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Optical and electrical conduction mechanisms of $[N(CH_3)_3H]CdCl_3$

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ABSTRACT

The X-ray powder diffraction patterns shows that at room temperature $[N(CH_3)_3H]CdCl_3$ crystallizes in the orthorhombic system with the Pbnm space group. The analysis of the data revealed the existence of optical allowed direct transition mechanisms with the band gap energy equal to 5.3 eV. The temperature dependences of the real part of dielectric permittivity show a relaxation process at high temperature that can be explained by the reorientational motion of alkyl chains. The alternative current (AC) electrical conduction in compound is governed by three processes, which can be attributed to several models: the correlated barrier hopping (CBH) model in phases I and II, the non-overlapping small polaron tunneling (NSPT) model in phases III and IV.

1. Introduction

Alkyl-Ammonium groups can be coupled via hydrogen bonding in different manners to a variety of inorganic matrices. The structural arrangement of the $AMCl_3$ (M:metal=Co, Cu, Zn, Cd...) formula, consists of infinite corner-sharing layers of chlorine octahedra with one layer of alkyl-ammonium group attached on each side. Recent studies of these compounds exhibit successive structural phase transitions that are associated with the reorientational dynamics of the alkyl-ammonium group or anionic group. Several properties interesting characterize these compounds such as the ferroelectricity, ferroelasticity and low dimensional magnetism [1–5].

In this context, we have successfully synthesized the $[N(CH_3)_3H]CdCl_3$ hybrid compound, which consist of infinite chains of face sharing $[CdC1_6]^-$ octahedral running parallel to the b-axis in Fig. 1. The trimethylammonium ion is located in the free space between the chains. The nitrogen and chlorine atoms are hydrogen-bonded with an N–H.... Cl. Following this relatively strong bond, the $[CdC1_6]^-$ octahedral are slightly elongated in the direction of the bonded chlorine atom [6]. They reported three phase transitions at T_1=355 K, T_2=372 K and T_3=415 K and the temperature decomposition of the material at around 446 K [7]..

The electrical analysis carried out on insulating materials is declined according to two aspects: measurements under alternative mode (alternative current AC) and others under continuous mode (direct current DC). The study in AC mode which is realized under low field reveals more in-depth the intrinsic mechanisms of conduction into the sample even if the electrodes have their role (electrode processes). The measurements of AC conductivity have been extensively used to understand the conduction process in organic-inorganic materials. Various models, such as the correlated barrier hopping (CBH), the overlapping large-polaron tunneling (OLPT), the non-overlapping small polaron tunneling (NSPT) and the quantum mechanical tunneling (QMT), have been proposed to explain the AC conduction mechanism. These templates are based on the relaxation induced by the hopping or tunneling of polarons or balance between sites atoms were developed to explain the frequency and temperature dependence of conductivity AC to several ranges limited temperature [8–10].

In this paper, we have analyzed the $[N(CH_3)_3H]CdCl_3$ organic-inorganic compound by means of X-ray diffraction. Thus, absorbance characteristics and the band gap energy of the crystals were determined by UV–vis spectrum. The conduction mechanism will be examined in the different phases.

2. Experimental

2.1. Synthesis

The $[N(CH_3)_3H]CdCl_3$ compound was synthesized according to the following reaction:

The $[N(CH_3)_3H]Cl$ and ($CdCl_2$) were dissolved in a (1 M) HCl aqueous solution in molar ratio of 2:1, then mixed and slowly evaporated at room temperature. After few days, parallelepiped-shaped colorless crystals appeared. The analysis of the obtained phase confirms the formation of $[N(CH_3)_3H]CdCl_3$.

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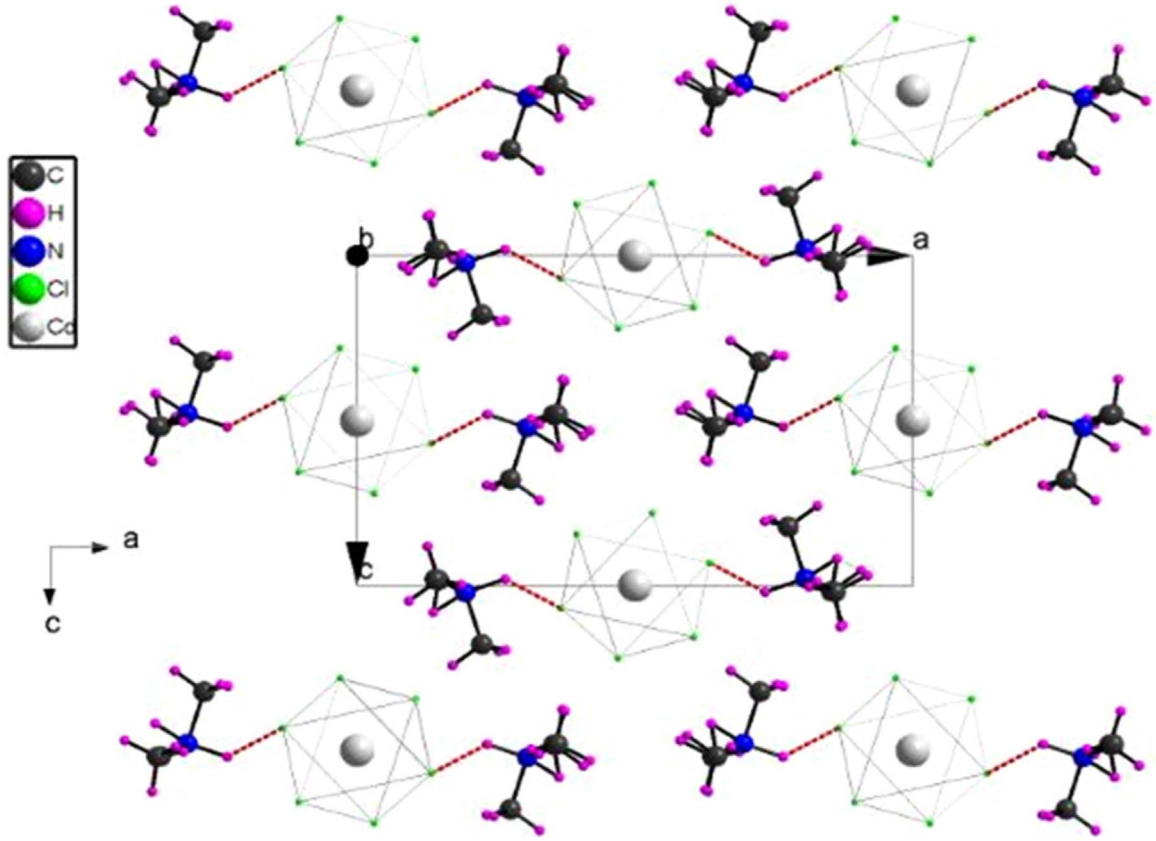

Fig. 1. Projection of part of the unit cell content of $[N(CH_3)_3H]CdCl_3$ along the b-axis. H bonds linking the $[CdCl_6]^-$ octahedra and $[(CH_3)_3NH]^+$ ions are represented by dotted lines.

2.2. Apparatus

The X-ray diffraction (XRD) pattern of powder was recorded at room temperature using a Philips PW 1710 diffractometer operating with copper radiation Cu K_α radiation ($\lambda_{K\alpha}$=1.5406 Å) in a wide range of Bragg angles 5°≤2θ≤80° angular range.

The structure refinement conducted by the Rietveld analysis [11] of the X-ray powder diffraction data using the FULLPROF software [12].

Then optical absorption spectra of the $[N(CH_3)_3H]CdCl_3$ were measured at room temperature using a conventional UV–vis absorption spectrometer (Shimadzu, UV-3101PC) in the wavelength range of 200–800 nm.

The AC conductivity data were measured on pellet disks of about 8 mm in diameter and 1 mm in thickness in the frequency range of 200 Hz to 1 MHz with the TEGAM 3550 ALF automatic bridge controlled by a microcomputer and a temperature controller. The measurements were carried at 323–433 K temperatures.

3. Results and discussion

3.1. Crystalline parameter

The X-ray diffraction of the $[N(CH_3)_3H]CdCl_3$ compound was carried at room temperature, using Rietveld's refinement program "Full Proof" and the experimental, calculated and difference powder XRD patterns were shown in Fig. 2..

The best refinement of the experimental profile is realized by the orthorhombic system with the Pbnm space group. The quality factor indicating the concurrence between the observed and the calculated profiles is χ^2=1.68. The refined lattice parameters are a=8.9789 (1) Å, b=14.4842 (3) Å, c=6.7033 (1) Å and V=871.784 $Å^3$; Z=4, which are in good agreement with the published results [7].

There have been several structural studies on the phase transitions

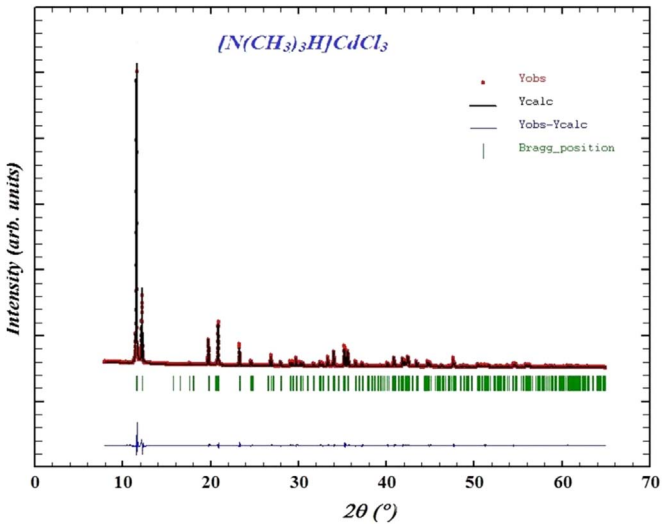

Fig. 2. X-Ray diffraction patterns at room temperature of $[N(CH_3)_3H]CdCl_3$ sample. The circles are the observed profile; the solid line is the calculated one. Tick marks below the profile indicate the position of allowed Bragg reflections.

that occur upon heating $[(CH_3)_3NH]$ $CdCl_3$ [6,13] have assigned the orthorhombic space group Pbnm to the high-temperature phase which exists between 342 K and 374 K. whereas above 374 K, the compound changes to hexagonal $P6_3/m$ structure.

3.2. Optical study

The absorbance spectrum of $[N(CH_3)_3H]CdCl_3$ at room temperature is shown in Fig. 3. The observed exciton peaks at 204, 270, 370 and 670 nm, which is very comparable to those found in other