$_n$NH$_3$]CuCl$_4$ as a function of temperature.
The very short value for lengths. In the $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]^{\text{2+}}$ ion, was shorter than that of C2, located further away from Cu$^{2+}$. Additionally, the $T_1$ value of C1, at the center of 5 CH$_2$, exhibited very short values. It is interesting to compare the results for $^{13}$C $T_1$ values for C1, C2, and C3 were obtained as a function of the inverse temperature from the slope of the logarithm of intensity versus the delay time plot (Figure 7). The $^{13}$C $T_1$ values increased rapidly from 10–100 ms. The $T_1$ behavior for random motions, with a correlation time $\tau_\rho$, could be elucidated by a fast motion. The $T_1$ value of C3, located close to the paramagnetic Cu$^{2+}$ ion, was shorter than that of C2, located further away from Cu$^{2+}$. Additionally, the $T_1$ of C1, at the center of 5 CH$_2$, exhibited very short values. It is interesting to compare the results for $^{13}$C $T_1$ according to the alkyl chain lengths. In the $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]$ cation, the marks of C1, C2, and C3 along the length of n are shown in Figure 8. The $^{13}$C $T_1$ values exhibited similar trends for n = 3, 4, and 5, with a very short value for n = 2, as shown in Figure 7. In the case of n = 5, unlike n = 2, 3, and 4, the $T_1$ value of C2 was different from those of C1 and C3. Overall, energy transfer was easier for the short alkyl chain length (n = 2).
The difference in $T_1$ motion for the spin-lattice relaxation times $T_1$ values for the CH$_2$ chain, indicating that the energy transfer was not easy. The thermal properties and structural dynamics of the [NH$_3$(CH$_2$)$_n$NH$_3$] cation in [NH$_3$(CH$_2$)$_n$NH$_3$]CuCl$_4$ ($n = 2, 3, 4, 5$) crystals were analyzed and compared using information obtained from TGA and NMR experiments. Thermal decomposition temperatures ($T_d$) decreased with an increase in the value of $n$, as observed in the TGA results of the four crystals. An enlarged view was observed near $T_d$; for $n = 2, 3, 4, 5$, $T_d$ values, when the case of 5% weight loss was set as $T_d$, were 533, 530, 527, and 514 K, respectively, indicating no improvement in thermal stability with an increase in the cation length (Figure 9). The $^1$H and $^{13}$C $T_1$ values exhibited a similar trend in increasing the methylene chain length, with $n = 2$ exhibiting shorter $T_{1p}$ values than $n = 3, 4, 5$; $T_{1p}$ increased with the increasing length of the CH$_2$ chain, indicating that the energy transfer was not easy. The difference in $T_{1p}$ values was mainly attributed to the cation length, with the shorter ($n = 2$) length exhibiting a smaller value, owing to the presence of paramagnetic Cu$^{2+}$ ions. $^1$H $T_{1p}$ values are very short after the inclusion of paramagnetic ions. The Cu$^{2+}$ ions in [NH$_3$(CH$_2$)$_n$NH$_3$]CuCl$_4$, which are paramagnetic and bonded with the inorganic layer through N–H···Cl hydrogen bonds, directly affected the $^1$H environment. With respect to the 2D structure of solar cell materials, the applicability of organic-inorganic hybrid compounds can be confirmed more clearly by knowing the energy transfer for a molecular motion for the spin-lattice relaxation times $T_{1p}$ along the length of a cation.

Figure 8. Names of carbons, according to their length, in the cation structure of [NH$_3$(CH$_2$)$_n$NH$_3$]CuCl$_4$ ($n = 2, 3, 4, 5$).

3. Discussion

![TGA curves of [NH$_3$(CH$_2$)$_n$NH$_3$]CuCl$_4$](image)

Figure 9. TGA curves of [NH$_3$(CH$_2$)$_n$NH$_3$]CuCl$_4$ ($n = 2, 3, 4, 5$) (inset: expansion of TGA curves near $T_d$).
4. Materials and Methods

\([\text{NH}_3(\text{CH}_2)_5\text{NH}_3]\text{CuCl}_4\) single crystals were grown by gradually evaporating an aqueous solution of \(\text{NH}_3(\text{CH}_2)_5\text{NH}_3\cdot2\text{HCl}\) (Aldrich, 98%) and \(\text{CuCl}_2\) (Aldrich, 97%) at a constant temperature of 300 K. The grown single crystals that were \(3 \times 3 \times 1.5\) mm in size exhibited a yellow color.

The XRD powder pattern experiments of the \([\text{NH}_3(\text{CH}_2)_5\text{NH}_3]\text{CuCl}_4\) crystal at several temperatures were measured in the measuring \(\theta\) range of 5–60° using an XRD system equipped with a Mo-K\(\alpha\) radiation source. The lattice parameters at various temperatures were determined by single-crystal X-ray diffraction (XRD) at the Seoul Western Center of the Korea Basic Science Institute (KBSI). A crystal block was picked up with paratone oil and mounted on a Bruker D8 Venture PHOTON III M14 diffractometer equipped with a graphite-monochromated Mo-K\(\alpha\) radiation source. Data were collected and integrated using SMART APEX3 (Bruker, 2016) and SAINT (Bruker, 2016). The absorption was corrected by a multi-scan method implemented in SADABS. The structure was solved using direct methods and refined by full-matrix least-squares on \(F^2\) using SHELXTL. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were added to their geometrically ideal positions.

TGA and DTA experiments were performed in the temperature range of 300–873 K on a thermogravimetric analyzer (TA Instruments) at a heating rate of 10 K/min with an N\(_2\) gas flow [42]. Additionally, a twin domain pattern, observed in the 300–680 K temperature range, was measured using an optical polarizing microscope by placing the prepared single crystals on a Linkam THM-600 heating stage.

NMR chemical shifts and spin-lattice relaxation times (\(T_1\rho\)) for \(^1\text{H}\) and \(^{13}\text{C}\) in \([\text{NH}_3(\text{CH}_2)_5\text{NH}_3]\text{CuCl}_4\) crystals were measured using a Bruker 400 MHz Avance II+ solid-state NMR spectrometer at the same facility, KBSI. The Larmor frequency was \(\omega_0/2\pi = 400.13\) MHz for \(^1\text{H}\) NMR, and \(\omega_0/2\pi = 100.61\) MHz for \(^{13}\text{C}\) NMR. To minimize the spinning sideband, the sample tube spinning speed was set to 10 kHz, and TMS was used as reference material to accurately measure the NMR chemical shifts. \(T_1\rho\) values were obtained using a \(\pi/2−\tau\) pulse, followed by a spin-lock pulse of duration \(\tau\), and the width of the \(\pi/2\) pulse for \(^1\text{H}\) and \(^{13}\text{C}\) was in the 3.2–3.9 \(\mu\)s range. The temperature was changed by adjusting the N\(_2\) gas flow and the heater current, and the NMR experiment was conducted in the 180–430 K temperature range.

5. Conclusions

We discussed XRD, TGA, and NMR experiments to investigate the crystal structure, thermal stabilities, and physical properties of \([\text{NH}_3(\text{CH}_2)_5\text{NH}_3]\text{CuCl}_4\) crystal. First, the monoclinic structure and lattice parameter were confirmed by XRD, and its thermodynamic property was observed at about 514 K without phase transition. NMR analysis indicated that the crystallographic environment of \(^1\text{H}\) in NH\(_3\) and that of \(^{13}\text{C}\) on C3, located close to NH\(_3\) at both ends of the cation, were changed, indicating a large structural change of CuCl\(_4\) connected to the N–H···Cl. The effects of the length of CH\(_2\) in the cation on the molecular motions and thermal properties will facilitate future research on their potential application in the research of environment-friendly hybrid perovskite solar cells.

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