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Raman and photoluminescence studies on intercalated lead iodide with pyridine and iodine

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Intercalated PbI_2 compounds were prepared by exposing crystalline films and crystalline powders of lead iodide to pyridine or iodine vapor at room temperature. Correlated studies of optical absorption, Raman scattering and low temperature photoluminescence (PL) reveal different properties in comparison with those of pure crystalline PbI_2 powder. Depending of the nature of intercalated molecules (organic or inorganic) the basic semiconducting properties of PbI_2 are dramatically modified. The main signature of iodine intercalated PbI_2 consists in a luminescence band peaking at 2.24 eV appearing at 77 K under 350 nm excitation light. In the case of pyridine intercalated PbI_2 a new intense band at about 3.3 eV in the absorption spectrum is observed. The the PL spectra of pyridine intercalated PbI_2 at 77 K change substantially when the excitation wavelength. The Raman spectra confirm the presence of pyridine between the PbI_2 layers.

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1. Introduction

The intercalation of layered materials with different molecules or atoms has become of great interest for the fundamental researches and for the technological applications. The properties of the new materials obtained by the intercalation process can be tuned by the proper choice of host-guest system. The intercalation imposes on the one hand to preserve in the host network the strong intra-layer bonds and on the other hand a diffusion process that manages the insertion in the crystalline structure, between the layers, of guest molecular or atoms species.

Among the layered materials, the PbI_2 as direct gap semiconductor focused the attention of researchers. In the bulk form, the structure of PbI_2 is featured by a strong intralayer chemical bonds and a weak interlayer interaction driven by van der Waals forces [1]. Each molecular layer is formed by a plane of metal atoms sandwiched between two planes of hexagonally arranged iodide atoms.

Alike of any semiconductor, in PbI_2 the energetic levels associated to the electrons density from the valence band result from a hybridization process of the electronic levels of the constituting ions. Thus the top of valence band is formed by an admixture of the 6*s* level of Pb^{2+} with a 5*p* level of I^- [2-4]. The lowest energy of the conduction band is built up to cation 6*p* state [2-5]. This means that the excitons near the fundamental absorption edge have a cationic character. By intercalation of different foreign molecules or atoms between the interlayer van der Waals spaces a lattice expansion along the *c* axis takes place and the two-dimensional connectivity of the original lamellar structure is destroyed. As a consequence the uppermost valence band is modified, i.e. the contribution of the 5*p* states of I^- ion is reduced and the $6s\rightarrow6p$ transition of Pb^{2+} acquires the feature of an intra-ion transition. In the case of PbI_2 intercalated with different molecules: hydrazine [5-7], aniline [8, 9] and ammonia [9] a shift of the cationic absorption band to higher energies was observed. Recently we have demonstrated that the ammonia intercalated PbI_2 is characterized by an intense broad emission band peaking at about 2.23 eV as signature in the photoluminescence spectra [10]. Also in the case of ammonia intercalated PbI_2, the increase of the distance between the layers has as result the appearance in the Raman spectrum of new sharp low-frequency lines placed below 100 cm^{-1} [9, 10]. The pyridine intercalated PbI_2 is regarded as a coordination compound resulting from a reaction between solid PbI_2 and the vapor of pyridine [11]. After reaction with organic vapors, the lead atom is six coordinated by two ligand nitrogen atoms and four iodides, bridged pair-wise to neighbouring lead atoms, forming an one-dimensional structure *c*-axis elongated.

The goal of this paper is to perform a comparative study of intercalated PbI_2 with pyridine and iodine corroborating the data obtained by optical absorption, Raman scattering and low temperature photoluminescence.

2. Experimental

In this work we used two kinds of samples: micrometric crystalline powder and crystalline films of PbI_2. The crystalline powder was obtained by mechanical crumbling of a PbI_2 single crystal grown from the melt. The films of lead iodide were made by vacuum evaporation and deposited on quartz substrates. Intercalation was achieved by exposing the films and powders samples to iodine or pyridine vapours at room temperature. As viewing fact one notice that the yellow

PbI_2 film and powder exposed to pyridine vapours, become colourless. The film returns partially yellow after removal from the solvent vapors. The dramatic changes are observed also to powder. The PbI_2 bright yellow powder change colour: white in the case of pyridine or dark yellow after exposure to iodine vapors.

Optical absorption spectra were recorded in the range 200-800 nm using a Perkin-Elmer spectrophotometer. The films allowed optical transmission data to be taken over a reasonable range of optical energies. All absorption spectra were measured at room temperature and baseline corrected.

The Raman studies were performed at room temperature under 1064 nm excitation wavelength using a FT Raman Bruker RFS 100 spectrophotometer.

The PL spectra at liquid nitrogen temperature (LNT) were recorded using a Horiba Jobin Yvon Fluorolog 3-22 spectrofluorimeter. The reported PL spectra are not corrected with spectral response of diffraction gratings and quantum efficiency of photomultiplier.

3. Results and discussion

Optical absorption spectra of the PbI_2 thin film before intercalation, during intercalation and after des-intercalation with pyridine are shown in Fig.1. The absorbency at about 2.49 eV indicates the band edge of PbI_2. Upon pyridine intercalation, this absorbency decreases for longer time exposure and additionally the optical spectra reveal a new intense absorption band around 3.34 eV (Fig. 1 b-f). Such a shift, already reported in papers having as topic the intercalation of PbI_2 with aniline [5-7] and hydrazine [8] was explained by the changes in the PbI_2 electronic band structure due to the interaction of host layered material with the guest molecules. An interaction between lead iodide and pyridine leading to the formation of a weakly coordination complex which can be easily thermally decomposed to yield starting products is reclaimed also in Ref. [11]. Thus the absorption band peaking at about 3.34 eV is a characteristic of adduct formed by lead iodide with pyridine molecules.

The optical data obtained for the PbI_2 film removed from the solvent vapours sustained the presumption that in our experiment a des-intercalation process takes place. In the optical absorption spectrum (Fig. 1g) the recovery process of PbI_2 is signalled by the reappearance of the band at 2.49 eV typical for the PbI_2 edge absorption.

As supplementary fact it has to be noticed that the optical spectrum of iodine intercalated PbI_2 is basically similar with that of PbI_2 thin film, no modification being observed after 4 weeks exposing time.

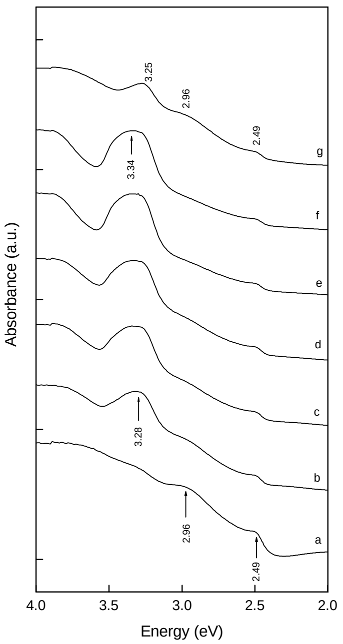

Fig. 1. The optical absorption spectra for PbI_2 thin film before intercalation (a), during intercalation (film exposed to the pyridine vapors for 3 days (b), 1 (c), 2 (d), 3 (e) and 4 (f) weeks) and after de-intercalation (g).

Fig. 2 illustrates how different are the Raman spectra recorded on PbI_2 crystalline powder (Fig.2A), iodine intercalated PbI_2 (Fig.2B) and the pyridine intercalated PbI_2 (Fig.2C). The former presents the well-known Raman spectrum recorded on a PbI_2 crystalline sample cleaved from a melt-grown crystal [12]. In the Raman spectrum of iodine intercalated PbI_2 only a small shift of the band situated at 75 cm^{-1} to 73 cm^{-1} has to be noticed. A more consistent modification is observed on the Raman spectrum of pyridine intercalated PbI_2 (Fig.2C) that practically retains the PbI_2 crystal signature by the presence of weak bands situated at 75 and 96 cm^{-1} combined with new Raman bands appearing at about 88, 119 and 135 cm^{-1}. A first explanation for the appearance of these new bands is linked to a compression effect resulting from the penetration of the pyridine molecules between iodine layers which activate Raman vibration modes situated in the low–frequency range of the spectrum. As in a previous paper the same effect was observed for the ammonia or polymer intercalated PbI_2 [10]. Another effect resulting from the formation of a coordination complex between PbI_2 and pyridine can be considered too. Up to now, as general signature in the Raman spectra of PbI_2 intercalated with different molecules is a strong Raman line situated at 30 cm^{-1} [10]. The interaction between pyridine and PbI_2 host lattice, for short the presence of pyridine between the PbI_2 layers, is noticed also by a small up-shift of the band situated at 992 cm^{-1} and the splitting of the band at 3057 cm^{-1}. More details concerning this fact will be found in a for-coming paper.

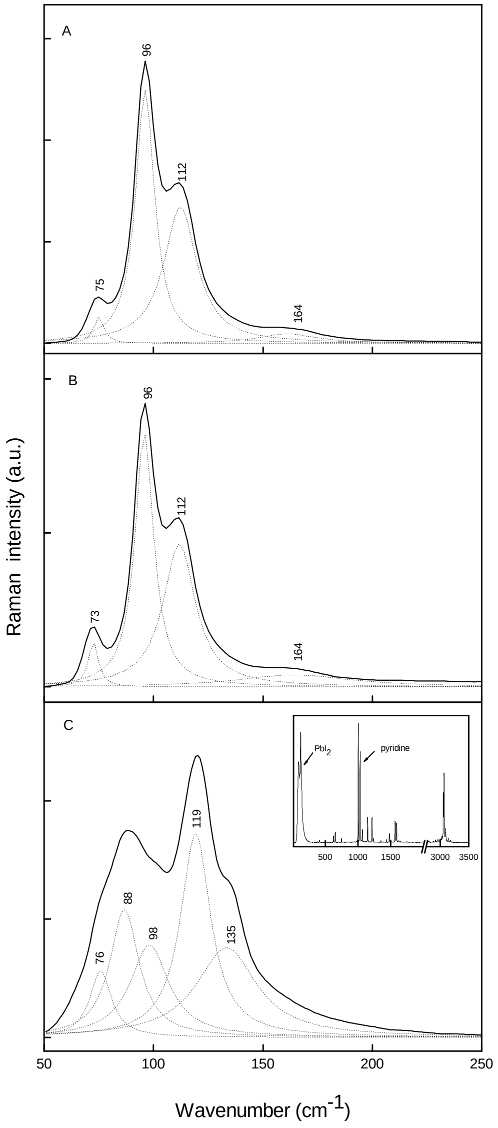

Fig. 2. Raman spectra at 1064 nm excitation wavelengths of PbI_2 crystalline powder (A), iodine intercalated PbI_2 (B) and pyridine intercalated PbI_2 (C).

The photoluminescence spectra of the PbI_2 intercalated with pyridine or iodine disclose different signatures depending on the intercalate type and excitation wavelength (Fig. 3). Under excitation light of 435 nm the PbI_2 crystalline powder display a PL spectrum (Fig. 3A) containing an intense excitonic emission band, with the maximum around of 2.49 eV, associated to the transition $3P_1 \rightarrow 1S_0$ of the Pb^{2+} and another two bands centred at 2.40 eV and 2.05 eV, labelled the D and G band, respectively [13]. The D band is linked to the volume properties. The wide and intense G band originates in a radiative electron-hole recombination process involving surface trapping levels [14]. Another band peaking around 1.75 eV related also of the surface defects characterizes the PL spectrum of PbI_2 crystalline powder. At the same excitation light the iodine intercalated PbI_2 (Fig. 3B, solid line) reveals a similar PL spectrum as PbI_2 crystalline powder. As normal difference resulting from the increased density of the volume defects induced by the diffusion of iodide into crystalline lattice an enhancement of the D band is observed. The effect is similar with that observed when the PbI_2 crystal is doped with the Ag^+ ions [15].

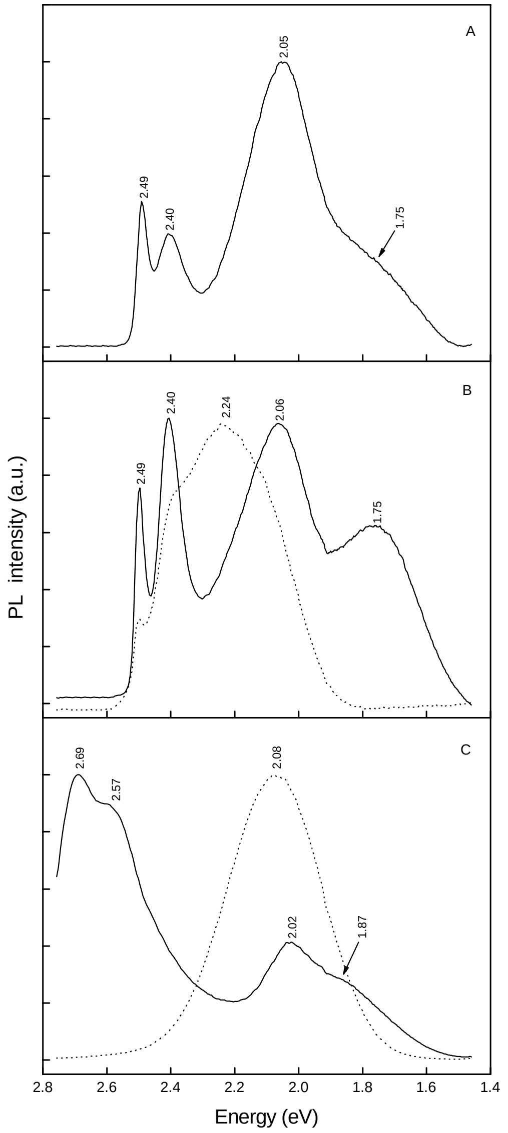

Fig. 3. Photoluminescence at liquid nitrogen temperature of PbI_2 crystalline powder (A), iodine intercalated PbI_2 (B) and pyridine intercalated PbI_2 (C); at two excitation wavelengths: 435 nm (solid lines) and 335 nm (dot lines).

The hypothesis is well sustained by the appearance of a wide band with the maximum at around 2.24 eV in the PL spectrum recorded at 335 nm excitation light (Fig. 3B, dot line). This band may have the same origin as the emission observed when the Pb^{2+} ions are dissolved in an alkali halide crystal [16]. It has to mention that other modifications are also noticed in the PL spectrum: the excitonic emission and the D band are very weak, the G band and the other band situated at 1.75 eV, are not more observed

For pyridine intercalated PbI_2 at 435 nm excitation light (Fig. 3C, solid line) the PL spectrum is dominated by a band with two components, one at 2.69 eV and another at 2.57 eV. We regard this band as a feature of the pyridine intercalated PbI_2 compound. A broad band peaking at 2.02 eV presenting a small asymmetry on the low energy side, disclosing a weak band at about 1.87 eV, is also presented in PL spectrum. Interesting is the total change of PL spectrum when the excitation is done at 335 nm (Fig. 3C, dot line), when it reveals only a broad and intense band with maximum at about 2.08 eV. A first attempt is to associate this band to a complex structure formed by pyridine molecules bound to the PbI_2 layers. More information regarding the origin of this complex band, situated at about 2.08 eV, will be furnished by luminescence decay studies which are in developing now.

4. Conclusions

We have studied by optical absorption, Raman scattering and photoluminescence at low temperature the intercalation of PbI_2 with iodine and pyridine. In the first case the diffusion of iodine molecules between PbI_2 layers generates defects in the crystal lattice similarly with a doping process. As distinct feature in the PL spectrum is a green emission observed predominantly when the excitation is done at higher energies (cca. 335 nm) at liquid nitrogen temperature. In the case of pyridine intercalated PbI_2 the mechanism of the intercalation process is much complicated. Additionally to a compression effect resulted from the penetration of the pyridine between iodine layers, the solvent molecules may react with the PbI_2 and formed a coordination complex. The Raman and PL spectra of the pyridine intercalated PbI_2 are very different with those of PbI_2 crystalline powder. Finally we demonstrated that by intercalation of different guest molecules the basic semiconducting properties of host PbI_2 are dramatically modified.

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