



Optical and dielectric relaxation of transition metal-based organic-inorganic hybrid materials



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ABSTRACT

The $[(\text{CH}_3)_3\text{NH}]\text{CdCl}_3$ (**1**) and $[\text{N}(\text{CH}_3)_3\text{H}]\text{CoCl}_3 \cdot 2\text{H}_2\text{O}$ (**2**) compounds were obtained by slow evaporation at room temperature and characterized by X-ray powder diffraction patterns. These compounds were crystallized in the orthorhombic system, in Pbnm and Pnma space groups, respectively. The optical properties were measured by means UV–Vis absorption spectrometry in order to deduce the absorption coefficient α and optical band gap E_g . The Tauc model was used to determine the optical gap energy of the synthesized compounds **1** and **2**. Data analysis revealed the existence of two optical transition mechanisms. The calculated values of the direct and indirect band gaps (E_{gd} , E_{gi}) for both samples were estimated between 5.41 and 5.30 eV for compound **1**; and between 4.02 and 3.82 eV for compound **2**. The dependence of the optical constants, the refractive index (n) and the extinction coefficient (k) of compounds **1** and **2** were calculated and the results discussed. The normal dispersion of refractive index of the samples was described using the Wemple–DiDomenico single oscillator method. The optical dispersion parameters E_0 and E_d were determined according to the above oscillator method. We employed dielectric spectroscopy to investigate the dipolar dynamics in the both compound. The evolution of the dielectric loss as a function of frequency showed a distribution of relaxation times; which is probably due to the reorientational dynamics of alkyl chains in compound **1**, analyzed with the Cole–Cole formalism. Various relaxation processes and their locations of compound **2** were analyzed according to the fitted data of the Havriliak–Negami (HN) function. Different relaxation processes were found to belong to non-debye relaxation. The dielectric constants were composed of two dielectric relaxation peaks, DC conduction and electrode polarization (EP) effect. The determined values of relaxation time are characteristic of the co-operative reorientation of the trimethylammonium cation.

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1. Introduction

Organic–inorganic hybrid materials are able to combine desirable characteristics from both organic and inorganic components. They have been extensively studied due to their rich physical properties, functionalities, and potential applications [1,2]. Trimethylammonium trichlorocadmium chloride $[\text{N}(\text{CH}_3)_3\text{H}]\text{CdCl}_3$ (**1**), denoted by (TrMcCd), belongs to a wide series of organometallic compounds with the general chemical formula $[\text{N}(\text{CH}_3)_3\text{H}]\text{MX}_3$ ($M = \text{Cd}, \text{Hg}, X = \text{Br}$ or Cl), and trimethylammonium trichlorocobaltate dihydrate $[\text{N}(\text{CH}_3)_3\text{H}]\text{CoCl}_3 \cdot 2\text{H}_2\text{O}$ (**2**), designated by

(TrMCo), which belongs to a large series of organic-inorganic compounds with the general chemical formula $[\text{N}(\text{CH}_3)_3\text{H}]\text{MX}_3 \cdot 2\text{H}_2\text{O}$ ($M = \text{Co}, \text{Mn}, \text{Fe}, \text{Ni}, X = \text{Br}$ or Cl). These compounds belong to the organic-inorganic hybrid material $\text{AMCl}_3 \cdot \text{H}_2\text{O}$ and AMCl_3 ($A = \text{N}(\text{CH}_3)_3\text{H}, \text{N}(\text{CH}_3)_4, \text{N}(\text{CH}_3)_2$). The members of the above group could pass through several phase transitions, whose particular properties have been closely determined [3–6]. Using high-resolution X-ray diffraction [7–10], optical absorption studies [11–13], electron-spin resonance (ESR) [14,15], high-pressure experiments [16] and lattice vibration [17]. The study of their optical properties is highly important for numerous applications as in optoelectronic devices.

Using optoelectronic materials requires the knowledge of their optical constants. Moreover, the optical measurements are extensively used for the characterization of the composition and the

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quality of materials. Therefore, the optical properties could also be closely linked with the atomic and electronic band structure of the material. Besides, the residues of the position of the optical characteristics by doing substitutions on the metal sites or halogen control over the specific structure of the metal halide across the proper selection of the organic cations which must provide a means to influence the optical properties.

Dielectric relaxation can be demonstrated by a fall in ϵ' and a maximum in the imaginary part of the permittivity ϵ'' , at the relaxation frequency f_r . The value of f_r may vary from low to high frequencies depending on the type of physical defects related to the dipoles considered. Defects may cause modifications of the short and/or long-range interactions.

For organic-inorganic materials, dielectric spectroscopy has become a valuable tool to probe the molecular structure and dynamics. This is one of the methods able to give valuable information on the thermal and frequency behavior of molecular scale composites [18]. In fact, it is highly complex due to electrode polarization [19] which is a ubiquitous phenomenon that occurs at the interface between an electrode and an ionic conductor.

In the present paper, the main aim is to determine the optical energy gap, optical conductivity and dispersion parameters relative to Trimethylammonium trichlorcadmium chloride and trimethylammonium trichlorcobaltate dihydrate. The dispersion of the refractive index was discussed in terms of the Wemple–DiDomenico single-oscillator model. In order to obtain an overview of the dielectric dispersion phenomenon, the dielectric properties of the hybrid compounds in the frequency regime studied are evaluated and the results correlated.

2. Experimental

Single crystals of TrMCd (compound **1**), they were prepared by slow evaporation at room temperature of the aqueous solution of hydrochloric acid (1M) containing a trimethylammonium chloride and cadmium chloride (CdCl_2) [20]. A few days later, colorless parallelepipedic-shaped monocrystals were obtained by slow evaporation at room temperature [20].

The single crystal of TrMCo (compound **2**) was grown at room temperature from an aqueous solution using an equimolar mixture of $(\text{CH}_3)_3\text{NHCl}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. The crystals were deep blue in color and they grew as elongated prisms [21].

Both samples were characterized by X-ray powder diffraction (XRD) using a Panalytical X'Pert Prompd powder diffractometer operating with copper radiation ($\lambda_{\text{Cu}} = 1.5406 \text{ \AA}$) in a range of Bragg's angle ($5^\circ \leq 2\theta \leq 65^\circ$) in both compounds. The unit cell parameters of the synthesized compounds were refined by the least square method from the powder data.

Afterwards, a pellet of about 8 mm in diameter and 1.2 mm in thickness was used for the UV–Vis absorption measurements. The optical absorption spectra of compounds **1** and **2** were measured at room temperature using a conventional UV–Vis absorption spectrometer (Shimadzu, UV-3101PC) in the wavelength range of 200–800 nm.

The dielectric measurements were performed using two electrodes configurations. The compound fine powder was pressed into a cylindrical pellet of an 8-mm diameter and 1-mm thickness. The dielectric response was measured in the heating mode from 390 K to 475 K using TEGAM 3550 ALF impedance analyzer in the frequency range 200 Hz to 1 MHz for compound **1** and for compound **2**, the dielectric measurement was carried out in the heating mode from 270 K to 340 K using NOVOCONTROL impedance analyzer in the frequency range 0.1 Hz– 10^7 Hz.

3. Results and discussion

3.1. X-ray diffraction analysis

The X-ray diffraction of the compounds **1** and **2** was carried out using a Panalytical X'Pert Prompd and analyzed by Full Proof software [22]. The pseudo-Voigt function was used for the simulation of the peak shapes. The experimental, calculated and difference powder XRD patterns were shown in Figs. 1 and 2.

All reflection peaks corresponding to 2θ values are indexed in Pbnm and Pnma space groups of compounds **1** and **2**, respectively. The obtained reliability factors and lattice parameters of both compounds given in Table 1 are in good agreement with the published results [20,21]. This indicates the purity of these materials, where the atoms of cadmium and cobalt exhibit an octahedral symmetry for both samples. For compound **1**, the cadmium atoms are each coordinated to six chlorine atoms [20]; whereas, for compound **2**, the cobalt atoms are each coordinated to four chlorine ones. The two remaining sites around cobalt contain water molecules, all of which act as bridging chlorines, such that the octahedral share edges to form infinite chains [21]. These materials therefore represent an excellent candidate for optical absorption studies of octahedral mixed ligand species of cadmium (II) and cobalt (II).

3.2. Optical absorbance spectra

The optical measurements of absorbance of compounds **1** and **2** were carried out in the range of 200–800 nm, as shown in Fig. 3. The obtained spectra show a sharp increase in absorption at wavelength near the absorption edge of the threshold wavelength for the onset of absorption at 204 nm and 265 nm for compounds **1** and **2**, respectively. The energy corresponding to this region determines the band gap of the samples [23], which are attributed to typical absorptions of excitation of free electron–hole pairs in the octahedra $[\text{CdCl}_6]$ and $[\text{CoCl}_4(\text{OH}_2)_2]$ based organic/inorganic layered structures in both compounds. This reveals a good impact of organic cations on the bonding features of the octahedral layers, which finally influences the physical properties of the inorganic sheets. These peaks are mainly due to a photo-induced exciton formed by the transition from the top of the valence band including

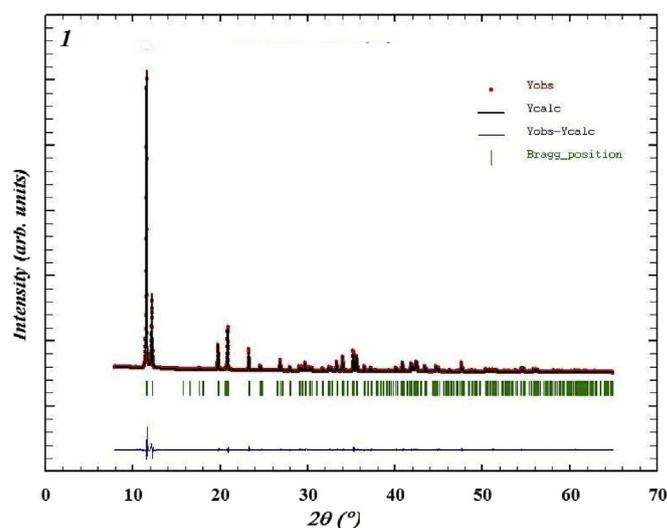


Fig. 1. X-Ray diffraction patterns at room temperature of TrMCd. The circles are the observed profile; the solid line is the calculated one. Tick marks below the profile indicate the position of allowed Bragg reflections [16].

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