Materials Chemistry and Physics 139 (2013) 770–774

Contents lists available at SciVerse ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Spectral ellipsometry study in the range of electronic excitations and band structure of $[(CH_3)_2CHNH_3]_4Cd_3Cl_{10}$ crystals

B. Andriyevsky [a,*], K. Dorywalski [a], M. Jaskólski [a], Z. Czapla [b,c], A. Patryn [a], N. Esser [d]

[a] Faculty of Electronics and Computer Sciences, Koszalin University of Technology, Śniadeckich Str. 2, PL-75-453 Koszalin, Poland
[b] Department of Physics, Opole University of Technology, Ozimska Str. 75, PL-45-271 Opole, Poland
[c] Institute of Experimental Physics, Wroclaw University, M. Born Sq. 9, PL-50-204 Wroclaw, Poland
[d] Leibniz-Institut für Analytische Wissenschaften-ISAS-e.V., Department Berlin, Albert-Einstein-Str.9, 12489 Berlin, Germany

HIGHLIGHTS

- ► Spectral ellipsometry in the VUV range is used for study of $(IPA)_4Cd_3Cl_{10}$ crystals.
- ► Band structure of $(IPA)_4Cd_3Cl_{10}$ crystal has been calculated for the first time.
- ► Origin of the lowest energy spectral band of dielectric function is determined.
- ► Width of temperature dependency of dielectric permittivity is large (near 50 K).
- ► Maximum of temperature dependency of dielectric permittivity is small (near 2%).

ARTICLE INFO

Article history:
Received 20 August 2012
Received in revised form
14 January 2013
Accepted 12 February 2013

Keywords:
Insulators
Optical properties
Phase transitions
Band-structure

ABSTRACT

Optical dielectric functions $\varepsilon(E)$ of the $(IPA)_4Cd_3Cl_{10}$ crystal were measured in the spectral range of fundamental electronic excitations 3.5–10 eV and in the temperature range of 310–400 K containing the phase transition point between the orthorhombic phases *Cmce* and *Pbca*. Measurements were performed by spectroscopic ellipsometry with using of synchrotron radiation. Electronic band structure, density of states and dielectric functions $\varepsilon(E)$ of $(IPA)_4Cd_3Cl_{10}$ were calculated and analyzed on the basis of the density functional theory. Top valence and bottom conduction bands were found to be formed mainly by the cadmium–chlorine complexes of the crystals.

1. Introduction

Halogenocadmate(II) compounds may exist in a variety of structural architectures owing to the chemical flexibility of these compounds, which may accommodate different organic counter-ions as well as inorganic components. This permits to create different crystal structures on the basis of the counterparts mentioned and thus to optimize their physical properties [1,2]. One of such compounds, the crystal tetra(isopropylammonium) decachlorotricadmate(II), $[(CH_3)_2CHNH_3]_4Cd_3Cl_{10}$, is characterized by three temperature stimulated phase transitions at 353, 294 and 259 K, that was found by calorimetry, X-ray diffraction, dielectric and dilatometric studies [3,4]. The crystal comprises two-dimensional cadmium(II) halide network of $[CD_3Cl_{10}]_n^{4-}$ in the *ac*-plane, that probably causes its cleavage perpendicularly to the *b*-axis (Fig. 1) implying the presence of strong enough chemical bonds in the *ac*-plane. Layered structure of the crystal implies weak chemical bonds between $[CD_3Cl_{10}]_n^{4-}$ and isopropylammonium (IPA) groups. This in turn permits larger flexibility of the isopropylammonium groups spatial positions and orientations, which is in agreement with existence of four structural phases in the $(IPA)_4Cd_3Cl_{10}$ crystal [3].

In the present work, results of theoretical and experimental study of the electronic properties of the $(IPA)_4Cd_3Cl_{10}$ crystal are obtained for the first time. Electronic band structure and related properties of $(IPA)_4Cd_3Cl_{10}$ are calculated for the phase II of the spatial symmetry group *Pbca* (no. 61). Experimental spectra of the effective dielectric permittivity $<\varepsilon>(E)$ of the crystal are measured in the photon energy range of 3.5–10 eV and for different

---

[*] Corresponding author. Tel.: +48 943478690; fax: +48 943433479.
E-mail addresses: bohdan.andriyevskyy@tu.koszalin.pl, bandriyevsky@gmail.com (B. Andriyevsky).

0254-0584/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.matchemphys.2013.02.030

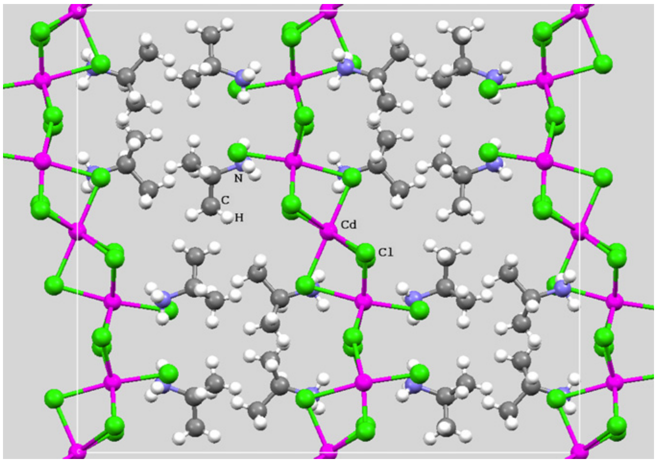

Fig. 1. View of $[(CH_3)_2CHNH_3]_4Cd_3Cl_{10}$ crystal structure in *bc*-plane (*b* is horizontal) for orthorhombic group of symmetry *Pbca*: Cd – magenta, Cl – green, N – blue, C – gray, H – white (picture is drawn using the cif-file of [3]). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

temperatures in the range of 310–400 K, comprising the phases I and II.

2. Methods of investigations

2.1. Experimental method

Spectroscopic ellipsometry was used for measurements of the dielectric permittivity ε of the crystal as function of the photon energy *E* in the range of electronic excitations 3.5–10 eV. Measurements were performed using the vacuum ultraviolet (VUV) rotating-analyzer ellipsometer attached to the 3m-NIM monochromator of Berlin electron storage ring for synchrotron radiation BESSY II. The setup is equipped with cooling and heating systems, which allows the ellipsometric measurements to be performed in the range of 10 K–500 K. More details of the experimental setup can be found elsewhere [5]. Experimental results obtained were presented in terms of the complex effective dielectric permittivity of crystal, $<\varepsilon> = <\varepsilon_1> + i<\varepsilon_2>$ [6], as functions of the photon energy *E* and temperature *T*. In the present work, temperature measurements were performed in the range of 310–400 K.

2.2. Method of theoretical study

For theoretical study of the crystal, the density functional theory based *ab initio* calculations were performed using the plane wave pseudopotential code Quantum ESPRESSO [7] (version 5.0). The Perdew–Zunger (pz) LDA exchange–correlation functional was used for the calculations [8]. The core electrons of the constituent atoms of $(IPA)_4Cd_3Cl_{10}$ were handled using the scalar nonlocal norm-conserving (nc) pseudopotentials of the Troullier–Martins type, Cd.pz-n-nc.UPF, Cl.pz-n-nc.UPF, N.pz-nc.UPF, C.pz-nc.UPF and H.pz-n-nc.UPF, generated using the “atomic” code by A. Dal Corso (Quantum ESPRESSO distribution). Some of the pseudopotentials used, Cd.pz-n-nc.UPF, Cl.pz-n-nc.UPF, and H.pz-n-nc.UPF, are with nonlinear core-correction (*n*). The cutoff energy was chosen at 410 eV. 29 *k*-points in the irreducible part of the Brillouin zone were used for the calculation of band structure (BS), 36 *k*-points were used for the calculation of density of states (DOS), and only the Γ-point was used for the calculation of the dielectric function $\varepsilon_2(E)$. The last limitation is necessary, because the large number of atoms ($N = 276$) in the unit cell of $(IPA)_4Cd_3Cl_{10}$ crystal demands large computational resources.

3. Results and discussion

Three principal groups of spectral bands may be selected in the photon energy range 3.5–10 eV of fundamental absorption in the dielectric function $<\varepsilon_2>(E)$ of $(IPA)_4Cd_3Cl_{10}$ at room temperature. These bands are centered at 4.9, 6.4, and 8.4 eV (Fig. 2a). Clear fine structure of the function $<\varepsilon_2>(E)$ consisting of at least 5 separate maxima is observed for the first spectral group centered at 4.9 eV, (Fig. 2a and b). These maxima (4.694, 4.886, 4.992, 5.066, 5.123 eV for the temperature 398 K) resemble molecular spectra resulted from the corresponding electron-vibration energy structure. However, the energy differences between neighboring maxima obtained, 0.192, 0.106, 0.074, 0.057 eV, are too large to be caused by repetitions of one vibration frequency. On the other hand, this series resembles spectra of electronic excitation for the hydrogen like atoms. Our attempts of analytical description using the relation, $E = P1 - P2/n^2$, for the maxima positions *E*, where *P*1 and *P*2 are constants, and $n = 1, 2, \ldots, 5$ were however unsuccessful. This relation approximates the experimental five element series mentioned satisfactorily only in the case when $n = 5, 6, \ldots, 9$. Due to the relatively small density of $(IPA)_4Cd_3Cl_{10}$ crystal ($\rho = 1.96\ \mathrm{g\ cm^{-3}}$), one can suggest also the relatively weak chemical bonding of the ionic type between IPA^+ and $CD_3Cl_{10}{}^{4-}$ molecular-like groups. This in turn implies the local character of electronic states and the

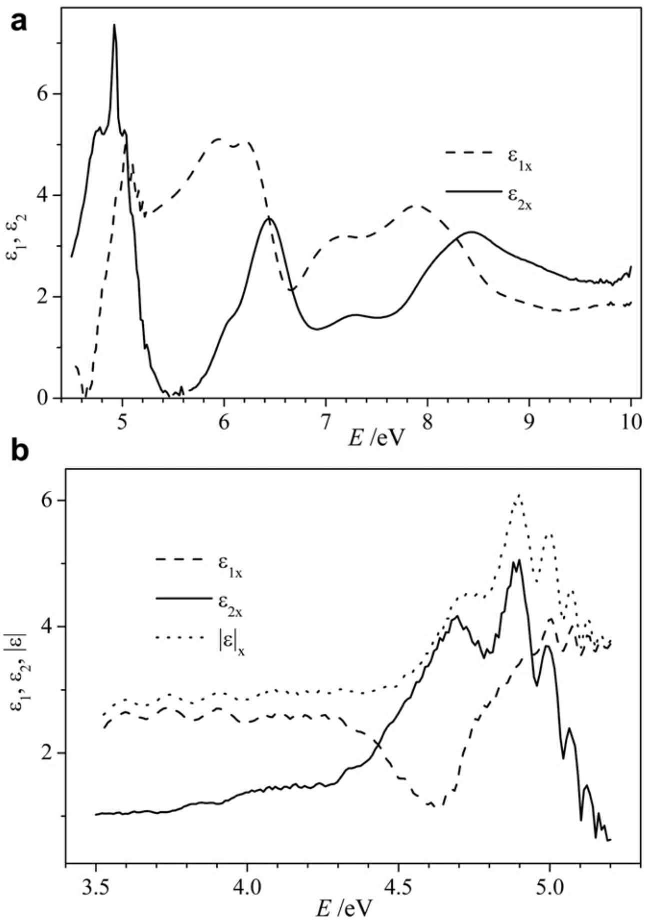

Fig. 2. Real (ε_1) and imaginary (ε_2) parts of effective dielectric function of $(IPA)_4Cd_3Cl_{10}$ in the ranges of 4.4–10.0 eV (a) and 3.5–5.2 eV (b), at the temperatures 312 K (a) and 398 K (b). $|\varepsilon|$ is an absolute value of the complex dielectric permittivity $|\varepsilon| = (\varepsilon_1^2 + \varepsilon_2^2)^{1/2}$.