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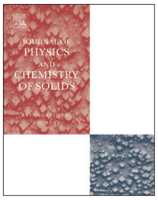

Effects of organic moieties on the photoluminescence spectra of perovskite-type tin bromide based compounds

George C. Papavassiliou [a,*], Maria-Sofia Vidali [a], Georgia Pagona [a], George A. Mousdis [a], Nikolaos Karousis [a], Ioannis Koutselas [b]

[a] Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48, Vassileos Constantinou Avenue, Athens 116-35, Greece
[b] Materials Science Department, School of Natural Sciences, University of Patras, Patras 265-04, Greece

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ABSTRACT

The photoluminescence (PL) and optical absorption (OA) spectra of some compounds of the type (SC)$SnBr_3$, $(BC)_2SnBr_4$, and (SC)$(BC)_2Sn_2Br_7$ (where SC is $CH_3NH_3^+$ or Cs^+; BC is $C_4H_9NH_3^+$, $CH_3C_6H_4CH_2NH_3^+$, $C_{12}H_{25}NH_3^+$, $C_{18}H_{37}NH_3^+$ and 1-naphthylmethyl ammonium group), in the forms of thin deposits on several substrates, are investigated. Generally, using the 350 nm as excitation line, the obtained PL spectra of compounds of the type $(BC)_2SnBr_4$ with short alkyl chain-length in the alkyl ammonium moiety, show broad and strong bands. For example, the PL spectra of compound $(C_4H_9NH_3)_2SnBr_4$ exhibit a weak band at *ca* 475 nm, attributed to free-excitons and a broad and strong band at *ca* 570 nm, attributed to radiative decay of self-trapped excitons in the inorganic moiety. This is a bright yellow-orange emission, which can be seen by naked eye, even at room temperature. In the case of the compounds with long alkyl chain-length in the alkyl ammonium moiety, the PL spectra are dominated by an excitonic band, which occurs close to the corresponding fundamental OA edge. The PL spectrum of (1-naphthylmethyl ammonium)$_2SnBr_4$ shows the strong red band with main maxima at *ca* 603 and 642 nm, arising from tetramers of naphthyl moieties. Also, the PL spectra of the compounds of the type (SC)$SnBr_3$ and (SC)$(BC)_2Sn_2Br_7$, after grinding, show strong bands at 600–620 nm.

1. Introduction

During the last five decades, a number of scientific papers concerning syntheses, structures and properties of perovskite-type compounds with general formulas (SC)MX_3 and $(SC)_{n-1}(BC)_2M_4 \times {}_{3n+1}$ (where SC is $CH_3NH_3^+$, Cs^+, K^+ *etc.*; BC is alkyl ammonium, arylalkyl ammonium, *etc.* group; M is Pb, Sn, Ge, Hg *etc.*; X is Cl, Br, I, and $n=1$, 2, 3 *etc.*) have been published so far (see for instance [1–32]). Only a few of them are based on tin-halide compounds (see for example [1,3,5,13–15,21]). The reported compounds were characterized as three-dimensional (3D) semiconductors of the type (SC)MX_3, two-dimensional (2D) or monolayer ($n=1$) of the type $(BC)_2MX_4$ semiconductors and quasi-two-dimensional (q-2D) bilayer or multilayer ($n \geq 2$) semiconductors. Moreover, some compounds with MX_3 units have been characterized as one-dimensional (1D) semiconductors. The position of the spectral bands occur in the order $\lambda(3D) > \lambda(2D) > \lambda(1D)$, where λ is the wavelength. They can be prepared from their solutions or from melts in single crystal form or in particulate forms (grinding powders, suspensions in several solvents, and dispersions in several matrices) [6,7,30–37]. In the particulate forms, the products of the reactions are in equilibrium with their precursors [8–10], *e.g.* as following:

$$\begin{aligned}&(CH_3NH_3)PbX_3 + (C_4H_9NH_3)_2PbX_4\\ &\Leftrightarrow (CH_3NH_3)(C_4H_9NH_3)_2Pb_2X_7 \quad \text{or} \quad 3D + 2D\\ &\Leftrightarrow q\text{–}2D\end{aligned}$$

Changes in the color and spectra have been observed during the transformation from one phase to another. For example, single crystals of $(CH_3NH_3)(C_4H_9NH_3)_2Pb_2Br_7$ are yellow in color with a weak luminescence. After grinding, they give a powder with a strong green luminescence [6,7,10,11]. This is due to the formation of (SC)$PbBr_3$ particles [10,11], and the strong luminescence (around 520 nm) is arising from the free-excitons of inorganic moiety [10]. Also, it has been discovered that the intensity of this excitonic band and luminescence of organic moieties depend on the nature of BC [9,17–20,22,23]. When BC is a conjugated group and the excitonic levels of inorganic moiety lie energetically in between the S_1 and T_1 states of organic moiety, energy transfer from excitons of inorganic to T_1 state of organic takes place and

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[*] Corresponding author. Fax: +30 210 7273794.
E-mail addresses: pseria@eie.gr (G.C. Papavassiliou), svidali@cc.uoi.gr (M.-S. Vidali), gpagona@eie.gr (G. Pagona), gmousdis@eie.gr (G.A. Mousdis), nkarou@eie.gr (N. Karousis), ikouts@upatras.gr (I. Koutselas).

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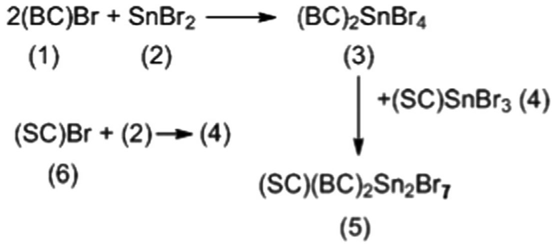
enhanced photoluminescence can be observed [8,9] (see also [31,32]). In the case of lead-halide materials, it has been found that several factors, such as the alkyl and arylalkyl chain-length in BC, play important role in the construction of the interlayer space and in the intermolecular interactions, which lead to several optical affects [17–22]. These compounds exhibit tunable properties in a wide range and they are suggested as candidate materials of several optical, electronic and optoelectronic applications *e.g.*, components of solar cells [12–21,24–29,32].

In this paper, the effects of organic moiety on the photoluminescence spectra of (SC)$SnBr_3$, $(BC)_2SnBr_4$ and (SC)$(BC)_2Sn_2Br_7$ (where SC is $CH_3NH_3^+$ or Cs^+; BC is, $C_4H_9NH_3^+$, $CH_3C_6H_4CH_2NH_3^+$, $C_{12}H_{25}NH_3^+$, $C_{18}H_{37}NH_3^+$ and $C_{10}H_7CH_2NH_3^+$ *i.e.*, 1-naphthylmethyl ammonium) are described. In some cases, the photoluminescence (PL) spectrum is dominated by a broad and strong band and the emission can be seen by naked eye. Also, the optical absorption (OA) spectra are described, for comparison.

2. Experimental

For the preparation of the required compounds, the following commercially available starting materials were used without further purification: Sn (MERCK 10786), $SnBr_2$ (ALFA 18808), $SnCl_2$ (FERAK 01663), HBr (ALDRICH 339345), CH_3NH_2 (ALDRICH 426466), $C_4H_9NH_2$ (ALDRICH 471305), $C_{12}H_{25}NH_2$ (ALDRICH 325163), $C_{18}H_{37}NH_2$ (ALDRICH 74350), $CH_3C_6H_4CH_2NH_2$ (ALDRICH 825606) and $C_{10}H_7CH_2NH_2$ (FLUKA 71020). The salts (SC)Br and (BC)Br were prepared easily by methods reported in [1,2,11]. The required compounds were prepared from their precursors, according to the following reactions:



Most of the samples of investigated materials were prepared by grinding the appropriate amounts of precursors in a agate mortar, followed by rubbing the sample on a substrate (quartz, glass, cellulose paper) at ambient conditions [10,37]. Thin deposits were also prepared from solutions (*e.g.* in acetone) or from melts [7]. In these cases, to minimize the influence of air (oxygen and water), the samples were prepared in an inert (Argon) atmosphere [39].

The spectra of freshly prepared samples were recorded at room temperature by instrumentation reported elsewhere [9,10,28].

3. Results and discussion

The starting material $SnBr_2$ is an anisotropic 3D semiconductor, and independently of the method of its preparation [33,38,39], is a white colored solid. It has been reported that the PL spectrum of $SnBr_2$ at low temperature values (*ca* 12 K) exhibits a band at *ca* 571 nm, which has been attributed to radiative decay of self-trapped excitons [27,33–35], and some weaker bands. The intensity of the 571 nm band decreases, when the sample is warmed above 50 K, and PL almost disappears at 100 K. Also, CH_3NH_3Br is a white colored solid, which does not show any PL band at room temperature. However, a mixture of CH_3NH_3Br and $SnBr_2$ becomes red in color after grinding, due to the formation of semiconductor $CH_3NH_3SnBr_3$ [11]. Fig. 1 shows that the PL and OA spectra of freshly prepared $CH_3NH_3SnBr_3$ differ from sample to sample, because of the particle size effect, as in the case of lead bromide analogs [6,8,10].

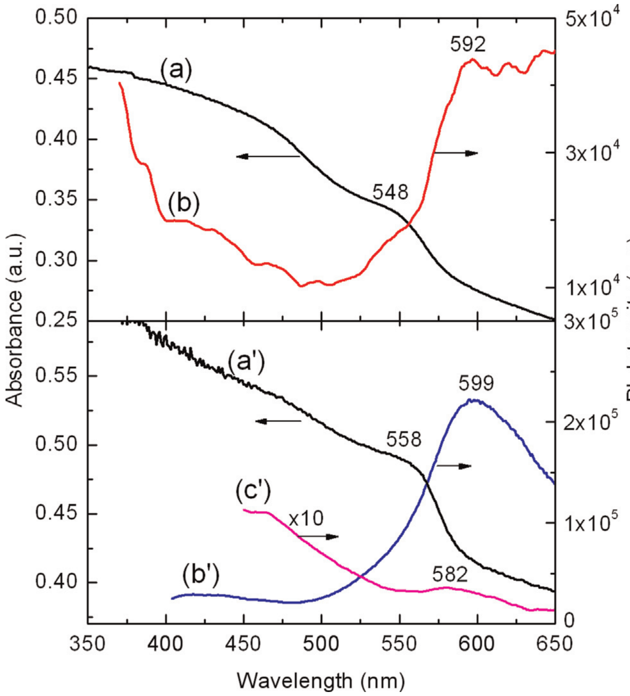


Fig. 1. Typical OA (a) and PL (b) spectra of freshly prepared $CH_3NH_3SnBr_3$, after grinding and rubbing the precursors on a quartz plate. Typical OA (a′) and PL (b′) spectra of $CH_3NH_3SnBr_3$ single crystals after grinding and rubbing on a quartz plate. Excitation 350 (b, b′) and 400 nm (c′).

The PL spectrum of a mixture of precursors CH_3NH_3Br and $SnBr_2$, after grinding and rubbing on quartz plates, shows a broad band with main maxima at 545, 592, 610 and 630 nm. The 545 nm band is attributed to free-excitons, in accordance to the position of OA fundamental absorption edge [1,2,11]. However, the PL (and OA) spectra of a thin deposit of $CH_3NH_3SnBr_3$, obtained from single crystals of materials, after grinding and rubbing on a quartz plate, are little different. With the 400 nm excitation the PL spectrum shows a relatively weak band at 582 nm, while the OA spectrum shows a shoulder at 558 nm, close to fundamental absorption edge [30]. The shoulder and the band are shifted to the shorter wavelengths after extensive grinding of the materials, as in the case of $CH_3NH_3PbBr_3$ [6]. This is due to the confinement of free-excitons to the small in size particles of materials. In a few words, the shape and intensity of PL and OA spectra of $CH_3NH_3SnBr_3$, varies from sample to sample (see also [1,2]) and the perfect reproducibility is difficult at ambient conditions. However, with 350 nm excitation the PL spectrum is dominated by a broad and strong band at *ca* 599 nm, attributed to the radiative decay of self-trapped excitons of $SnBr_3$ moiety, as it is observed from other semiconductors [11,33–36]. The differences in the position and the intensity between the PL spectra b′ and c′, perhaps is a consequence of the amount of energy transfer of several states to the trapped exciton state.

The compounds based on $C_2H_5NH_3$ and $C_3H_7NH_3$ do not exhibit strong PL bands, arising from excitonic states, but behave as 1D semiconductors of the type (BC)MX_3 [4–7].

In the cases of 2D systems of the type $(BC)_2SnBr_4$, in which the big cation (BC) is an alkyl ammonium $CH_3(CH_2)_nNH_3^+$ ($n \geq 3$) or arylalkyl ammonium $Ar(CH_2)_nNH_3^+$ group, the behavior is more explicable than that observed in 3D (and 1D) compounds. The PL and related properties do not depend on the particle size of the samples, even for suspensions [10,11]. They depend on the number