Organic-Inorganic Hybrid Compounds Based on Lead Halide Units: Preparation from Melts and through Grinding Effects

George C. Papavassiliou, George A. Mousdis, and George C. Anyfantis

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48, Vassileos Constantinou Ave., Athens 11635, Greece

Reprint requests to Prof. G. C. Papavassiliou. Fax: (30210) 7273794. E-mail: pseria@eie.gr

Z. Naturforsch. 2010, 65b, 516 – 520; received November 27, 2009

Organic-inorganic hybrid compounds based on lead halide units of the formula \((\text{CH}_3\text{NH}_3)_2(\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3)_2\text{Pb}_3(\text{Br}_x\text{Y}_{1-x})_{10}\) \((Y = \text{Cl, I})\) were prepared from melts, and their optical absorption as well as photoluminescence spectra, before and after grinding the compounds, were investigated. The luminescence of the materials after grinding is strong and is observed with naked eye. By changing the mole fraction \(x\), the strong photoluminescence in the range from ca. 400 nm to ca. 600 nm could be tuned. These effects indicate that the hybrid compounds are promising materials for potential applications.

Key words: Organic-Inorganic Hybrids, Optical Properties

Introduction

During the last twenty years a large number of organic-inorganic hybrid compounds based on metal halide units have been prepared and studied (see refs. [1 – 15] and refs. cited therein).

Compounds of the type \((\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3)_2\text{MX}_4\) \((M = \text{Pb, Sn}; X = \text{I, Br, Cl})\) behave as two-dimensional (2D) semiconducting systems, and those of the type \((\text{CH}_3\text{NH}_3)_{n-1}(\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3)_2\text{MX}_2(n+1)\) \((n = 2: \text{bilayer}; n = 3: \text{trilayer}; n \geq 3: \text{multilayer})\) behave as quasi-two-dimensional (q-2D) semiconducting systems, while those of the type \((\text{CH}_3\text{NH}_3)_n\text{MX}_3\) or \((\text{CH}_3\text{NH}_3)_{n-1}(\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3)_2\text{MX}_3(n+1)\) with \(n \gg 3\) behave as three-dimensional (3D) semiconducting systems. Investigations of the optical properties on single crystals of \((\text{CH}_3\text{NH}_3)_{n-1}(\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3)_2\text{MX}_3(n+1)\) have shown that the excitonic optical absorption (OA) and photoluminescence (PL) bands are shifted to longer wavelengths with increasing number of layers \((i.\ e., n)\). For large values of \(n\) the excitonic band occurs close to that of the corresponding 3D material \((\text{CH}_3\text{NH}_3)_n\text{MX}_3\) [4, 5]. For example, single crystals or polycrystalline pellets of the 2D system \((\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3)_2\text{PbBr}_4\) obtained from solutions [8, 13e] or from melts [10] exhibit a sharp excitonic PL band at ca. 408 nm, and crystals of the 3D system \((\text{CH}_3\text{NH}_3)_3\text{PbBr}_3\) exhibit an excitonic PL band at ca. 530 nm. It has also been observed that, after intensive grinding of crystals of the q-2D and 3D compounds, considerable shifts of the PL (and OA) bands and an enhancement of the PL bands is induced. For example, in the cases of \((\text{CH}_3\text{NH}_3)_2(\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3)_2\text{Pb}_3\text{Br}_{10}\), (q-2D) and \((\text{CH}_3\text{NH}_3)_3\text{PbBr}_3\) (3D) the PL bands occur at ca. 520 nm after grinding the crystals [8, 9]. The green photoluminescence of the ground samples is observed with naked eye. The PL spectrum of the “unknown” thin film, prepared from a solution of \((\text{CH}_3\text{NH}_3)_2(\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3)_2\text{Pb}_2\text{Br}_7\), exhibits a strong band at ca. 510 nm [7a], while the PL spectrum of a nanocrystalline sample of \(\text{CsPbBr}_3\) (\(\sim 7.6\) nm) under low excitation intensity exhibits a band at ca. 523 nm [7b] (see also ref. [7c]). The PL bands of the corresponding iodides occur at ca. 710 nm after grinding [8]. However, the preparation of the corresponding chlorides by conventional methods, in single crystalline form, is difficult because of the poor self-assembly and/or low solubility [11a].

In this paper, the preparation from melts [4, 10] of some lead halide compounds mainly with the formula \((\text{CH}_3\text{NH}_3)_2(\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3)_2\text{PbBr}_{10}\) \((Y = \text{Cl, I})\) as well as the preparation of similar compounds based on some other cations, \(e.\ g., \text{Cs}^+, \text{C}_{10}\text{H}_{12}\text{NH}_3^+, \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_3^+\), are described. Also, the optical absorption and photoluminescence spectra of these compounds before and after grinding were investigated. The results are compared with those ob-
tained from single crystals or polycrystalline samples of similar compounds, prepared from solutions, as well as with those obtained for other luminescent inorganic systems.

**Optical Behavior and Discussion**

Fig. 1 shows the PL spectrum of \((\text{CH}_3\text{NH}_3)_2(\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3)_2\text{Pb}_3\text{Br}_{10}\) obtained from melts, before grinding (i.e., from a polycrystalline pellet), as well as the OA and PL spectra of the material after grinding (i.e., thin deposit on quartz plates). The PL spectrum before grinding (Fig. 1a) shows a weak and broad band from ca. 400 to 500 nm. This shape of the band indicates that the material obtained from melts is in a glassy state. The maxima or shoulders at ca. 414, 431, 450, and 470 nm correspond to the excitonic bands of the (infinite) species \(\text{PbBr}_4\), \(\text{PbBr}_7\), \(\text{Pb}_3\text{Br}_{10}\), and \(\text{Pb}_4\text{Br}_{13}\), respectively. The PL spectrum shows a weak band at ca. 530 nm, which corresponds to the excitonic band of the (infinite) species \(\text{PbBr}_3\) [4–6]. The PL spectrum of the crystalline material obtained from solutions shows that the excitonic peaks of these species are distinct, and at the same positions [4,5]. However, in all cases the relative intensities of the PL bands differ from sample to sample (see also refs. [4,8,9,13]). After grinding, the short-wavelengths PL bands remain weak or disappear and a new PL band at ca. 527 nm appears (Fig. 1b). The sample exhibits a green luminescence, which can be observed with the naked eye. The OA spectrum of a ground sample (thin deposit on quartz plate) shows an OA band edge at ca. 540 nm (Fig. 1c). The results were found to be the same as those obtained from similar bromides, almost independent of the method of preparation of the compounds (from solution or melt), the nature of the (large) cation (\(\text{CH}_3\text{NH}_3^+\), \(\text{C}_10\text{H}_21\text{NH}_3^+\), \(\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_3^+\), etc.) and the number of layers \((n \geq 2)\). 3D systems (e.g., \(\text{CH}_3\text{NH}_3\text{PbBr}_3\)) need a large amount of grinding in order to become strongly luminescent (see also refs. [7–9]). The same results were also obtained from compounds containing a monovalent metal cation (e.g., \(\text{Cs}^+\), instead of \(\text{CH}_3\text{NH}_3^+\)). Fig. 2 shows the spectrum of \(\text{Cs}_2(\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3)_2\text{Pb}_3\text{Br}_{10}\), after grinding on a quartz plate. The PL spectrum does not change after transferring the sample to a (filter) paper. The iodide analogs showed the new PL band at ca. 710 nm and the chloride analogs at ca. 400 nm (see also refs. [8,9]). The results are summarized in Table 1.

The strong PL band observed after grinding (G) of an infinite system (IS) \(\text{Pb}_3\text{Br}_{10}^4^-\) may be due to the formation of small particles (SP) of \(\text{PbBr}_3^-\) in the organic matrix (e.g., \(\text{CH}_3\text{NH}_3^+\) and \(\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3^+\)), according to Eq. 1.

\[
\text{Pb}_3\text{Br}_{10}^4^- (\text{IS}) \xrightarrow{G} 3 \text{PbBr}_3^- (\text{SP}) + \text{Br}^- \quad (1)
\]

or, generally, for any q-2D or 3D system, the formation
of $MX^-$ particles, according to the Eq. 2 or 3 (see also refs. [7 – 9]).

$$M_nX^{(n+1)-}_{3n+1} \xrightarrow{G} nMX^-(SP) + X^- \quad (2)$$

$$MX^- (IS) \xrightarrow{G} MX^- (SP) \quad (3)$$

The PL spectra of 2D systems, such as $(\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3)_2\text{PbBr}_4$ [8], do not show the strong PL band (e. g., at 520 nm) after grinding the crystals. This means that Eq. 2 is valid only for $n > 2$.

Some interesting results were obtained with mixed halides, e. g., of the type $(\text{CH}_3\text{NH}_3)_2(\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3)_2\text{Pb}(\text{Br}_x\text{Y}_{1-x})_{10}$, where $Y$ is Cl or I. In each sample, before grinding, the PL spectrum showed a number of excitonic bands. But after grinding, the PL spectrum showed mainly a strong PL band, which may be due to the formation of small particles, i. e. $\text{Pb}(\text{Br}_x\text{Y}_{1-x})_3^-$, according to Eq. 4 or, generally, for any $q$-2D or 3D system according to Eq. 5.

$$\text{Pb}_3(\text{Br}_x\text{Y}_{1-x})_{10}^- (SP) \xrightarrow{G} 3\text{Pb}(\text{Br}_x\text{Y}_{1-x})_3^- (SP) + \text{Br}_xY_{1-x}^- \quad (4)$$

$$M_n(X,Y_{1-x})^{(n+1)-}_{3n+1} (IS) \xrightarrow{G} nM(X,Y_{1-x})_3^- (SP) + X,Y_{1-x}^- \quad (5)$$
NH₃)₂Pb₃(Br₃Y₁₋ₓ)₁₀, after grinding. One can see that the strong PL (and the OA band-edge) of the ground materials can be tuned to a desired wavelength (from ca. 400 to ca. 600 nm), by controlling the composition of BrₓY₁₋ₓ. The position of the PL bands as function of the mole fraction (x) was found to be linear. For example, the position of the PL bands of BrₓCl₁₋ₓ (Fig. 3) obeys approximately the equation λₚL = 403 + 125 x (nm). Also, it was observed that the position of the PL band does not depend of the nature of the cations (e. g., CH₃NH₃⁺, Cs⁺, C₆H₅CH₂CH₂NH₃⁺, C₁₀H₂₁NH₃⁺, Cs₅H₃CH₂CH₂NH₃⁺) and/or the number of layers (n > 2). The OA band edges of the ground materials follow the strong PL bands (see Table 1). According to Eq. 4, the new OA and PL bands of Fig. 3 are due to the strong PL bands (and the OA band-edge) of the ground compounds.

**Starting materials**

The following starting materials were used without further purification: PbI₂ (Alfa Aesar 12724), PbBr₂ (Alfa Aesar 10720), PbCl₂ (Alfa Aesar 55704), methylamine aqueous solution (41 %) (Fluka 65580), 4-methylbenzylamine (Fluka 73164), decylamine (Aldrich 30692), 2-phenylethylamine (Merck 807344), hydrochloric acid 25 % (Merck 312), hydrobromic acid 47 % (Merck 304) and CsBr (Alfa Aesar 87639). Hydroiodic acid 57 % (Merck 341) was used after purification with H₂PO₃ 50 % (Fluka 94210). The precursors CH₃NH₃X, CH₃C₆H₄CH₂NH₃X, C₁₀H₂₁NH₃X and C₆H₅CH₂CH₂NH₃X (X = I, Br, Cl) were obtained by treating the amines with the corresponding acids.

**Preparation of the compounds**

Before the preparation of hybrid halides from melts, the amounts of the starting materials were calculated, in order to be in accordance mainly with the following formula

(CH₃NH₃)₂(CH₃C₆H₄CH₂NH₃)₂Pb₃(BrₓY₁₋ₓ)₁₀

Then, the following general method was applied [10]. The starting materials (lead halides and other halides), in the form of fine powders, were mixed together. For example, for the preparation of (CH₃NH₃)₂(CH₃C₆H₄CH₂NH₃)₂PbBr₁₀, 110 mg (0.3 mmol) of PbBr₂, 22.6 mg (0.2 mmol) of CH₃NH₃Br and 40.6 mg (0.2 mmol) of CH₃C₆H₄NH₃Br were used. Another example is the preparation of (CH₃NH₃)₂(CH₃C₆H₄CH₂NH₃)₂PbBr₁₀Cl₄, by using 110 mg (0.3 mmol) of PbBr₂, 13.5 mg (0.2 mmol) of CH₃NH₃Cl and 31.4 mg (0.2 mmol) of CH₃C₆H₄NH₃Cl. This compound could be prepared by using PbCl₂ and PbBr₂, instead of PbBr₂ only, and organic ammonium bromides, instead of chlorides. During the mixing of the starting materials, a solvent-free reaction [18] or the intercalation of PbX₂ into the organic crystals [11a] takes place and changes in the color are observed (e. g. from colorless to pale-orange). Then, the mixture of the powders was transferred to a glass tube and heated to a temperature close to the melting points of the organic components. During this treatment, first the lead halide is dissolved in the organic melt, then the hybrid is formed, and the product solidifies immediately. Sometimes small crystals of hybrid materials are formed [10]. The preparation of hybrids from melts is easier than from solutions. The spectroscopic data (OA and PL) of a single crystal of (CH₃C₆H₄CH₂NH₃)₂PbBr₄ obtained from solutions are identical with the corresponding data of a sample of the material obtained from melts [10]. This result indicates that the stoichiometry of the materials is identical in both cases. Similar results are expected for other hybrids.

**Addendum**

Another possible interpretation of the PL enhancement of these (composite) metal halides after grinding is based on the Foerster (or fluorescence) resonant energy transfer [19] in which particles obtained from MⁿX₃;n₊₁ (IS) act as donors and particles obtained from MⁿX₃;n₊₄ (IS) or MX₃ (IS) as acceptors.

**Experimental Section**

**Starting materials**

The following starting materials were used without further purification: PbI₂ (Alfa Aesar 12724), PbBr₂ (Alfa Aesar 10720), PbCl₂ (Alfa Aesar 55704), methylamine aqueous solution (41 %) (Fluka 65580), 4-methylbenzylamine (Fluka 73164), decylamine (Aldrich 30692), 2-phenylethylamine (Merck 807344), hydrochloric acid 25 % (Merck 312), hydrobromic acid 47 % (Merck 304) and CsBr (Alfa Aesar 87639). Hydroiodic acid 57 % (Merck 341) was used after purification with H₂PO₃ 50 % (Fluka 94210). The precursors CH₃NH₃X, CH₃C₆H₄CH₂NH₃X, C₁₀H₂₁NH₃X and C₆H₅CH₂CH₂NH₃X (X = I, Br, Cl) were obtained by treating the amines with the corresponding acids.

**Preparation of deposits**

Thin deposits on quartz plates were obtained by grinding the compounds on the plates. The ground samples could be transferred from one substrate, e. g. quartz, to another, e. g. (filter) paper, by rubbing with several solvents, e. g. acetone.
Optical absorption spectra of thin deposits on quartz plates were recorded on a Perkin-Elmer, Lambda 19 spectrophotometer. Photoluminescence spectra were recorded on a Jobin Yvon-Spek, Fluorolog 3 spectrophotometer, using the front-face collection method. All measurements were performed at room temperature.