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Alternating-current conductivity and dielectric relaxation of bulk iodoargentate

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ABSTRACT

An inorganic-organic hybrid compound $Cu(en)_2Ag_2I_4$ (en = ethylenediamine) (**1**) was synthesized and single crystal structurally characterized. Along the [001] direction, the inorganic parts form an infinite 1-D chain and $[Cu(en)_2]^{2+}$ cations are separated by inorganic chain. The electrical conductivity and dielectric properties of **1** have been investigated over wide ranges of frequency. The alternating-current conductivities have been fitted to the Almond–West type power law expression with use of a single value of S. It is found that S values for **1** are nearly temperature-independent, which indicates that the conduction mechanism could be quantum mechanical tunneling (QMT) model. The dielectric loss and electric modulus show single dielectric relaxation process. The activation energy obtained from temperature-dependent electric modulus compare with the calculated from the dc conductivity plots.

1. Introduction

The inorganic–organic hybrid compound is a fertile topic of research, mainly because such compounds may combine useful properties from the inorganic as well as the organic moieties within a crystalline molecular scale composite [1,2]. In these systems, the inorganic building-block of silver(I) halide occupy an important position for their versatile topology structures and enthralling properties such as good electrical mobility, band gap tenability, mechanical and thermal stability. So far, considerable progress is being made toward the goal of obtain specific architectures: for example, the chiral framework iodoargentates with tridymite topology [3], the Ag_{10} quadruple helicate, and undecanuclear silver clusters containing an unusual μ_9-iodide [4]. In these compounds, the organic portion is usually an organic ammonium cation, balancing the negative charge from the inorganic part. Recently, such hybrid compounds incorporating novel templates have emerged, and these templates include transition-metal complexes [5] and bifunctional organic cations [6]. In particular, the introduction of second metal–organic subunits provides not only charge balance for the inorganic substructure but also influencing physical properties via structural alterations [7]. The study of electrical properties of theses materials is a dynamic field of research since a number of applications can be foreseen such as photovoltaic devices, light emitting diodes, schottky diodes and field effect transistors.

Dielectric relaxation spectroscopy is a very useful technique in solid state electrical system, because it can resolve the conduction components by differentiating among the transport properties of complex system [8]. The dielectric relaxation methods are commonly used in studies of ionic conductivity and molecular dynamics in different dielectric materials, such as glasses, crystal and liquids [9,10]. It is well known that the measurements of alternating current (ac) conductivity can provide the underling mechanisms of the dielectric relaxation [11,12].

In this paper, we presented the synthesis and crystal structure a AgI-based inorganic-organic hybrid compound bis (ethylenediamine) copper(II) di-iodido-bis[iodidosilver(I)] (abbreviated as $Cu(en)_2Ag_2I_4$, **1**). The dielectric and conductivity investigations both as a function of temperature and frequency were carried on **1** using impedance spectroscopy.

2. Experimental

2.1. Preparation sample of 1

$KAgI_2$/DMF solution was prepared as follows: The *N*,*N*-dimethylformamide (DMF) solution of $AgNO_3$ was added to 20 ml of the saturated KI/DMF solution, and little precipitate was immediately formed and stirred until the mixture became the clear solution. Subsequently, a DMF solution of $Cu(NO_3)_2 \cdot 3H_2O$

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and 2 ml ethylenediamine were added into $KAgI_2$/DMF solution. The resulting solution was kept at room temperature for two weeks, and black block crystals (**1**) were formed in ca. 85% yield based on Cu, which is higher than other literature reported [13].

2.2. Physical measurements

Thermogravimetric (TG) experiments were performed with a TA2000/2960 thermogravimetric analyzer at a warming rate of 10 K/min under a nitrogen atmosphere. TG plot of compound 1 was shown in Fig. S1. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). The diffraction pattern was shown in Fig. S2, confirming the phase purity of the as-prepared sample. Temperature and frequency dependent dielectric constant, ε', total conductivity, σ (ω), the impedance, Z, dielectric loss, tan (δ), and electric modulus, M'', measurements were carried out employing Concept 80 system; the powdered pellet was coated by gold films on the opposite surfaces and sandwiched by the copper electrodes and the ac frequencies span from 1 to 10^7 Hz.

2.3. X-ray crystallography

Selected crystals of 1 were centered on an Oxford Diffraction Xcalibur diffractometer equipped with a Sapphire 3CCD detector and a graphite monochromated Mo Kα ($\lambda = 0.71073$ Å). Measurements were performed at 296 K for 1. The data collection routine, unit cell refinement, and data processing were carried out with the program CrysAlis [14]. Structures were solved by the direct method and refined by the full-matrix least-squares procedure on F^2 using SHELXL-97 program [15]. The non-Hydrogen atoms were anisotropically refined using the full-matrix least-squares method on F^2. The crystallographic details about data collection and structural refinement are summarized in Table 1.

Table 1
Crystal data and structural refinements of **1** at 296 K.

Temperature	296 K
Chemical formula	$C_{14}H_{16}N_4AgCuI_4$
CCDC number	991701
Formula weight	907.10
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	c2/m
a (Å)	10.580(4)
b (Å)	13.309(5)
c (Å)	6.854(3)
α(°)	90
β (°)	118.68(6)
γ (°)	90
V(Å^3)/Z	846.7(6)/2
Density (g cm^{-3})	3.558
Abs coeff. (mm^{-1})	10.808
F(000)	806.0
Data collect θ range	1.43–25.98
Index range	$-11 \leq h \leq 13$ $-15 \leq k \leq 16$ $-7 \leq l \leq 8$
Reflns collected	823
R_{int}/R_{sigma}	0.0427/0.0519
Independent reflns	797
Data/restraints/parameters	823/0/41
Goodness-of-fit on F^2	1.189
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0629$ $wR_2 = 0.2129$
Final R indices for all data	$R_1 = 0.0637$ $wR_2 = 0.2132$

3. Results and discussion

3.1. Crystal structure descriptions

Compound **1** crystallizes in the monoclinic space group C2/m, and an asymmetric unit contains one Ag^+ ion and one I^- anion together with one $Cu(en)_2{}^{2+}$ cation (as depicted in Fig. 1a). The bond lengths and angles are in agreement well with the values in the reported compounds and are listed in Table 2 [13]. The silver atoms are four-coordinated from two different types of I^- anions to give distorted AgI_4 tetrahedron. The $[Ag_2I_4]^{2-}$ subunit are constructed by sharing I–I edge of AgI_4 tetrahedron. Each $[Ag_2I_4]^{2-}$ subunit are linked together via edge-sharing mode to form an infinite 1-D chain along the [0 0 1] direction. The smaller angle of I–Ag–I leads to reduction of the Ag···Ag contact of the neighboring $[Ag_2I_4]^{2-}$ subunit (Ag···Ag = 3.090 Å), which is shorter than Van der Waal's radius sum of silver (3.44 Å). In $[Cu(en)_2]^{2+}$ cation, each copper atom is coordinated by four nitrogen atoms of two ethylenediamine molecules. The CuN_4 core exists in square planar geometry. Along the c-axis direction, the neighboring $[Cu(en)_2]^{2+}$ cation stacks into uniform cation column, which is separated by inorganic chain (Fig. 1b). Furthermore, there exist weak hydrogen bond interactions between —NH_2 group of en molecular and iodine of $[Ag_2I_4]^{2-}$ subunit (Fig. S3). Such weak hydrogen bond interactions connect the adjacent anions and cations into two-dimensional molecular solid.

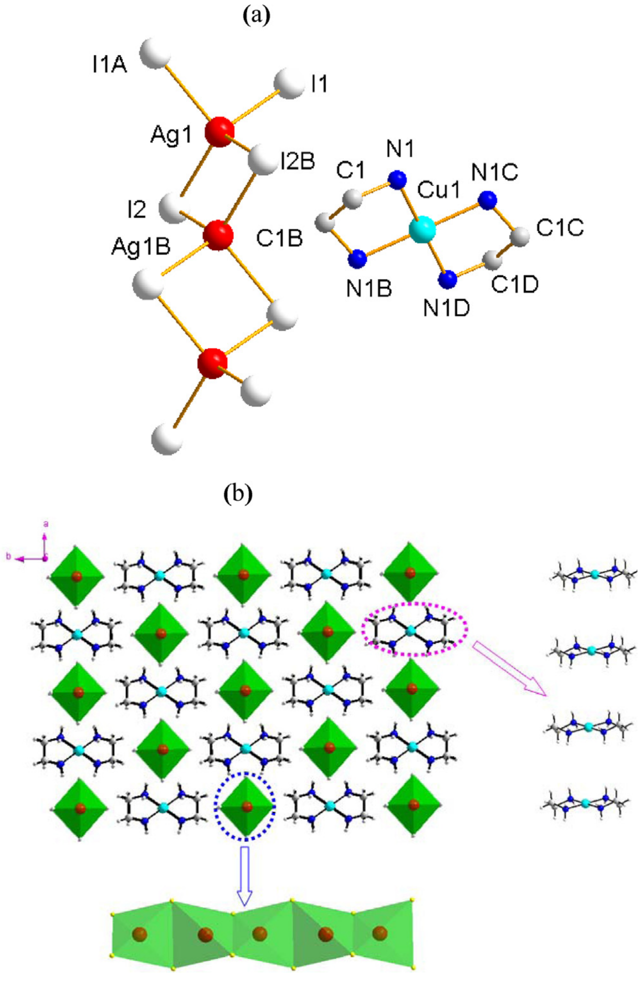

Fig. 1. (a) Asymmetric unit with non-H atomic labeling. (b) View of the crystal packing structure along the c-axis. Symmetry codes: $A = 2 - x, 1 - y, 3 - z$; $B = 2 - x, y, 2 - z$; $C = x, -1 - y, z$; $D = 2 - x, 1 - y, 2 - z$.