

Powder x-ray diffraction and Rietveld analysis of $(C_2H_5NH_3)_2CuCl_4$

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RAPID COMMUNICATION

Powder x-ray diffraction and Rietveld analysis of $(C_2H_5NH_3)_2CuCl_4$*

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Structural properties of the organic-inorganic hybrid $(C_2H_5NH_3)_2CuCl_4$ (EA_2CuCl_4) have been investigated by means of x-ray powder diffraction and Rietveld analysis. A structural phase transition from *Pbca* to *Aba2* occurs at $T_4 = 240$ K, which results in a paraelectric–ferroelectric phase transition. The release of the Jahn–Teller distortion with increasing temperature toward T_4 is revealed by the structural analysis.

Keywords: organic-inorganic hybrid, x-ray diffraction, $(C_2H_5NH_3)_2CuCl_4$

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1. Introduction

It is well known that a ferroelectric material undergoes a phase transition from a high-temperature phase that behaves as an ordinary dielectric to a low-temperature phase that has a spontaneous polarization. A primary requirement for the existence of ferroelectricity (FE) is a structural distortion from the prototypical high-symmetry phase that removes the center of symmetry and allows an electric polarization. There are 31 point groups that allow a spontaneous electric polarization P.[1,2]

However, an ambiguous case has been ignored in organic-inorganic hybrid system $(C_2H_5NH_3)_2CuCl_4$ (EA_2CuCl_4).[3–6] As a member of the family of compounds with composition $(C_nH_{2n+1}NH_3)_2MCl_4$, where M is a divalent metal (M = Mn^{2+}, Cd^{2+}, Fe^{2+}, and Cu^{2+}), its potentials are not only in hydrogen storage, catalysis, etc, but also attractive as a magnetoelectric, two-dimensional magnetocaloric, and electrocaloric material.[7–10] The layered cupric halide compound EA_2CuCl_4 has been investigated as a ferroelectric material with a large remnant value 37 μC/cm^2 of electric polarization P by P–E loop and pyroelectric current measurements below its FE transition temperature $T_c \approx 247$ K, whereas its space group of crystal structure has been reported as centrosymmetry below room temperature (RT: space group, *Pbca*; $a = 21.18$ Å, $b = 7.47$ Å, and $c = 7.35$ Å).[3,11] An electrically polar state is generally produced by the loss of inversion symmetry of the crystal structure, driven by spin order, displacive mechanism or hydrogen-bond ordering scheme in a ferroelectric material. Thus identifying the space group of EA_2CuCl_4 is indeed an essential issue.

EA_2CuCl_4 crystallizes in a layered perovskite structure consisting of nearly isolated layer of corner-sharing $CuCl_6$ octahedra separated by two layers of ethyl-ammonium cations $(C_2H_5NH_3)^+$ at RT [see Fig. 3(b)], where the ethyl-ammonium bilayer and the anionic inorganic layer are stacked ionically by Coulombic force. The hydrogen bonding between the ammonium head and halogens determines the orientation and conformation of the organic cation.[12] The crystal structure at RT is orthorhombic and belongs to the space group *Pbca*. The $CuCl_6$ octahedra are strongly deformed due to the in-plane Jahn–Teller (JT) distortion. The shorter and longer Cu–Cl bond lengths are ∼ 2.28 Å and ∼ 2.98 Å, respectively.[11]

Upon lowering temperature, EA_2CuCl_4 undergoes five phase transitions at $T_1 = 364$ K (*Bbcm*), $T_2 = 356$ K (*Bbcm*→$P2_1/c$), $T_3 = 330$ K ($P2_1/c$ →rhombic *Pbca*), T_4 = 247 K, and $T_5 = 232$ K. The previous investigations on crystal structure or phase transition evolution with temperature and pressure have been focused on the high temperature region at T_1, T_2, and T_3 by means of dilatometric, dielectric, V-UV absorption spectra, x-ray diffraction (XRD), hydrostatic pressure, etc.[11,13–16] However, available structural data are not sufficient to confirm the existence of phase transition from centro to non-centro symmetry at T_4 since the compound EA_2CuCl_4 shows a phase transition from paraelectricity to FE.[3] Here we devote to the studies of structural phase transition at lower temperature T_4 by XRD method.

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2. Experimental details

Crystals of EA_2CuCl_4 are obtained by a solvothermal condition method from an aqueous solution, which contains stoichiometrically $C_2H_5NH_2{\cdot}HCl$ and $CuCl_2{\cdot}2H_2O$. The solution is put in a 100 ml flat beaker then heated for 3 days at 70 °C in a thermostat. Then the beaker is placed at RT for several days for crystallization by the method of slow evaporation. The obtained crystals are transparent yellow square plates, typically 5×5 mm^2 (*ab* plane) in area and 0.25 mm in thickness. The crystals are stored in Ar protective atmosphere. Differential scanning calorimetry (DSC) measurement as an aid to determine the characteristic temperatures of the EA_2CuCl_4 are performed in air atmosphere at a heating rate of 10 K/min. The XRD experiments of powder are performed at various temperatures with increasing temperature using a Rigaku x-ray diffractometer (SmartLab 9 kW) with Cu Kα_1 radiation ($\lambda = 1.541$ Å). Data are collected by step scanning over the angular range $20° \leq 2\theta \leq 60°$ and analyzed by the Rietveld method implemented in the program FULLPROF. Powder XRD patterns have confirmed the structure and phase purity of the obtained samples, revealing the single phase perovskite structure with space group *Pbca* at RT, which is in agreement with literature.[17] The single-crystal XRD pattern suggests that the crystal is naturally grown along [100] direction.[10]

3. Results and discussion

The phase transition temperatures T_4 of 218 K and 243 K are indicated by DSC measurements during cooling and heating processes, as shown in Figs. 1(a) and 1(b), respectively. The warming and cooling curves show a big thermal hysteresis (25 K), implying a first-order phase transition at T_4. The magnitude of heat flow signal of T_4 is quite small compared to that of T_2 (space group: *Bbcm* to $P2_1/c$ with cooling T). It may imply that the crystal structure is transformed by simple symmetry operator or the incomplete phase transition occurs. It is worth noting that the DSC curves do not show other trace of phase transitions.

Figure 2 shows the powder XRD patterns with $2\theta = 20°$ to 60° for the temperatures of 10, 70, 100, 170, 200, 220, 240, 260, and 300 K. It is clear that the diffraction single peaks of 24°, 29°, 36°, and 49° split into double peaks with increasing temperature, which indicates that a structure phase transition has occurred around T_4. To determine accurate lattice parameters and atomic positions, Rietveld analyses are carried out for all the temperatures. It is found that the structure phase with space group D_{2h}^{15}-*Pbca* and the initial sets of Cu at 4a (0, 0, 0) where all Cu sites are crystallographically equivalent changes into a phase with space group *Aba2* and the sets of Cu at 4a (z, 0, 0) at T_4. The symmetry group on "Cu^{2+}" site is operated from "−1" to "2". Rietveld analyses of the XRD data at 10 K and 300 K are summarized in Table 1.

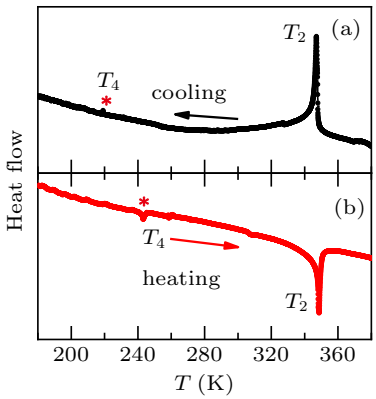


Fig. 1. Experimental DSC curves during cooling (a) and heating (b) processes for EA_2CuCl_4. The symbol "*" indicates a hysteresis phase transition temperature T_4 of 218 and 243 K.

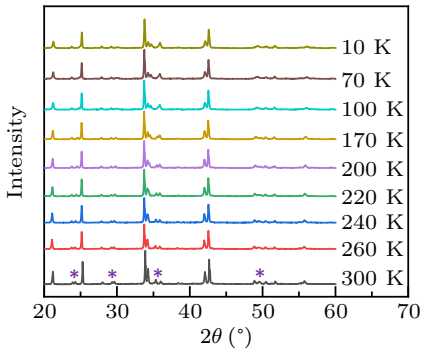


Fig. 2. XRD patterns for EA_2CuCl_4 at various temperatures. The splitting peaks' position with increasing temperature is indicated by symbol "*".

Table 1. Structural parameters and crystallographic positions determined from the Rietveld profile refinements of the powder XRD patterns for EA_2CuCl_4 at 10 K and 300 K, respectively. Here Cl1 refers to the apical chloride, Cl2 refers to the basal chloride which lies in the plane of the layer.

Parameters	10 K	300 K
Space group	*Aba2*	*Pbca*
a (Å)	21.1929	21.2324
b (Å)	7.4658	7.4806
c (Å)	7.1211	7.3640
Cu site	4a (0, 0, 0.0703)	4a (0, 0, 0)
Cl1 site	8b (0.1061, 0.0127, 0.1140)	8c (0.1134, 0.0019, –0.0020)
Cl2 site	8b (0.0021, 0.2613, 0.3697)	8c (–0.0172, 0.2809, 0.3132)
N site	8b (0.0969, 0.4474, 0.1191)	8c (0.0977, 0.1864, –0.3034)
C1 site	8b (0.1636, 0.5279, 0.0141)	8c (0.1025, 0.0780, 0.6300)
C2 site	8b (0.2120, 0.5938, 0.0457)	8c (0.1745, 0.5380, 0.0700)
R_{wp}	16.7	14.3
R_{exp}	9.5	9.0

Figures 3(a)–3(d) show the representative XRD Rietveld refined patterns and the corresponding sketches of crystal structures. XRD patterns at RT [Figs. 3(a) and 3(b)] are almost identical to the data collected by Steadman *et al.*[17] The slightly larger *c* axis at RT may originate from the different crystal growth condition or chemicals. The structure can be refined in the space group *Aba2* with lower R_{wp} factor than that in *Pbca* below 240 K [Figs. 3(c) and 3(d)]. From Fig. 3(c), one can see that the secondary phase with space group *Pbca*

is detected with minor trace indicated by the symbol "*" at 10 K despite a perfect fitted structure (*Aba2*) is revealed with $R_{wp} = 16.7\%$. Similarly, at other temperatures below 240 K, the minor second phase (*Pbca*) is also obtained based on the XRD patterns that show extra diffraction peak [600]. This indicates that the phase transition into main phase with non-centro symmetry (*Aba2*) from centro symmetry (*Pbca*) at T_4 is incomplete, which is in agreement with the behavior of DSC results. Both the incomplete phase transition and simple modification of symmetry operator at T_4 stunt the intensity of DSC.

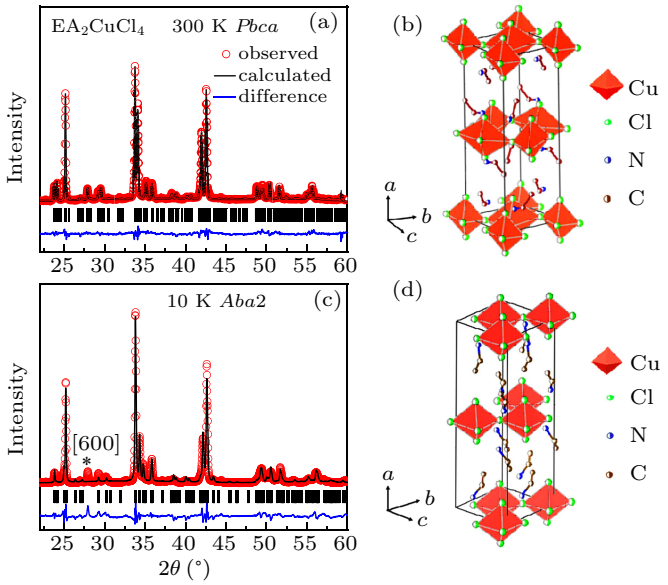


Fig. 3. Representative Rietveld refined patterns and the corresponding sketches of crystal structures for EA_2CuCl_4 at (a), (b) 300 K and (c), (d) 10 K. Observed (dots), calculated (black line), diffraction peaks (vertical lines), and the difference profile from FULLPROF analysis are shown. The symbol "*" in (c) indicates the [600] direction of residual secondary phase with space group *Pbca*.

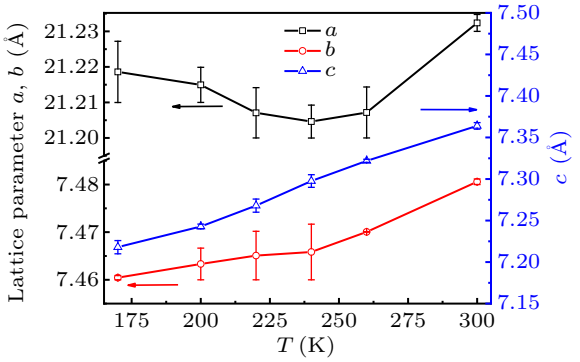


Fig. 4. Temperature dependence of the lattice parameters *a*, *b*, and *c*.

The temperature dependence of the lattice parameters *a*, *b* and *c* is shown in Fig. 4. It can be seen that *b* and *c* decrease with the lowering temperature monotonously while *a* shows a minimum value at T_4. It may originate from the release of in-plane JT distortion of $CuCl_6$ octahedron, as shown in Fig. 5. Upon lowering temperature, the distance of bond Cu–Cl1 (out-of-plane) almost maintains constant whereas the distance of Cu–Cl2(1) (in-plane) is abruptly squeezed and Cu–Cl2(2) (in-plane) is elongated at T_4. Figure 5 shows that the bond distances of Cu–Cl2(1) and Cu–Cl2(a) of the $CuCl_6$ octahedron converge to the value of Cu–Cl1 bond at T_4 then maintain almost unchangeable with decreasing temperature. It implies that the organic chain of EA between $CuCl_6$ layers is modified along *a* axis and contributes to the expansion of *a* axis below T_4 due to the phase transition. At the same time, one can see a distinct distortion which still occurs just below T_4.

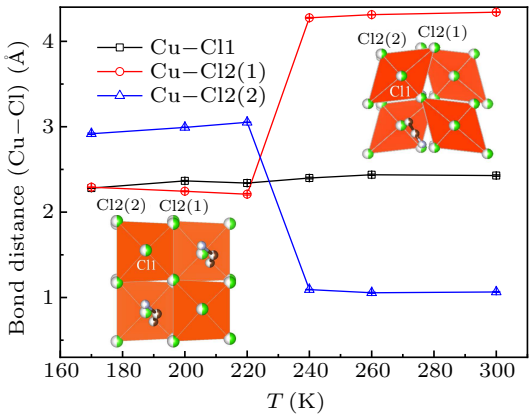


Fig. 5. Temperature dependence of the bond distances of Cu–Cl1, Cu–Cl2(1) and Cu–Cl2(2) for $CuCl_6$ octahedron. The insets illustrate the in-plane (*bc* plane) schematic structures of $CuCl_6$ octahedron for clarification.

Such a structural change could influence the electronic or spin state of the system. Cu^{2+} is a strong JT ion and JT effect (in-plane distortion) of $CuCl_6$ octahedron is significantly released. The behavior of the reduction of JT distortion may active the reorientation of EA chains among four equivalent orientations inside the cavity of $CuCl_6$ octahedron and induces an order–disorder transition of hydrogen bonds thus leading to FE.[3,13,18,19] The reported dielectric and electric polarization measurements do show appreciable anomalies around 240 K.[10] This experimental result proves that there is coupling between the electrical property and the order parameter. An interpretation on FE emergence around T_4 is addressed.

4. Conclusion

We have observed a structural phase transition from *Pbca* to *Aba2* of EA_2CuCl_4 crystal at T_4 by XRD analysis. An in-plane JT distortion of octahedron $CuCl_6$ is released and the organic chain is modified at 240 K. This structural phase transition is solidly evidenced to couple the electric property of EA_2CuCl_4.

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