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

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Organic-inorganic hybrid compounds based on lead halide units of the formula $(CH_3NH_3)_2$-$(CH_3C_6H_4CH_2NH_3)_2Pb_3(Br_xY_{1-x})_{10}$ (Y = 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 $(CH_3C_6H_4CH_2NH_3)_2MX_4$ (M = Pb, Sn; X = I, Br, Cl) behave as two-dimensional (2D) semiconducting systems, and those of the type $(CH_3NH_3)_{n-1}$ $(CH_3C_6H_4CH_2NH_3)_2M_nX_{3n+1}$ (n = 2: bilayer; n = 3: trilayer; $n \geq 3$: multilayer) behave as quasi-two-dimensional (q-2D) semiconducting systems, while those of the type $(CH_3NH_3)MX_3$ or $(CH_3NH_3)_{n-1}(CH_3C_6H_4CH_2NH_3)_2M_nX_{3n+1}$ with $n \gg 3$ behave as three-dimensional (3D) semiconducting systems. Investigations of the optical properties on single crystals of $(CH_3NH_3)_{n-1}$-$(CH_3C_6H_4CH_2NH_3)_2M_nX_{3n+1}$ 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 $(CH_3NH_3)MX_3$ [4, 5]. For example, single crystals or polycrystalline pellets of the 2D system $(CH_3C_6H_4CH_2NH_3)_2PbBr_4$ 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 $(CH_3NH_3)PbBr_3$ 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 $(CH_3NH_3)_2(CH_3C_6H_4CH_2NH_3)_2Pb_3Br_{10}$, (q-2D) and $(CH_3NH_3)PbBr_3$ (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 (CH_3NH_3)-$(CH_3C_6H_4CH_2NH_3)_2Pb_2Br_7$, exhibits a strong band at *ca.* 510 nm [7a], while the PL spectrum of a nanocrystalline sample of $CsPbBr_3$ (~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 $(CH_3NH_3)_2(CH_3C_6H_4CH_2NH_3)_2Pb_3(Br_xY_{1-x})_{10}$ (Y = Cl, I) as well as the preparation of similar compounds based on some other cations, *e. g.*, Cs^+, $C_{10}H_{21}NH_3{}^+$ and $C_6H_5CH_2CH_2NH_3{}^+$, 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-

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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 $(CH_3NH_3)_2$-$(CH_3C_6H_4CH_2NH_3)_2Pb_3Br_{10}$ 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 $PbBr_4$, Pb_2Br_7, Pb_3Br_{10}, and Pb_4Br_{13}, respectively. The PL spectrum shows a weak band at *ca.* 530 nm, which corresponds to the excitonic band of the (infinite) species $PbBr_3$ [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-wavelenths 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 ($CH_3C_6H_4CH_2NH_3^+$, $C_{10}H_{21}NH_3^+$, $C_6H_5CH_2CH_2NH_3^+$, *etc.*) and the number of layers ($n \geq 2$). 3D systems (*e. g.*, $CH_3NH_3PbBr_3$) 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.*, Cs^+, instead of $CH_3NH_3^+$). Fig. 2 shows the spectrum of $Cs_2(CH_3C_6H_4CH_2NH_3)_2Pb_3Br_{10}$, 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.

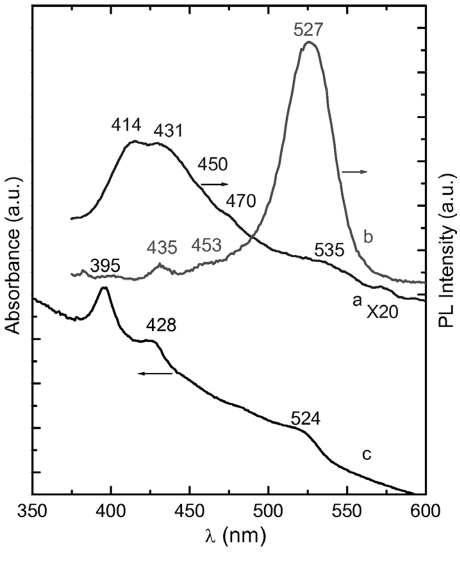

Fig. 1. PL (a, b) and OA (c) spectra of $(CH_3NH_3)_2(CH_3C_6$-$H_4CH_2NH_3)_2Pb_3Br_{10}$ obtained from melts, before (a) and after (b, c) grinding the sample; excitation 350 nm.

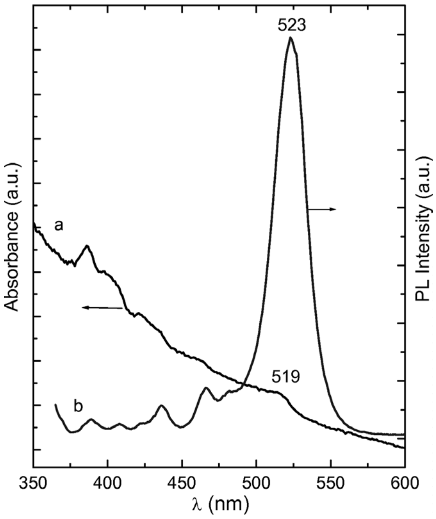

Fig. 2. OA (a) and PL (b) spectra of $Cs_2(CH_3C_6H_4$-$CH_2NH_3)_2Pb_3Br_{10}$, after grinding on a quartz plate; excitation 350 nm.

The strong PL band observed after grinding (G) of an infinite system (IS) $Pb_3Br_{10}^{4-}$ may be due to the formation of small particles (SP) of Pb Br_3^- in the organic matrix (*e. g.*, $CH_3NH_3^+$ and $CH_3C_6H_4CH_2NH_3^+$), according to Eq. 1,

$$Pb_3Br_{10}^{4-}\,(IS) \xrightarrow{G} 3\,Pb\,Br_3^-(SP) + Br^- \qquad (1)$$

or, generally, for any q-2D or 3D system, the formation

Table 1. Position (nm) of the PL band and the OA band edges of the compounds after grinding.

Compound	PL	OA	Prepared from	Refs.
$(CH_3NH_3)PbCl_3$	408	416	solution	[4]
$(CH_3NH_3)PbCl_3$	405	415	melt	this work
$(CH_3NH_3)_2(CH_3C_6H_4CH_2NH_3)_2Pb_3Cl_{10}$	403	410	melt	this work
$(CH_3NH_3)_2(C_9H_{19}NH_3)_2Pb_3Cl_{10}$	405	412	melt	this work
$(CH_3NH_3)_2(CH_3C_6H_4CH_2NH_3)_2Pb_3Br_2Cl_8$	423	435	melt	this work
$(CH_3NH_3)_2(CH_3C_6H_4CH_2NH_3)_2Pb_3Br_4Cl_6$	458	470	melt	this work
$(CH_3NH_3)_2(C_{10}H_{21}NH_3)_2Pb_3Br_4Cl_6$	456	468	melt	this work
$(CH_3NH_3)_2(CH_3C_6H_4CH_2NH_3)_2Pb_3Br_6Cl_4$	475	493	melt	this work
$(CH_3NH_3)_2(CH_3C_6H_4NH_3)_2Pb_3Br_8Cl_2$	505	515	melt	this work
$(CH_3NH_3)_2(C_{10}H_{21}NH_3)_2Pb_3Br_8Cl_2$	510	520	melt	this work
$(C_s)PbBr_3$	530	540	melt	this work
$(CH_3NH_3)PbBr_3$	510 – 530	520 – 540	melt	this work
$(CH_3NH_3)PbBr_3$	515 – 530	525 – 540	solution	[4, 9b]
$(CH_3NH_3)_2(CH_3C_6H_4CH_2NH_3)_2Pb_3Br_{10}$	513 – 523	520 – 525	solution	[8a, 9a]
$(H_3NH_3)_2(CH_3C_6H_4CH_2NH_3)_2Pb_3Br_{10}$	527	545	melt	this work
$(Cs)_2(CH_3C_6H_4CH_2NH_3)_2Pb_3Br_{10}$	523	530	melt	this work
$(CH_3NH_3)_2(C_9H_{19}NH_3)_2PbBr_{10}$	525	535	melt	this work
$(CH_3NH_3)_2(C_6H_5CH_2CH_2NH_3)_2Pb_3Br_{10}$	530	540	melt	this work
$(CH_3NH_3)_1(C_6H_5CH_2CH_2NH_3)_2Pb_2Br_7$	520	530	melt	this work
$(CH_3NH_3)_1(C_6H_5CH_2CH_2NH_3)_2Pb_2Br_7$	510	520	solution	[7], this work
$(CH_3NH_3)_1(C_9H_{19}NH_3)_2Pb_2Br_7$	520	530	melt	[5], this work
$(CH_3NH_3)_2(CH_3C_6H_4CH_2NH_3)_2Pb_3Br_8I_2$	595	610	melt	this work
$(CH_3NH_3)PbI_3$	750	760	melt	this work
$(CH_3NH_3)PbI_3$	753	765	solution	[4, 9b]
$(CH_3NH_3)_2(CH_3C_6H_4CH_2NH_3)_2Pb_3I_{10}$	720	730	melt	this work
$(CH_3NH_3)_1(CH_3C_6H_4CH_2NH_3)_2Pb_2I_7$	710	715	solution	[8a, 9b]

of MX_3^- particles, according to the Eq. 2 or 3 (see also refs. [7 – 9]).

$$M_nX_{3n+1}^{(n+1)}(\mathrm{IS}) \xrightarrow{\mathrm{G}} n\,MX_3^-(\mathrm{SP}) + X^- \tag{2}$$

$$MX_3^-\,(\mathrm{IS}) \xrightarrow{\mathrm{G}} MX_3^-\,(\mathrm{SP}) \tag{3}$$

The PL spectra of 2D systems, such as $(CH_3C_6H_4CH_2NH_3)_2PbBr_4$ [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 $(CH_3NH_3)_2(CH_3C_6H_4CH_2NH_3)_2Pb_3(Br_xY_{1-x})_{10}$, 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.* $Pb(Br_xY_{1-x})_3^-$, according to Eq. 4 or, generally, for any q-2D or 3D system according to Eq. 5.

$$\begin{aligned} &Pb_3(Br_xY_{1-x})_{10}^{4-}(\mathrm{SP}) \xrightarrow{\mathrm{G}} \\ &\quad 3\,Pb(Br_xY_{1-x})_3^-\,(\mathrm{SP}) + Br_xY_{1-x}^- \end{aligned} \tag{4}$$

$$\begin{aligned} &M_n(X_xY_{1-x})_{3n+1}^{(n+1)-}\,(\mathrm{IS}) \xrightarrow{\mathrm{G}} \\ &\quad nM(X_xY_{1-x})_3^-\,(\mathrm{SP}) + X_xY_{1-x}^- \end{aligned} \tag{5}$$

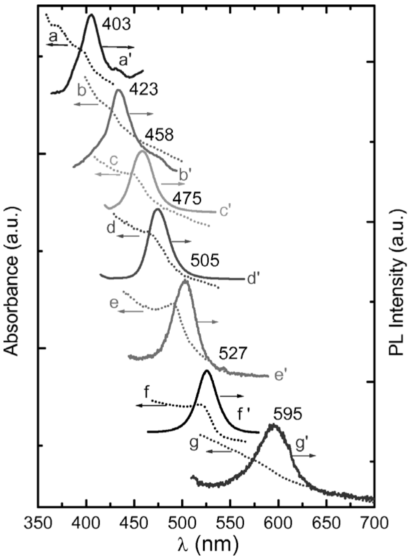

Fig. 3. OA (a, b, c, d, e, f, g) and PL (a′, b′, c′, d′, e′, f′, g′) spectra of some compounds of the formula $(CH_3NH_3)_2(CH_3C_6H_4CH_2NH_3)_2Pb_3(Br_xY_{1-x})_{10}$ after grinding, where $(Br_xY_{1-x})_{10}$ is Br_0Cl_{10} (a, a′), Br_2Cl_8 (b, b′), Br_4Cl_6 (c, c′), Br_6Cl_4 (d, d′), Br_8Cl_2 (e, e′), $Br_{10}Cl_0$ (f, f′) and Br_8I_2 (g, g′); excitation 350 (a′, b′, c′), 400 (d′, e′), 450 (f′), 500 nm (g′).

Fig. 3 shows the OA and PL spectra of some samples of the type $(CH_3NH_3)_2(CH_3C_6H_4CH_2$-

$NH_3)_2Pb_3(Br_xY_{1-x})_{10}$, 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 Br_xY_{1-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 Br_xCl_{1-x} (Fig. 3) obeys approximately the equation $\lambda_{PL} = 403 + 125\,x$ (nm). Also, it was observed that the position on the PL band does not depend of the nature of the cations (*e. g.*, $CH_3NH_3^+$, Cs^+, $CH_3C_6H_4CH_2NH_3^+$, $C_{10}H_{21}NH_3^+$, $C_6H_5CH_2CH_2NH_3^+$) 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 small particles of $PbCl_3$ (a, a′), $PbBr_{0.6}Cl_{2.4}$ (b, b′), $PbBr_{1.2}Cl_{1.8}$ (c, c′), $PbBr_{1.8}Cl_{1.2}$ (d, d′), $PbBr_{2.4}Cl_{0.6}$ (e, e′), $PbBr_3$ (f, f′) and $PbBr_{2.4}I_{0.6}$ (g, g′) formed after grinding. The shape of these particles, coming from the q-2D parents, is expected to be different from that of particles coming from the corresponding 3D ones, because of the differences in the structure of q-2D and 3D systems (see for example refs. [1, 5, 6]). In the cases of the compounds rich in iodine as well as the tin analogs, the results are qualitatively the same, but some additional bands are observed, because of the decomposition of the compounds in air [6] and/or the formation of mixed-valent hybrids [12a]. The tunability of PL and OA bands in the organic-inorganic hybrid systems described herein is similar to that observed for inorganic semiconductor quantum dots, such as small particles of $CdSe_xS_{1-x}$ or $Zn_xCd_{1-x}S$ (see refs. [6, 16, 17] and refs. cited therein). The results concerning the PL bands from the ground samples indicate that the new organic-inorganic hybrid compounds could be candidates for potential applications, such as scintillators [11b] and microcavities [13d].

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 M_nX_{3n+1} (IS) act as donors and particles obtaind from M_nX_{3n+4} (IS) or MX_3 (IS) as acceptors.

Experimental Section

Starting materials

The following starting materials were used without further purification: PbI_2 (Alfa Aesar 12724), $PbBr_2$ (Alfa Aesar 10720), $PbCl_2$ (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 H_3PO_2 50 % (Fluka 94210). The precursors CH_3NH_3X, $CH_3C_6H_4CH_2NH_3X$, $C_{10}H_{21}NH_3X$ and $C_6H_5CH_2CH_2NH_3X$ (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

$$(CH_3NH_3)_2(CH_3C_6H_4CH_2NH_3)_2Pb_3(Br_xY_{1-x})_{10}$$

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 $(CH_3NH_3)_2(CH_3C_6H_4CH_2NH_3)_2Pb_3Br_{10}$, 110 mg (0.3 mmol) of $PbBr_2$, 22.6 mg (0.2 mmol) of CH_3NH_3Br and 40.6 mg (0.2 mmol) of $CH_3C_6H_4NH_3Br$ were used. Another example is the preparation of $(CH_3NH_3)_2(C_6H_4CH_2NH_3)_4Pb_3Br_6Cl_4$, by using 110 mg (0.3 mmol) of $PbBr_2$, 13.5 mg (0.2 mmol) of CH_3NH_3Cl and 31.4 mg (0.2 mmol) of $CH_3C_6H_4CH_2NH_3Cl$. This compound could be prepared by using $PbCl_2$ and $PbBr_2$, instead of $PbBr_2$ only, and organic ammonium bromides, instead of chlorides. During the mixing of the starting materials, a solvent-free reaction [18] or the intercalation of PbX_2 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 that from solutions. The spectroscopic data (OA and PL) of a single crystal of $(CH_3C_6H_4CH_2NH_3)_2PbBr_4$ 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.

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.

Apparatus

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-Spex, Fluorolog 3 spectrophotometer, using the front-face collection method. All measurements were performed at room temperature.

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