SOME ORGANIC-INORGANIC HYBRID SEMICONDUCTORS OBTAINED FROM MELTS

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During the last ten years, a number of three- and low-dimensional organic-inorganic hybrid semiconductors based on metal halide units have been prepared and (for some reviews see [1-3]). It has been found that these compounds could be used as elements in nonlinear optical devices [4], light emitting diodes [5], optical microcavities [6] and as channels in thin-film field effect transistors [7]. Mainly, the structural, optical and related properties of compounds, crystallized or deposited on substrates from their solutions in several solvents, have been reported [1-3, 8-14]. There is only little information on properties of hybrid compounds obtained from melts [12]. Very recently, a number of compounds have been prepared from melts and characterized crystallographically [15]. The compounds $[CH_3C_6H_4CH_2NH_3]_2SnI_4$, $[CH_3C_6H_4CH_2NH_3]_2PbI_4$, $[CH_3C_6H_4CH_2NH_3]_2PbBr_4$, $[CH_3C_6H_4CH_2NH_3]_2PbCl_4$, $[C_6H_5(CH_2)_2NH_3]_2PbI_4$, $[C_6H_5(CH_2)_4NH_3]_2PbI_4$, $[C_4H_9NH_3]_2PbBr_4$, have been prepared from melts into glass tubes and found to be two-dimensional (2D) compounds, *i.e.*, isostructural to those obtained from solutions.

In this paper, the sample preparation of these compounds from melts as well as their optical absorption (OA), photoluminescence (PL), photoluminescence excitation (PLE) and photoconductivity (PC) spectra are described. The results are compared to those obtained from solutions.

The samples were prepared in an inert (*e.g.*, in Ar) atmosphere and/or in the ambient atmosphere (*i.e.*, in air). Finely grinded powders consisting of the appropriate amounts of the starting materials, *i.e.*, alkylammonium or benzylammonium halides and MX_2 (M=Sn, Pb; X=I, Br, Cl), were prepared firstly. The powders were transferred to glass tubes or on quartz plates and heated at the melting point temperatures of the organic components. The inorganic component is dissolved first in the organic melt and immediately, the hybrid is crystallized. If the organic component is in excess of the inorganic one, small crystals of the hybrid are obtained after melting, slow cooling and washing with *e.g.*, CH_2Cl_2. For the preparation of the films, a rolling pin-like tube from

A. Graja et al. (eds.),
Molecular Low Dimensional and Nanostructured Materials for Advanced Applications, 319–322.

glass was used to attach the melts on the quartz plates. Thus, homogeneous deposits were obtained after cooling. The deposits on quartz plates were used for the observation of the OA, PL and PLE spectra. Thin deposits in between the gaps of two gold-electrodes fixed on bakelite substrates were prepared by a similar way using a hot tip to melt the powders. These deposits were used for the observation of PC (and PL) spectra. The obtained samples were characterized by powder X-ray diffraction. Only, the ambient conditions OA, PL, PLE and PC spectra were recorded by instrumentation described elsewhere [13].

Fig. 1. shows the OA and PL spectra of $[CH_3C_6H_4CH_2NH_3]_2SnI_4$, $[CH_3C_6H_4CH_2NH_3]_2PbI_4$, $[CH_3C_6H_4CH_2NH_3]_2PbBr_4$, $[CH_3C_6H_4CH_2NH_3]_2PbCl_4$ deposited on quartz plates from melts, in an inert atmosphere. Also, Fig. 2 shows the OA, PL and PC spectra of $[C_6H_5(CH_2)_2NH_3]_2PbI_4$ samples obtained from melts. In all cases, the spectra show (sharp) excitonic bands of which the position, shape and intensity depend on the nature of M and X.

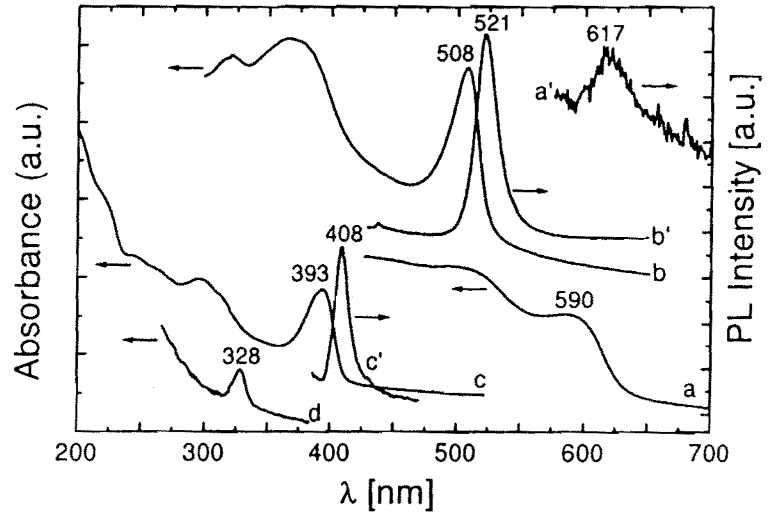

Figure 1. OA(a, b,c,d) and PL (a',b',c') spectra of $[CH_3C_6H_4CH_2NH_3]_2SnI_4$ (a,a'), $[CH_3C_6H_4CH_2NH_3]_2PbI_4$ (b,b'), $[CH_3C_6H_4CH_2NH_3]_2PbBr_4$ (c,c'), $[CH_3C_6H_4CH_2NH_3]_2PbCl_4$ (d) thin deposits obtained from melts.

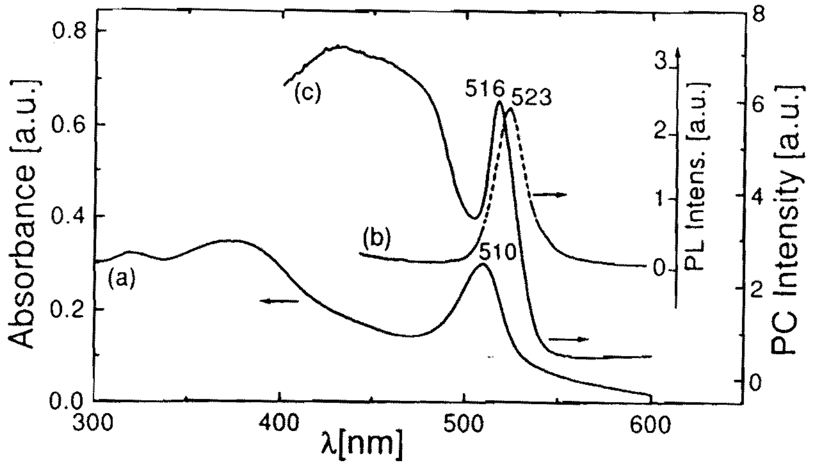

Figure 2. OA (a), PL (b) and PC (c) spectra of $[C_6H_5CH_2CH_2NH_3]_2PbI_4$ samples obtained from melts.

The spectra were found to be identical to the corresponding spectra of thin films obtained from solutions (see [10,12,13]). However, the excitonic PC bands of samples obtained from melts were found to be more intense and sharper than those obtained from solutions. Similar results were obtained from some other 2D compounds. The OA, PL and PC excitonic peak positions of some compounds obtained from melts and solutions are listed in Table 1. Fig. 3 shows the PL and PC spectra of $[CH_3C_6H_4CH_2NH_3]_2PbI_4$ and $[C_6H_5CH_2CH_2NH_3]_2PbI_4$ samples prepared from melts in an inert atmosphere and in air.

Table 1. Excitonic PL, OA, PC peak positions (nm) of some organic-inorganic hybrids

Compound	PL (M)	OA (M)	PC (M)	PL (L)	OA (L)	PC (L)
$[CH_3C_6H_4CH_2NH_3]_2SnI_4$	617	590	600	610	588	604
$[CH_3C_6H_4CH_2NH_3]_2PbI_4$	521	508	520	527	515	535
$[CH_3C_6H_4CH_2NH_3]_2PbBr_4$	408	393	410	411	409	409
$[CH_3C_6H_4CH_2NH_3]_2PbCl_4$	335	328		335	328	
$[C_6H_5(CH_2)_2NH_3]_2SnI_4$	620	590	620	624	586	620
$[C_6H_5(CH_2)_2NH_3]_2PbI_4$	523	510	516	518	511	525
$[C_6H_5\,(CH_2)_4NH_3]_2PbI_4$	506	484		510	485	
$[C_4H_9NH_3]_2PbBr_4$	417	403	413	415	403	409

PL(M), OA(M) and PC(M) are the PL, OA and PC peaks of compounds prepared from melts, while PL(L), OA(L) and PC(L) the peaks of compounds prepared from solutions, respectively.

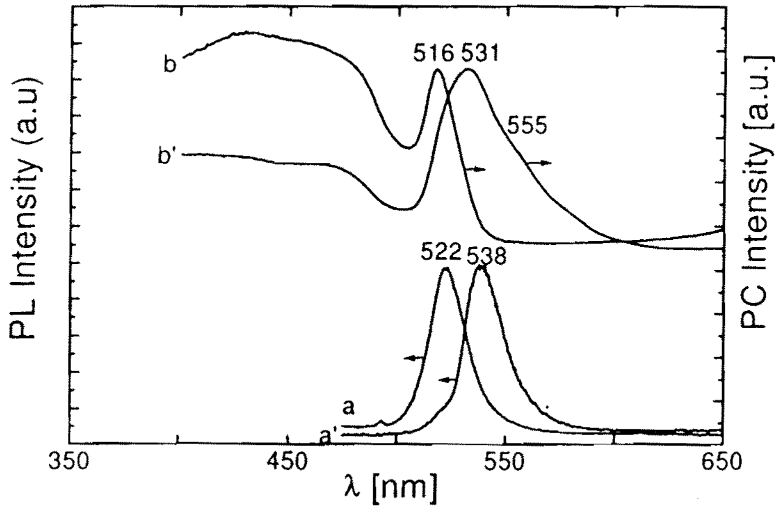

Figure 3. PL (a, a') and PC (b, b') spectra of $[CH_3C_6H_4CH_2NH_3]_2PbI_4$ (a, a') and $[C_6H_5CH_2CH_2NH_3]_2PbI_4$ (b, b') samples prepared from melts in an inert atmosphere (a, b) and in air (a', b')

One can see that, instead of the (free) exciton PL and PC peaks (522 and 516nm), some new peaks are observed at longer wavelengths (538, 531 and 555nm), arising from the bound exciton states and/or from impurity states.

The spectra of $PbBr_4$ and $PbCl_4$ containing samples prepared in air are almost the same as the corresponding spectra of the samples prepared in an inert atmosphere. The reason is that the $PbBr_4$ and $PbCl_4$ based compounds are stable in air, independently of the method of preparation. Weak bound-exciton peaks were observed in the air prepared samples at low temperatures, only.

The quasi-2D compounds $(CH_3NH_3)_{n-1}[CH_3C_6H_4CH_2NH_3]_2Pb_nBr_{3n+1}$, $(CH_3NH_3)_{n-1}[C_6H_5(CH_2)_2NH_3]_2Pb_nBr_{3n+1}$, and $(CH_3NH_3)_{n-1}[C_4H_9NH_3]_2Pb_nBr_{3n+1}$ ($n \geq 3$) obtained from melts exhibit weak OA bands at *ca* 473-512 nm and strong PL bands at ca 504 - 518 nm, as in the cases of compounds obtained from solutions [10,13].

It is clear that the optoelectronic behavior of organic-inorganic hybrid semiconductors obtained from melts is the same as that of the semiconductors obtained from solutions. Consequently, an alternative method, *i.e.*, that from melts, could be applied for the construction of optoelectronic devices [15]. By this method, instead of that from solutions, the problems arising from pinholes and exclusive solvents could be avoided [15].

References

1. Ishihara, T. (1995) in T. Ogawa and Y. Kanemitsu (eds.), *Optical Properties of Low-Dimensional Materials*, World Science, Singapore, pp. 288-339.
2. Papavassiliou, G.C. (1997) *Progr. Solid State Chem.* **25**, 125.
3. Mitzi, D.B. (1999) *Progr. Inorg. Chem.* **48**, 1.
4. Kondo, T., Iwamoto, S., Hayase, S., Tanaka, K., Ishi, J., Mizuno, M., Ema, K. and Ito, R. (1998) *Sol. State Commun.* **105**, 503.
5. Hattori, T., Taira, T., Era, M., Tsutsui, T. and Saito, S. (1996) *Chem. Phys. Lett.* **254**, 103; Gebauer, T. and Schmid, G. (1999) *Z. Anorg. Allg. Chem.* **625**, 1124; Chondroudis, K. and Mitzi, D.B. (1999) *Chem. Mater.* **11**, 3028.
6. Fujita, T., Sato, Y., Kuitani, T. and Ishihara T. (1998) *Phys. Rev. B* **57**, 12428.
7. Kagan, C.R., Mitzi D.B. and Dimitrakopoulos C.D. (1999), *Science* **286**, 945.
8. Mousdis, G.A., Papavassiliou, G.C., Raptopoulou, C.P. and Terzis, A. (2000) *J. Mater. Chem.* **10**, 515; Papavassiliou, G.C., Mousdis, G.A., Terzis, A. and Raptopoulou, C.P. (1999), *Z. Naturforsch.* **54b**, 109.
9. Papavassiliou, G.C., Mousdis, G.A., Raptopoulou, C.P. and Terzis, A. (1999) *Z. Naturforsch.* **54b**, 1405.
10. Papavassiliou, G.C., Mousdis, G.A., Raptopoulou, C.P. and Terzis, A. (2000) *Z. Naturforsch.* **55b**, 536.
11. Papavassiliou, G.C., Mousdis, G.A., Koutselas, I.B., Raptopoulou, C.P., Terzis, A., Kanatzidis, M.G. and Axtell III, E.A. (1998) *Adv. Mater. Opt. Electron.* **8**, 263; Papavassiliou, G.C., Mousdis, G.A. and Koutselas, I.B. (1999) *Adv. Mater. Opt. Electron.* **9**, 265; (2001) *Ibid.*, in press.
12. Papavassiliou, G.C., and Koutselas, I.B. (1995) *Synth. Metals* **71**, 1713; Papavassiliou, G.C., Patsis, A.D., Lagouvardos, D.J. and Koutselas, I.B. (1993) *Ibid.* **55-57**, 3889.
13. Papavassiliou, G.C., Mousdis, G.A. and Koutselas, I.B. (2001) *Synth. Metals* **121**, 1339; (2001) *Chem. Monthly* **132**, 113; (2001) *Int. J. Modern Phys. B*, in press.
14. Braun, M., Tuffentsammer, W., Wachtel, H. and Wolf, H.C. (1999) *Chem. Phys. Lett.* **303**, 157; (1999) **307**, 373; Era, M., Maeda, K. and Tsutsui, T. (1998) *Ibid.* **296**, 417; Mitzi, D.B., Chondroudis, K. and Kagan, C.R. (1999) *Inorg. Chem.* **38**, 6246.
15. Papavassiliou, G.C., Terzis, A. Mousdis, G.A. and Papaioannou, G.J., *Private Commun.*