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On the optical properties of micro- and nanometric size PbI₂ particles

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Abstract

Scanning electron microscopy, Raman scattering, UV–VIS absorption spectroscopy and low temperature photoluminescence (PL) were used to examine small particles produced by the chemical reaction between Pb(NO₃)₂ and KI in different liquid media: water, methanol, ethanol and acetonitrile. By stoichiometric changes in the synthesis reaction, platelets of PbI₂ and rods probably of KPbI₃ are produced. Regardless of shape and size, these particles exhibit almost the same PL, which consists of two intense bands centred around the 2.5 (E band) and 2.0 eV (G band), in turn similar to that of a crystalline slide or a micrometric powder, both prepared from a PbI₂ single-crystal grown from the melt. Crystalline PbI₂ platelets exhibit an E band with two components, at 2.49 (E_F band) and 2.47 eV (E_T band), originating in the recombination of the free and trapped excitons produced by inter-band irradiation. A close relation between the enhancement of the E_T and G band reveals that they are linked to the surface defects. For the rod-like particles, the PL spectrum is somewhat similar to that of a Pb²⁺ ion introduced into an alkaline halide lattice, which as for any ns² ion displays two emission bands, A_T and A_X, whose correspondents are E and G bands.

1. Introduction

Today, in the materials science field, a great interest is shown in the quantum confinement effects generated in low-dimensional systems, and among these, the nanoparticles of various semiconductors are taken primarily into consideration. On the nanometric scale, the large ratio of surface area to particle volume strongly influences all electrical and optical properties, and for semiconductor materials the blue shift of the absorption edge is one of the most well known size-dependent phenomena. No less interesting is the study of nanophase materials

physically confined in various hosts. For this, the main problem is to produce nanoparticles with a narrow size distribution, uniformly distributed in the host matrix. Their shape can also be important for the generation of specific properties. Layered semiconductor compounds are well suited for the studies of anisotropic confinement along different crystallographic axes. Among these materials, a good candidate is PbI_2 , which has as its structural repeat unit a layer of lead, hexagonally packed, sandwiched between two layers of iodine ions. In the bulk, the PbI_2 crystal features a strong intralayer chemical bonding and a weak interlayer van der Waals interactions [1].

Lead iodide is a direct band gap semiconductor that at low temperature and excitation in the fundamental absorption band exhibits an intense excitonic photoluminescence (PL), at 2.5 eV (E band), accompanied by two weak additional emission bands centred at 2.44 and 2.07 eV, labelled the D and G band, respectively [2], whose intensities depend on the quality of the crystal. The D band links more to the volume properties, and the G to the surface quality of the crystal. The D band increases by doping the crystal with Ag^+ ions [3], and the G band depends more on the density mechanical defects, dislocations and grain boundaries [2]. The G band can be created and enhanced easily, up to two orders of magnitude, by pulse evaporation in vacuum at a temperature above 520 K, photolytical decomposition and mechanical scratching with an abrasive paper. Originating in a thin layer at the crystal surface, the G band disappears by the removal of the top layer of the sample, while the D does not. Photolytical generation of the G band indicates a stoichiometric modification, produced by a photodecomposition process that occurs on the crystal surface. Originally, the G band was explained as originating in aggregates of Pb^{2+} ions, perturbed by the vicinity of anionic vacancies thermal generated [2]. Recently, the same G band was reported in the emission spectrum of PbI_2 nanometre-sized particles [4–6], and its disappearance, after an annealing treatment of the PbI_2 nanoparticles under an iodine atmosphere, is a valuable argument that it has to be associated with stoichiometric defects [7].

In general, the main evidence for a quantum confinement effect generated in the nanometre-size particles is the optical absorption edge moving to the higher energy. The reported data regarding the properties of PbI_2 nanoparticles are very different; the main difference concerns the shift of the fundamental absorption edge, a small one of about 10 meV that increases reciprocally with the particle radius [5], and another, much greater, of 1.25 eV [7–10]. Since the same large and abrupt shift was also observed for BiI_3 particles, it was considered a general feature for small clusters of the layered semiconductors PbI_2 and BiI_3 [8]. Although, by transmission electron microscopy (TEM) or atomic force microscopy (AFM), convincing pictures of nanometric particles as platelets and rods were seen [5, 7, 8, 10], the great difference between the reported shift of the fundamental absorption edge has remained unexplained.

If the above data are regarded from the point of view of the procedure used for the preparation of PbI_2 nanoparticles, one find that a small blue shift of the absorption edge is observed systematically with samples prepared by the sol–gel technique [4–6], while a large blue shift seems to characterize the particles resulting from the chemical reaction of NaI or KI with $\text{Pb}(\text{NO}_3)_2$ in different solvents [7–11]. In this context, one can raise the question if the two preparation methods lead to the same type of particles. Recently, the yield of nanorod-like particles, whose optical properties are the same as those of an imperfect PbI_2 crystalline sample, i.e., a excitonic emission blue shifted with few millielectronvolts and a well developed G emission band has been reported [12]. From a crystallographic point of view these data are hardly comprehensible; PbI_2 , having a layered structure, must form by crystallization hexagonal platelets rather than rod-like particles. That is why we have thought that finding an explanation for these discrepancies is an exciting challenge.

In the following, we show that the large blue shift of the absorption edge, of about 1.25 eV, reported as a quantum confinement effect in the low-dimensional systems of PbI_2 , has to be

associated with the presence of rod-like particles which appear as other by-products from the reaction between Pb(NO₃)₂ and KI. The genesis of such rod-like particles, in addition to hexagonal platelets, is proved by scanning electron microscopy (SEM) pictures. The weight of platelets and rods can be modified by changing the liquid used as the host medium and/or the stoichiometric ratio of compounds implied in the chemical reaction of preparation. Correlated studies of UV–VIS optical absorption, Raman light scattering and photoluminescence support a different chemical composition for the two types of particles, i.e. PbI₂ for the platelets and probably KPbI₃ for the rods.

2. Experimental details

Lead iodide microcrystals were prepared according to the procedure described in [7], from the chemical reaction of KI with Pb(NO₃)₂ in water, methanol (MeOH), ethanol (EtOH) and acetonitrile (ACN) solvents of Merck quality without further purification. Suspensions of PbI₂ were prepared at room temperature as follows. 5 cm³ of 0.01 M aqueous solution of lead nitrate was added to 100 cm³ of the solvent of interest. Into this solution, under vigorously ultrasonic homogenizing, was added 5 cm³ of 0.05 M aqueous potassium iodide. The sudden appearance of a yellow colour is the first evidence of the formation of PbI₂ crystallites, which are collected on a polished silicon plate used as a support for SEM and optical measurements, i.e. optical absorption, luminescence and Raman light scattering.

A Varian Cary 2300 spectrophotometer was used to measure the absorption spectra in UV–VIS. The luminescence spectra at liquid nitrogen temperature (LNT) were recorded in reflection at right-angle geometry under continuous excitation using a Coherent Innova 90 argon ion laser as the excitation light source. The emission spectrometer was a SPEX double monochromator, equipped with a cooled EMI photomultiplier and a photon counting system.

The Raman spectra were recorded at room temperature in backscattering geometry with a Jobin Yvon T64000 spectrophotometer equipped with a microprobe allowing the laser spot to be focused on the sample within a micrometre scale. This facility has permitted an individual Raman inspection of particles of different size and shape. Polarized Raman studies were performed using a half-wave plate and a polarizing filter placed in the exciting laser beam and in Raman scattered light, respectively.

3. Results and discussion

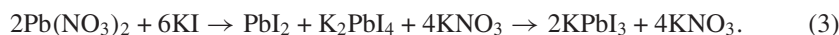
PbI₂ and KNO₃ as end-products of the reaction



appear as colloidal particles, dispersed in the synthesis medium, which slowly form a deposit on the bottom of the preparing vessel. Such a deposit should contain particles of different shape and size: hexagonal platelets of PbI₂ and rods of KNO₃. Depending on their solubility in the liquid used as host medium, the deposit may contain only one or both types of particles. In water, which is a good solvent for KNO₃, the deposit will contain only particles of PbI₂ as hexagonal platelets of different size.

The whole process is much more complicated. Small alterations in the preparation procedure, such as modifications of the concentration of the interacting compounds, the use of different host liquids, the stirring strength of reacting mixture, and the mingling order of reacting compounds, i.e. KI put over Pb(NO₃)₂ or inverse, all lead to significant changes in the properties of the particles collected as a powder from the bottom of the preparing vessel. The most important is the change of stoichiometric ratio by an excess of one compound, or

using for the reaction (1) liquids with different solvating power for the reacting compounds. Reactions (2) and (3) illustrate how, by stoichiometric modification of the reaction (1), one can obtain other by-products, such as KPbI_3 , K_2PbI_4 .



In these circumstances, the procedure of preparation described in [7], which operates with a modified stoichiometric ratio, may lead to the formation of lead iodide particles and other by-products too, of different shape and chemical composition. The main problem is to identify these particles.

Figure 1 presents the scanning electron microscopy (SEM) pictures of the particles resulted from the reaction between $\text{Pb}(\text{NO}_3)_2$ and KI carried out in water, MeOH, EtOH and ACN. One sees that in MeOH (figure 1(b)) and EtOH (figure 1(c)) both platelets and rod-like particles are formed, while in water (figure 1(a)) and ACN (figure 1(d)) there are either platelets and rods. In general, the size of these particles increases with the quantity of reacting compounds and the elapsed time from the achievement of synthesis mixture. Apart from the case when ACN was used as host liquid, the particles formed immediately the potassium iodide was added to the lead nitrate solutions had a mean size of about ~ 100 nm.

The formation of two types of particles is also demonstrated by optical absorption spectra.

In figure 2, the spectra S_1 , S_{21} , S_{22} and S_3 are for the colloidal suspensions achieved in water, MeOH, EtOH, and ACN, respectively, and the spectrum C shows the optical absorption edge, ~ 2.44 eV at room temperature, of a PbI_2 sample cleaved from a melt grown single crystal. In the spectra S_1 , S_{21} , S_{22} , the growth of absorbency observed at 2.48, 2.46 and 2.52 eV indicates the optical absorption edge in PbI_2 colloidal particles, which in comparison with the crystalline sample (C curve) are blue shifted. The different absorbency values above are related to platelets of PbI_2 of different mean size, i.e. a quantum confinement effect generated in the low-dimensional particles of PbI_2 . In addition, the spectra S_{21} , S_{22} as well as S_3 reveal an intense absorption band around 3.5 eV. This band, already reported in earlier papers devoted to the synthesis of small particles of layered semiconductors of PbI_2 , HgI_2 and BiI_3 [7–10], was attributed to I_3^- ions [11]. Such an explanation does not contravene our supposition that other by-products are formed by reaction (2) too, one of these being the particles of KPbI_3 . Corroboration of the SEM pictures, from figures 1(a) and (d), with the absorption spectra S_1 and S_3 , presented in figure 2, suggests that the hexagonal platelets and rod-like particles could correspond to PbI_2 and KPbI_3 , respectively.

SEM pictures disclose two types of appearance of the rods: as isolated units spread randomly among platelets, as one sees in figures 1(b) and (c), and expanded tufts starting from the same point, figure 1(d), which suggests that they originate in a common seed. One must notice that the mean size of the particles formed in MeOH, EtOH as well as in water increases if the reacting mixture is left standing for a longer period of time. Regardless of the liquid used as host medium for the reaction (2), all rod-like particles shown in figures 1(b)–(d), exhibit the same Raman spectrum, but it is different from the spectrum of KNO_3 .

A particular genesis of the rod-like particles is observed when ACN is used as host liquid. In this case, immediately the synthesis mixture is carried out, in the deposit formed on the bottom of the preparation vessel one finds mainly hexagonal small platelets whose Raman spectrum is identical with that of lead iodide. Afterwards these platelets transform slowly into thin rods forming expanded tufts, and after approximately 24 h the whole deposit formed on the bottom of preparation vessel contains only rod-like particles. The transformation rate of platelets into rods depends on the stoichiometric ratio of reacting compounds, increasing with the weight of KI. Such a process could be described by the two steps of reaction (3): in

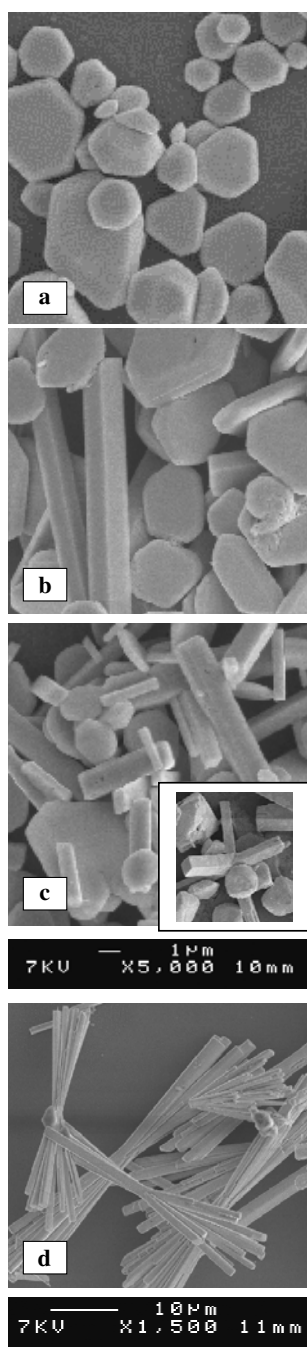


Figure 1. SEM pictures of the particles produced by the reaction between $\text{Pb}(\text{NO}_3)_2$ and KI in water (a), methanol (b), ethanol (c) and acetonitrile (d).

the beginning platelets of PbI_2 are formed, which afterwards, in the presence of K_2PbI_4 , are transformed in rods of KPbI_3 . The same transformation of PbI_2 platelets into rod-like particles is also observed in methanol and ethanol, under a greater excess of KI.

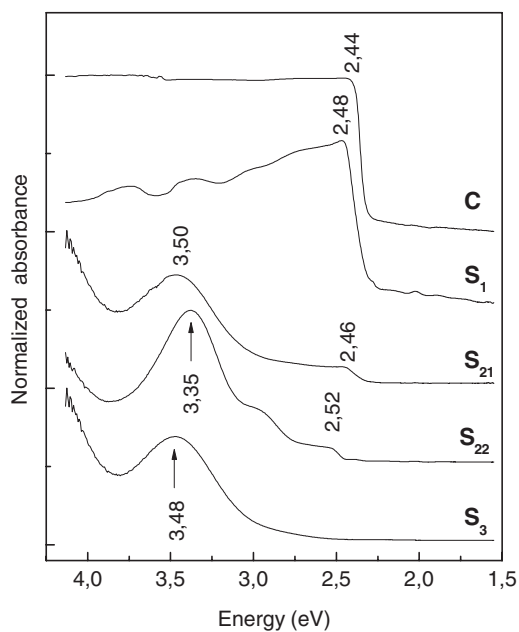


Figure 2. The optical absorption spectra of colloidal particles prepared by the reaction between $\text{Pb}(\text{NO}_3)_2$ and KI in water (S_1), methanol (S_{21}), ethanol (S_{22}) and acetonitrile (S_3). The spectrum (C) is for a PbI_2 slide cleaved from a single crystal grown from the melt.

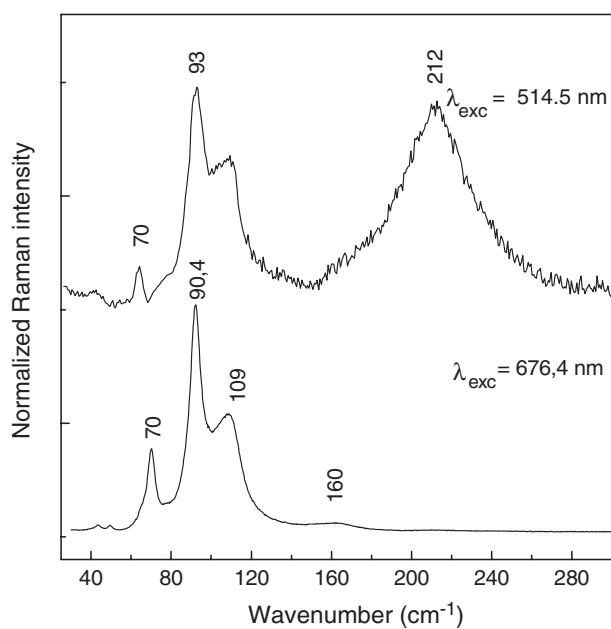


Figure 3. The Raman spectra of PbI_2 platelets synthesized in water at resonant excitation, $\lambda_{\text{exc}} = 514.5 \text{ nm}$ (2.41 eV), i.e. near the fundamental absorption band ($\sim 2.44 \text{ eV}$) and nonresonant excitation, i.e. $\lambda_{\text{exc}} = 676.4 \text{ nm}$ (1.83 eV).

The Raman spectra recorded on individual particles seems to give the most convincing proof that the platelets and rods belong to different compounds. For platelets, figure 3 display

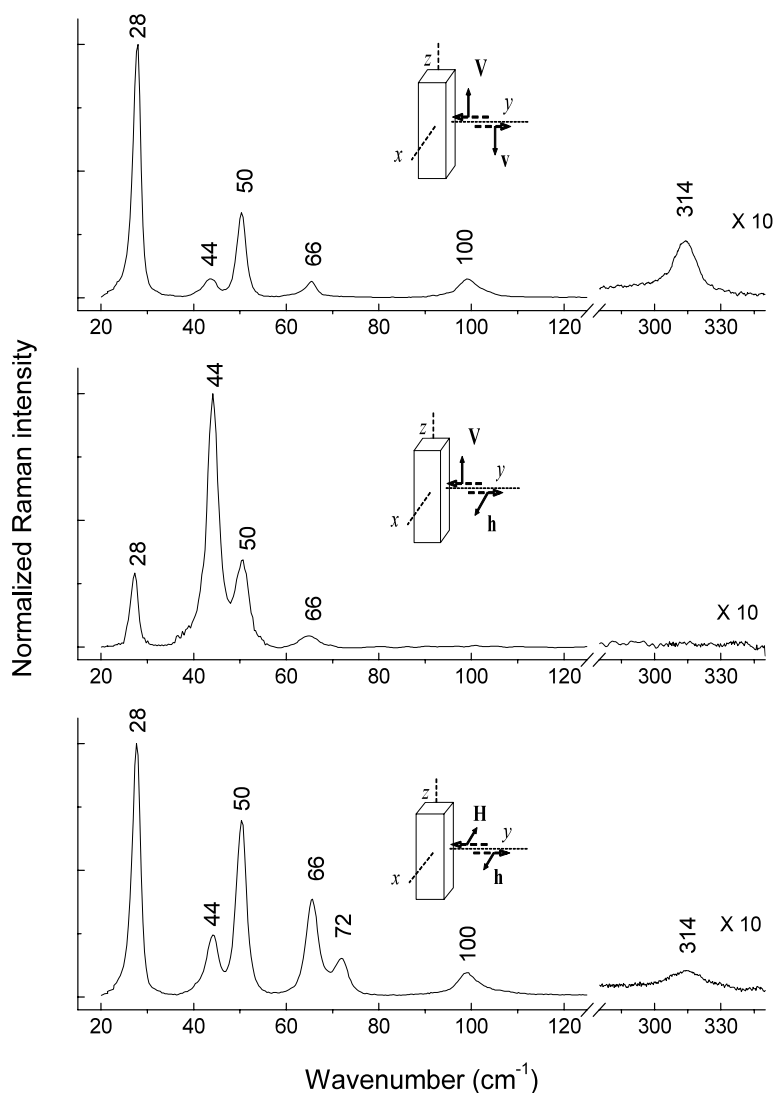


Figure 4. Polarized Raman spectra at $\lambda_{\text{exc}} = 676.4$ nm of rod-like particles.

the well-known Raman spectrum of lead iodide, which is identical with that recorded on a crystalline sample cleaved from a melt grown crystal [13]. As a distinguishing feature, we notice for these particles the generation of a resonant Raman scattering effect observed when the laser excitation energy ($\lambda_{\text{exc}} = 514.5$ nm; 2.41 eV) approaches the fundamental absorption band, (~ 2.44 eV). In this case, the appearance of new lines as well as an important changes of the relative intensity of different Raman lines are the main features observed [13].

The Raman spectra for rods depend strongly upon the direction of observation and excitation relative to the principal axes of the particles. This dependence, shown in figure 4, suggests for rod-like particles an orthorhombic crystalline system, which is supported also by the SEM pictures, i.e. the 90° interpenetrating twins that are a crystallographic detail frequently observed among orthorhombic crystals grown from solution. In this frame is important to notice that crystals of $\text{KPbI}_3 \cdot 2\text{H}_2\text{O}$, in the form of thin pale-yellow needles,

were obtained by saturating the aqueous solution of alkali iodide with PbI_2 [14]. The structure of $\text{KPbI}_3 \cdot 2\text{H}_2\text{O}$ belongs to the $Pnma$ orthorhombic crystalline system, the space group D_{2h} , with four $\text{KPbI}_3 \cdot 2\text{H}_2\text{O}$ formula units per unit cell ($Z = 4$) and $a = 10.168 \text{ \AA}$, $b = 4.577 \text{ \AA}$ and $c = 22.484 \text{ \AA}$ [14]. In this case, the Raman active phonon modes A_g , B_{1g} , B_{2g} and B_{3g} [15] can be revealed using specific measuring configurations denoted $x(zz)y$ that describe the direction of incident radiation, incident polarization, observed polarization and direction of observation, respectively. Parentheses give the components of the derived polarizability tensor, which associate with different phonon modes. Thus, for rod-like particles the A_g phonons appear in the measuring configurations (xx) , (yy) and (zz) , B_{1g} in (xy) , B_{2g} in (xz) and B_{3g} in (yz) . The spectra presented in figure 4 link only with the components (zz) top, (zx) middle and (xx) bottom. For a complete Raman characterization of an individual rod-like particle, the approach of all the measuring configurations mentioned should be necessary. Unfortunately, a more detailed Raman study on individual particles of micronic size is not at all easy to perform. Consequently, we limit ourselves to mentioning the similarity of the Raman spectra of figure 4 with those of CsPbCl_3 in the $Pnma$ orthorhombic structure [16]. As shown, the polarized Raman spectrum of rod-like particles reveals a line at 28, two sets of doublets situated at $(44, 50)$ and $(66, 72) \text{ cm}^{-1}$ and others three lines at 100, 240 and 314 cm^{-1} .

Similarly, with CsPbCl_3 one expects the phonon spectrum in figure 4 to contain three transverse optical (TO) and three longitudinal optical (LO) phonons. The higher intensity of the Raman lines situated at low frequencies than at higher ones indicates that the crystal is more polarizable at low frequencies; this means that $\omega_{LO} > \omega_{TO}$, where ω_{LO} and ω_{TO} are the frequencies of the longitudinal and transverse modes. For this reason, we believe that the weak Raman lines at 100, 240 and 314 cm^{-1} must be associated with the longitudinal modes and the others with the transverse modes. The TO doublets at $(44, 50)$ and $(65, 72) \text{ cm}^{-1}$ may appear by the removal of degeneracy by the low space group symmetry of D_{2h} .

In the perspective of reactions (2) and (3), and based on the Raman signature of rod-like particles, similar to that of CsPbCl_3 , we are tempted to believe that these additional particles generated in the frame of the chemical reaction between $\text{Pb}(\text{NO}_3)_2$ and KI are, most probably, KPbI_3 crystals.

The micro-particles resulting from the reaction between $\text{Pb}(\text{NO}_3)_2$ and KI, regardless of their shape and size, exhibit at liquid nitrogen temperature (LNT) under continuous excitation at $\lambda_{\text{exc}} = 476.5 \text{ nm}$ a similar photoluminescence (PL) that consists of two intense bands, one at about 2.5 eV and another around 2.0 eV. This result is intriguing, taking into account that both the SEM pictures and Raman spectra show that the synthesis reaction carried out in water, MeOH and ACN leads to different particles in shape and composition: only platelets of PbI_2 , platelets and rods, and only rods of KPbI_3 , respectively. However, from a more attentive analysis of the PL spectra shown in figure 5, one discovers some differences between the platelet and rod emissions. In the following, we will take as reference the PL spectrum of PbI_2 single crystals at LNT, shown in figure 6(a), which display an excitonic band consisting of two components, one at 2.49 eV (E_F band) and another at 2.47 eV (E_T band). The first band, which is very intense, originates in the recombination of the free excitons created by the band-to-band irradiation. The latter, with its intensity depending on the crystal quality, represents the contribution coming from the recombination of the excitons trapped in the imperfections of the crystal lattice as dislocations, grain boundaries and cleavage defects [3]. The same defects are involved in the appearance of the band situated at around 2.0 eV, known as the G band. It may appear as a very weak PL band in the samples cleaved from a PbI_2 single-crystal ingot, figure 6(a), and much enhanced in samples having the surface damaged mechanically, figure 6(b). The enhancement of the G band may also be achieved by submitting the crystal to a photolysis process or thermal annealing in vacuum at about 520 K [2]. A much

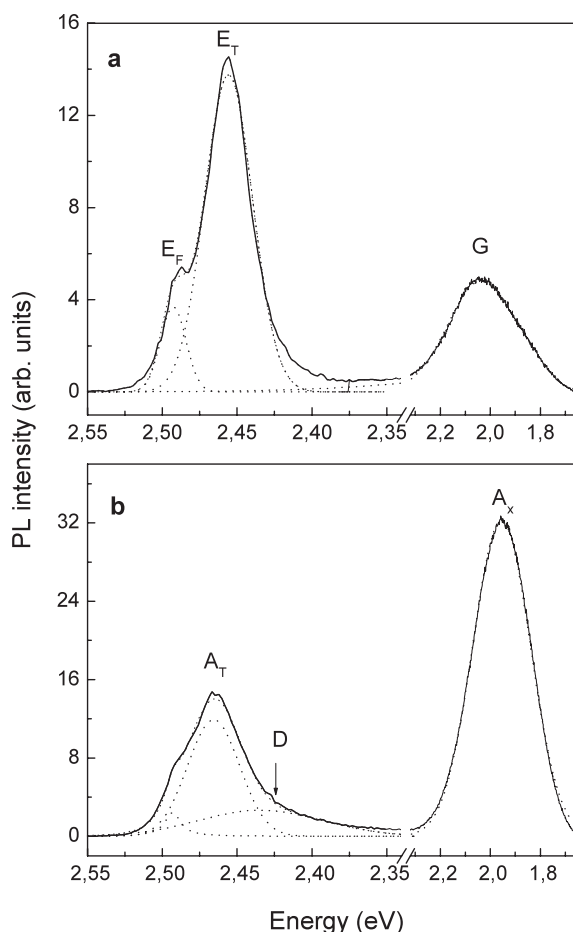


Figure 5. LNT photoluminescence of micro-particles produced by the reaction between $\text{Pb}(\text{NO}_3)_2$ and KI in water (a) and acetonitrile (b); $\lambda_{\text{exc}} = 476.5 \text{ nm}$.

clearer demonstration is seen in figure 6(c), which presents the PL spectrum at LNT of a dried micrometric crystalline powder of PbI_2 dispersed in water by vigorous ultrasonics. The PbI_2 powder was obtained by mechanical crumbling of a PbI_2 single crystal grown from the melt.

The role of the surface, as an exciton trapping centre, is revealed by the increase of the E_T band, which in figure 6(c) almost equals the E_F emission coming from the free exciton recombination. At the same time, an important enhancement of the G band is observed. This is interpreted as a radiative electron–hole recombination process associated with the Pb^+ ions created under band-to-band irradiation. The relation between the presence and the enhancement of the G band is explained by the fact that the Pb^+ ions, as an intermediate product of the photolysis of PbI_2 , are located near to the surface of the crystal. It is worth noticing that similar emission bands at about 1.97 and 2.06 eV, related to the volume properties of the PbI_2 crystal, can be produced by doping the crystal with Ag^+ and Cu^+ , respectively, [3, 17]. As with the G band, these originate in radiative electron–hole recombination that takes place on the acceptor centre induced by the impurity ions.

Returning to the E_F and E_T bands, presented in figure 6(a), we notice their narrow width of about 0.018–0.02 eV, a typical feature for excitonic emission. On increasing the density of

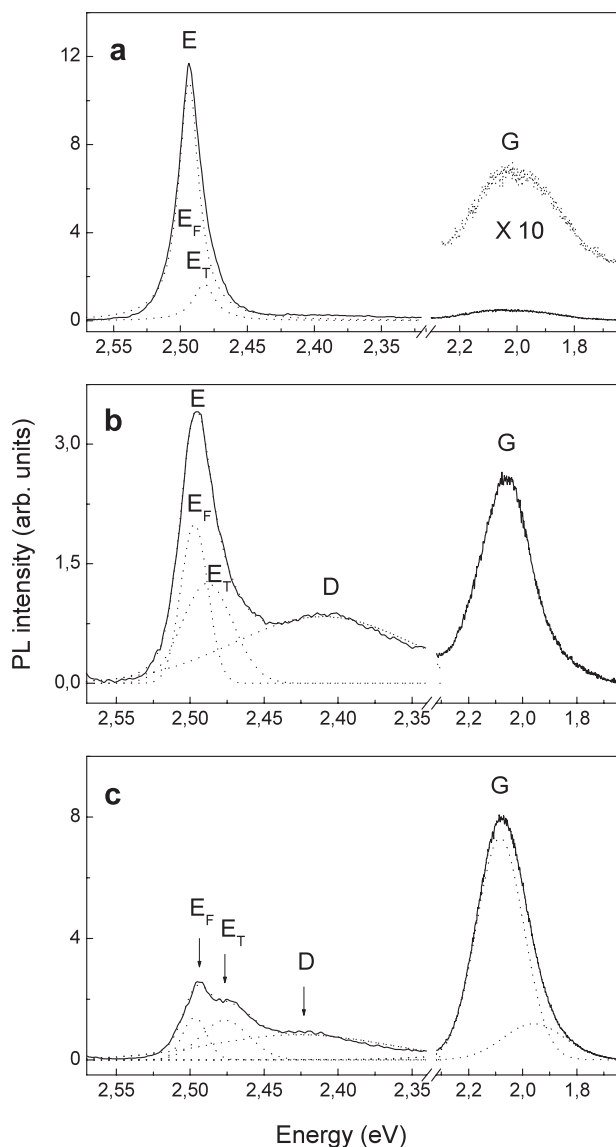


Figure 6. LNT photoluminescence of PbI₂ samples prepared from a melt-grown single crystal: cleaved crystalline slide (a), cleaved crystalline slide with the surface damaged mechanically (b), micrometric crystalline powder obtained by mechanical crumbling, vigorously ultrasonicated in aqueous solution and finally dried in vacuum (c); $\lambda_{\text{exc}} = 476.5$ nm.

surface defects, the E_T band increases and broadens suddenly up to 0.032–0.35 eV. Seemingly, the same E_T band with a full-width at half-maximum (FWHM) of around 0.032 eV is observed in figures 5(a) and (b), where the PL spectra of two quite different particles, PbI₂ platelets and KPbI₃ rods, are presented. *A priori*, the band around 2.5 eV originates in the radiative deexcitation of the Pb²⁺ ions, fixed in two different crystalline lattices; the fact that one observes very similar PL spectra could be a simple coincidence. In the both cases, the excitation by laser light of 476.5 nm produces a transition $1S_0 \rightarrow 3P_1$ of the Pb²⁺ ions, which for platelets

and rods means an inter-band and intra-ion transition, respectively. In the former case, the PL has to have the characteristics of a radiative recombination process, linked to the exciton and electron–hole pair, while in the latter it must be similar to the PL of the Pb²⁺ ion introduced into an alkaline halide lattice, and as for any *ns*² ion, it displays two emission bands, labelled A_T and A_X, which in the NaI and KI crystals are located at 3.03 eV (408 nm) and 2.06 eV (600 nm), respectively [18]. The positions and intensities of these bands depend strongly on the dispersion state of the impurity in the host lattice. A complex mechanism of dipole (impurity–cationic vacancy) aggregation, depending on the impurity concentration and the host matrix, leads to a pile-up of impurities around dislocations and grain boundaries. In KI and NaI crystals, this process evolves quite differently from all the other Pb-doped alkali halides. When the impurity reaches a high degree of aggregation, giving birth to a precipitation phase of the type PbI:_nNaI or PbI:_nKI, the PL spectrum becomes almost a mirror-like image of the excitation one, the A_T band is replaced by a new one, down-shifted at 2.65 eV (468 nm), which has the characteristics of an excitonic emission, and the A_X band almost disappears. In the intermediate stages of aggregation, the variations of the A_X band are not very significant; it can be considered as a G band.

Coming back to the rod-like particles of KPbI₃, they could be regarded as an intermediate compound belonging to the PbI:_nKI system, whose signature in the PL spectrum is two emission bands like those mentioned above, A_T and A_X. Then, the similarity between the PL spectra presented in figures 5(a) and (b) must indeed be considered a simple coincidence. Thus, for the micro-particles of PbI₂, in figure 5(a) the two components E_F and E_T found in the PL band peaking around 2.5 eV originate in radiative cationic exciton recombination, involving free and trapped excitons. Enhancement of E_T band reveals the role played by the surface of the particle as an exciton trapping centre, and the G band has the same significance as in the case of figure 6, i.e. for a crystalline sample with defects of surface. On the other hand, the PL spectrum from figure 5(b) has a different origin; it also belongs to the Pb²⁺ ion embedded in a crystal lattice, different from an ordinary KI one, but whose emission bands at about 2.5 and 2 eV play the role of the A_T and A_X bands of a Pb²⁺ ion situated in the crystalline lattice of KI or NaI.

4. Conclusions

By correlated studies of scanning electron microscopy, Raman spectroscopy, optical absorption and low temperature photoluminescence (PL) we have demonstrated that by the reaction between Pb(NO₃)₂ and KI, carried out in different liquids media as water, methanol, ethanol and acetonitrile, platelets of PbI₂ and rods of probably KPbI₃, with micrometric and nanometric size are formed. By changing the stoichiometry of the synthesis reaction one modifies the yield of platelets and rods. The formation of two types of particles explains the great differences between the reported data concerning the shift of the fundamental absorption edge, of about 10 meV and 1.25 eV, associated in both cases with a quantum confinement effect generated in the low-dimensional systems of PbI₂ layered semiconductor compounds.

Regardless of shape and size, these particles exhibit a similar photoluminescence that consists of two intense bands centred around 2.5 (E band) and 2.0 eV (G band), which in turn is similar to that of a crystalline slide or a micrometric powder, both prepared from a PbI₂ single-crystal grown from the melt. Crystalline PbI₂ platelets exhibit an E band with two components, at 2.49 (E_F band) and 2.47 eV (E_T band), originating in the recombination of the free and trapped excitons produced by inter-band irradiation. The close relation between the enhancement of the E_T and G bands reveals that they are linked to surface defects. For the rod-like particles, the PL spectrum is similar to a certain extent to that of a Pb²⁺ ion introduced

into an alkaline halide lattice, which as for any ns^2 ion displays two emission bands, labelled A_T and A_X whose correspondents are E and G bands.

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