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Quantum well effect in bulk PbI_2 crystals revealed by the anisotropy of photoluminescence and Raman spectra

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Abstract

On subjecting a bulk 2H- PbI_2 crystal to vacuum annealing at 500 K followed by a sudden cooling at liquid nitrogen temperature stacking faults are generated that separate distinct layers of nanometric thickness in which different numbers of I–Pb–I atomic layers are bundled together. Such structures, containing two, three, four, five etc I–Pb–I atomic layers, behave as quantum wells of different widths. The signature of such a transformation is given by a shift towards higher energies of the fundamental absorption edge, which is experimentally revealed by specific anisotropies in the photoluminescence and Raman spectra. The quantum confining effect is made visible by specific variations of a wide extra-excitonic band (G) at 2.06 eV that originates in the radiative recombination of carriers (electrons and holes), trapped on the surface defects. The excitation spectrum of the G band, with p polarized exciting light, reveals a fine structure comprised of narrow bands at 2.75, 2.64, 2.59 and 2.56 eV, which are associated with the PbI_2 quantum wells formed from two, three, four and five I–Pb–I atomic layers of 0.7 nm thickness. Regardless of the polarization state of the laser exciting light of 514.5 nm (2.41 eV), which is close to the band gap energy of PbI_2 (2.52 eV), the Raman scattering on bulk as-grown PbI_2 crystals has the character of a resonant process. For p polarized exciting light, the Raman scattering process on vacuum annealed PbI_2 becomes non-resonant. This originates from the quantum well structures generated inside the crystal, whose band gap energies are higher than the energy of the exciting light.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The properties of any material vary substantially when its physical size is reduced below a specific length scale, usually on the nanometric dimension. In low-dimensional systems, the electronic energy levels which belong to the valence and conduction bands are not as continuous as in the bulk and, due to the confinement of the electronic wavefunction, a discrete structure of the electronic density states is formed. The low-dimensional systems may be (i) two dimensional (2D) and include thin films, layer structures, quantum wells and superlattices; (ii) one dimensional (1D), in which linear chain structures are identified; (iii) zero dimensional (0D), such as quantum dots, colloids and clusters [1, 2].

Among layered materials a good example is PbI_2 , which has, as a rigid structurally repeated unit, an I–Pb–I layer of 0.7 nm thickness [3]. The bulk crystal is composed of atomic I–Pb–I layers arranged successively and perpendicularly along the *c* axis. PbI_2 features a strong intralayer chemical bonding and weak interlayer van der Waals interactions [4]. The PbI_2 crystal shows at low temperature a strong photoluminescence originating from exciton recombination and trapped electron–hole pairs which have been formed by the band-to-band irradiation [5]. A coupled electron–hole pair, referred to as an exciton, is characterized by a strong electrostatic attraction distributed within a sphere of radius called the Bohr exciton radius. The different electrostatic attraction determines their relative localization within regions of different

nanometric size [1, 2]. When the crystalline particle size decreases, the recombination of electron–hole pairs gives rise to a light emission called band edge luminescence whose peak position shifts towards higher energies. Termed the *quantum confinement effect*, it occurs when one or more of the dimensions of a nanocrystal is made very small, its size approaching the exciton size. In PbI_2 , such effects were clearly observed in nanometric crystalline powder and on thin films formed from two, three, four and more I–Pb–I layers [6–9]. In this context the question arises of whether such an effect can be observed in a bulk PbI_2 crystal. The answer can be affirmative, but it depends on the ability to disrupt the stacking sequence of layers in isolated packages with different numbers of I–Pb–I layers alternating along the c axis. This suggests a crystallographic transformation by which *stacking faults* are generated in the crystalline sample. It is similar to a polytypic transformation which results in variations in the sequences of stacking layers along the layer normal to the hexagonal c -axis. Indeed, more than 30 different polytypes of PbI_2 have been identified [10]. In an as-grown 2H crystal a polytypic transformation can be induced by vacuum annealing at 400–600 K [11–15]. The reversible [10, 16] or irreversible [17] nature of the polytypic transformation induced by the increases and decreases of the temperature remains without complete elucidation. However, optical microscopy reveals faults in the stacking continuity of the crystalline layers along the c axis when the sample is cooled abruptly to liquid nitrogen temperature from an annealing temperature at ~ 500 K. In the remainder of this paper this treatment will be referred to as the quenching thermal treatment (QTT). The stacking faults produced in this way may detach closed packed I–Pb–I layers of nanometric limited thickness, which should behave as quantum wells of different widths. The ‘flaky’ structural property of PbI_2 facilitates the creation of a high density of stacking faults in which most of the trapping centers (iodine vacancies, Pb^+ ions, dislocations) for excitons and free carriers are localized. Thus, in the PL spectrum of PbI_2 , as a single crystal or crystalline powder, at least two emission bands are detected: one originating from the radiative recombination of excitons, including self-trapped excitons, and the other stemming from the radiative recombination of the trapped carriers, labeled the G band [18]. Relative to the edge absorption, these bands are characterized by a small and a large Stokes shift. This detail is important in the observation of the signature of stacking faults in the PL spectrum. The excitonic emission, located close to the band edge absorption (~ 2.5 eV), being strongly absorbed, provides information about the surface layers of the crystal, while the G band, situated in the domain of transparency of the crystal (~ 2 eV), may stem from the interior of the crystal, from deeper layers. In this context, the quantum well system generated by stacking faults in the interior of the PbI_2 crystal, along the c axis, will be perceived better by variations of the G band than the blue-shift of the narrow excitonic emission band, which normally indicates a quantum confinement effect. In addition, the G band shows different properties when it is observed along or perpendicular to the c axis. All these facts emphasize the complex nature of the luminescence in PbI_2 crystals and

that a study of the G band anisotropy with respect to the c crystalline axis might be efficient in revealing an alternating layer configuration of different thicknesses, reminiscent to quantum well structures formed via stacking faults.

In this work, we demonstrate that on vacuum thermal annealing the PbI_2 crystal undergoes a transformation resulting in the formation of different layered structures including two, three, four, five and more I–Pb–I layers that alternate along the c crystalline axis. By anisotropic photoluminescence and Raman scattering studies, we were able to demonstrate that these structures, of nanometric thicknesses, behave as quantum wells.

2. Experimental details

Four types of PbI_2 samples were used: (i) crystalline blades cleaved perpendicular to the c axis from a single crystal grown by the Bridgman method; (ii) crystalline blades cut along the c axis; (iii) micrometric crystalline powder produced by grinding a piece of PbI_2 single crystal; (iii) blades resulting from a micrometric crystalline powder compressed non-hydrostatically at 0.58 GPa. The last sample consists of a poly-crystal with many internal interfaces. The polarized and unpolarized PL spectra (emission and excitation) at liquid nitrogen temperature (LNT) were recorded in reflection at right angle geometry under continuous excitation using a HORIBA Jobin Yvon FLuorolog-3 model FL3-2. The Raman spectra were recorded under 676.4 and 514.5 nm excitation in backscattering geometry with a Jobin Yvon T64000 spectrometer equipped with a microprobe allowing the laser spot to be focused on the sample within a micrometer scale. Thermal annealing performed in vacuum (5×10^{-5} mbar) at 500 K was followed by a sudden cooling at LNT.

3. Results and discussion

Figure 1 shows the complexity of PL spectra of PbI_2 at LNT under band-to-band optical excitation. The PL of a single-crystalline slide of PbI_2 cleaved perpendicular to the c axis from a pure single crystal ingot (inset figure 1(A)) is dominated by a strong excitonic emission (E band), with its maximum at 2.495 eV. Depending on the sample quality or, more precisely, how many surface defects were produced by cleaving, a new wide band, peaking around 2.0 eV, is formed (figure 1(A)). Termed the G band, it is strongly enhanced by thermal annealing, photolytic decomposition and mechanical scratching with an abrasive paper. It originates from the radiative recombination of excitons and photo-carriers trapped at the crystal surface. This explanation is supported by the observation that it disappears after removal of the top layer of sample. The nature of the traps involved in the generation of the G band is reflected in the excitation spectra. Thus in figures 1(B₁) and (B₂) the solid curves represent the emission spectrum of a surface scratched sample and the excitation spectrum associated with the G band, respectively. The two peaks in the excitation spectrum, at 2.46 and 2.52 eV, indicate that the G band originates in radiative recombination both

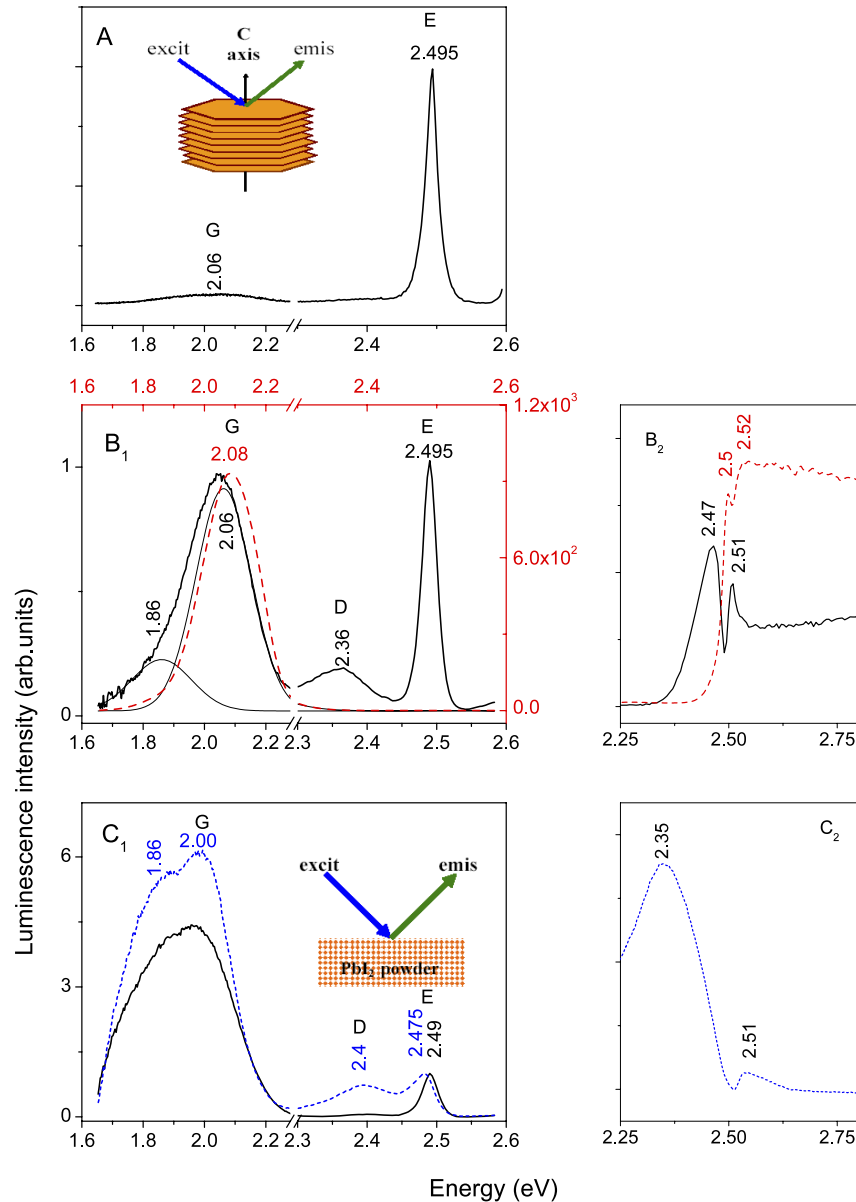


Figure 1. (A) Photoluminescence at LNT of a PbI_2 slice cleaved from an as-grown crystal; (B) crystalline slide with surface defects produced mechanically before (solid curve) and the same sample after vacuum thermal annealing at 500 K (dashed curve); (C) PbI_2 microcrystalline powder (dotted curve) and PbI_2 platelet obtained by non-hydrostatic compression at 0.58 GPa (solid curve). The corresponding excitation spectra of the G band are presented in figures (B₂) and (C₂).

of the trapped excitons and the trapped carriers which were formed by the band-to-band irradiation.

Enhancement of the G band, by up to three orders of magnitude, may also be observed by subjecting the PbI_2 crystal to a QTT (figure 1(B), dashed curve). In this way stacking faults are produced, which in turn localize trapping centers for the photo-generated electrons, which afterward recombine with the holes, giving rise to the G emission band whose excitation spectrum is shown in figure 1(B₂) by the dashed curve. In comparison to the excitation spectrum shown by the solid curve in figure 1(B₂), two significant modifications can be immediately perceived: (i) a small blue-shift of about 0.02 eV of the band edge absorption that reveals an enlargement of the band gap energy and (ii) a weaker contribution of the excitons, represented by the band at 2.5 eV, in the generation

of the G band. This indicates that, in the formation of the G band, the contribution of radiative recombination of photo-generated carriers is greater than excitonic. One argument for this is the increase of the decay time of the G band after QTT, which is the same kind of variation as that after mechanical scratching (figure 2). Another argument is suggested by the photoconductivity measurements at LNT. A PbI_2 crystalline slide, after a band-to-band irradiation during which the traps formed by the thermal annealing are filled, displays a photoconduction band situated in the spectral range of the G band when the excitation light is scanned from low to high energies [19].

The crystalline powder behaves differently; it represents a situation in which the density of surface defects is greatest. In this case, the G band is accompanied by two bands at about

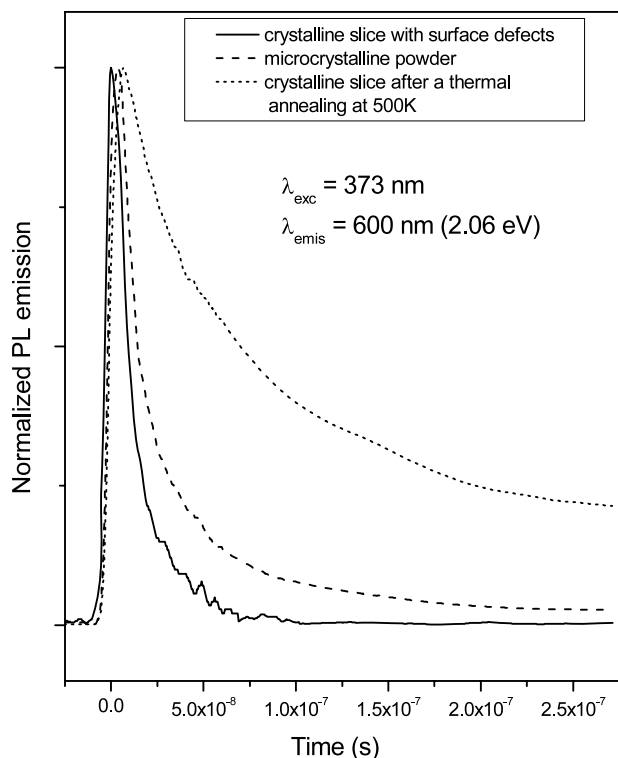


Figure 2. G emission band decay at LNT of a PbI_2 crystalline slice with surface defects produced mechanically (black curve), microcrystalline powder (dashed curve) and crystalline slide after vacuum thermal annealing at 500 K (dotted curve). The excitation light of 337 nm was from a pulsed nitrogen laser.

1.86 and 2.36 eV; the latter is labeled as the D band. The D band appears in the crystalline sample with a scratched surface as well as in PbI_2 powder, in both cases being evidently a ‘flaky’ structure that, in turn, is connected with the presence of stacking faults. Compressing the PbI_2 crystalline powder at 0.58 GPa causes a compact polycrystalline pastille to be formed, in which the ‘flaky’ structure is suppressed and the D band in the PL spectrum is no longer visible, (figure 1(C₁)).

A high density of surface trapping centers implies a large number of trapped carriers that afterward recombine radiatively. Their provenance is revealed in the excitation spectrum by a band whose maximum is situated at a lower energy than the band edge absorption. Such a result is indicated by the maximum at 2.35 eV that appears in the excitation spectrum of the G band in the PbI_2 crystalline powder, figure 1(C₂). Noticing that the position of this excitation maximum almost coincides with the position of the D emission band, we are tempted to associate this with the stacking faults at which the crystal point defects are accumulated. Here, by the radiative recombination of trapped carriers, the G band is generated.

Finally, taking into account that stacking faults appear as a disruption of the continuous stacking of the I–Pb–I atomic planes along the c axis, the D emission band connected with their existence must reveal anisotropic properties with respect to the crystallographic axis. In this sense figure 3 is relevant. It presents the PL spectrum at LNT as a function of the

orientation of the c crystalline axis versus the measuring plane, i.e. in the plane and perpendicular to the measuring plane. With these configurations a new feature comes to light, namely, that the D band behaves isotropically when the c crystalline axis is contained in the scattering plane and anisotropically when the c crystalline axis is perpendicular to the scattering plane. In the latter case the intensity of the D band was more intense when a p polarized exciting light was used. This result supports the assumption that the D band emission is associated with stacking faults in the PbI_2 layered crystalline structure.

Evidently, such defects in the architecture of a PbI_2 crystal should be revealed by Raman spectroscopy. Indeed, this presumption is supported by figure 4. Referring to the assignment of Raman bands in the 2H- PbI_2 polytype, two main Raman bands are observed: one at 74 cm^{-1} associated with the E_g vibration modes (shear type deformation of the layer) and the other at 96 cm^{-1} associated with A_{1g} vibrational modes (breathing deformation) [20, 21]. A wide band at 112 cm^{-1} appears to be the A_1 (LO) mode superposed on the second order mode. The anisotropy of a PbI_2 crystal may be revealed in the Raman spectra using two measuring configurations. In figure 4, the A configuration is adapted for the observation of Raman bands at 74 and 112 cm^{-1} , while the B configuration is more appropriate to reveal the Raman band at 96 cm^{-1} . Thermal annealing changes the spectra, and a new line at 86 cm^{-1} appears. It is considered the Raman signature of the stacking faults induced in the PbI_2 . Worth noting is that a similar Raman band, strongly sample dependent, has been reported appearing at 83 cm^{-1} by thermal annealing carried out by laser irradiation [22]. It was attributed to the interface phonons (IF), which propagate along the planar defects produced by stacking faults. Observation of the IF modes in a backscattering geometry is less forbidden for the PbI_2 ‘flaky’ sample prepared by thermal annealing.

Remaining in the field of anisotropic properties of PbI_2 , the question arises as to whether the emission G band could indicate the formation of different sequences of I–Pb–I atomic layers along the c crystalline axis that should manifest as quantum wells of different widths.

In this sense figure 5 is relevant. It presents the excitation spectra of the G band after a QTT measured in two polarization states of the exciting light. The backward excitation spectra, I_{R1} and I_{R2} , were obtained with exciting light polarized in the crystalline I–Pb–I plane (p polarization) and with light polarized along the c axis, i.e. perpendicular to the I–Pb–I plane (s polarization). The excitation spectra obtained in the two configurations are markedly different: fine structure is exhibited by narrow excitation bands at 2.75, 2.67, 2.6, 2.56, 2.515 and 2.432 eV for the p polarization while in the s polarization only two maxima, at 2.515 and 2.432 eV, were detected.

Regardless of the intensity of the G band, the fine structure revealed in the excitation spectrum cannot be observed in the geometry sketched in figure 1(A). This fact becomes comprehensible if the reasoning is developed in terms of a quantum confinement effect that appears in nanometric layered structures. The G band originates in the radiative recombination of trapped electrons and holes independently

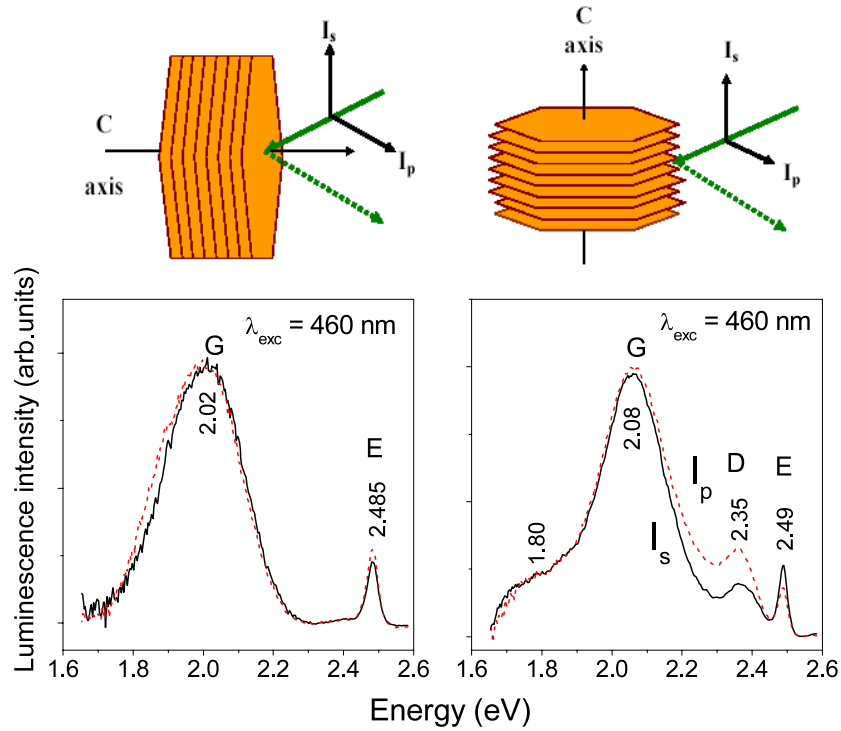


Figure 3. Photoluminescence anisotropy at LNT of bulk PbI_2 crystal after vacuum thermal annealing at 500 K. At the top of the figure are shown the two measuring configurations used. $\lambda_{\text{exc}} = 460$ nm.

confined in quantum well structures oriented perpendicular to the c axis. In the bulk PbI_2 architecture, the generation of stacking faults separating groups of I–Pb–I layers linked together in structures of nanometric thickness is equivalent to the generation of quantum well sequences of different widths that manifest themselves anisotropically [23]. In this way it becomes explicable why the G luminescence band excited with p polarized light gives rise to an excitation spectrum consisting of a series of lines that mark the band-to-band transition in PbI_2 layer structures of different thicknesses. The alternating structures along the c crystalline axis including two, three and more I–Pb–I atomic layers behave as quantum wells whose band gap is shifted gradually towards higher energies. Figure 5(C), obtained by optical microscopy, illustrates the alternation of bundles of layers along the c crystalline axis. Nevertheless, it is hard to imagine a quantum well effect in the bulk material even if the material is layered. We remind the reader here that the most convincing quantum well effect on PbI_2 crystalline structure was demonstrated by absorption and luminescence studies performed on thin films of nanometric thickness [7]. The absorption spectra on films including two, three, four, five and more I–Pb–I layers have provided evidence for a blue-shift of the fundamental absorption band. In this context, it must be mentioned that the peak positions of the narrow excitation bands presented in figure 5 coincide with the absorption peak positions presented in [7], which were obtained on nanometric PbI_2 thin films. This fact is invoked as argument for a quantum well effect observed even in a bulk layered material. Worth noting is the good coincidence between the sequence of fine excitation lines found in figure 5 at 2.75, 2.67, 2.6 and 2.56 eV and those reported in [7]

(2.75, 2.64, 2.59 and 2.56 eV), which were obtained by absorption spectroscopy on thin nanometric films containing two, three, four and five I–Pb–I layers. In terms of quantum wells these maxima are related to the shift of the fundamental absorption band towards higher energies when the number of I–Pb–I layers bundled together decreases. In this case the fundamental absorption band is expressed by $E = E_g + \Delta E$, where E_g is the energy of the bulk band edge absorption and $\Delta E \approx \frac{\hbar^2 \pi^2}{2ML_c^2}$ is the shift produced in a nanocrystalline layer of L_c size. In a weak confinement regime the term ΔE , dominated by the Coulomb electron–hole interaction energy, is related to the exciton confinement. In this case M , the mass of the exciton, is given by $M = m_e^* + m_h^*$, where m_e^* and m_h^* are the effective masses of the electron and hole. In the strong confinement regime the Coulomb interaction is small, the excitons are not formed and the electrons and holes are confined independently. The term ΔE becomes $\Delta E \approx \frac{\hbar^2 \pi^2}{2\mu L_c^2}$, where μ is the reduced exciton mass, $\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$ [2].

Because the experimental data concern the G emission band that originates in the radiative recombination of electrons and holes trapped independently at the surface defects and the exciton signature is less important (for example, the dashed curves in figures 1(B₁) and (B₂)), we are inclined to favor a stronger confinement effect developed even in the bulk PbI_2 crystal. At first sight, such a conclusion may be thought astonishing because, up to the present, a quantum well effect has been observed only on isolated nanometric thin films.

A supporting point in this interpretation is furnished by the Raman spectra performed under resonant light excitation.

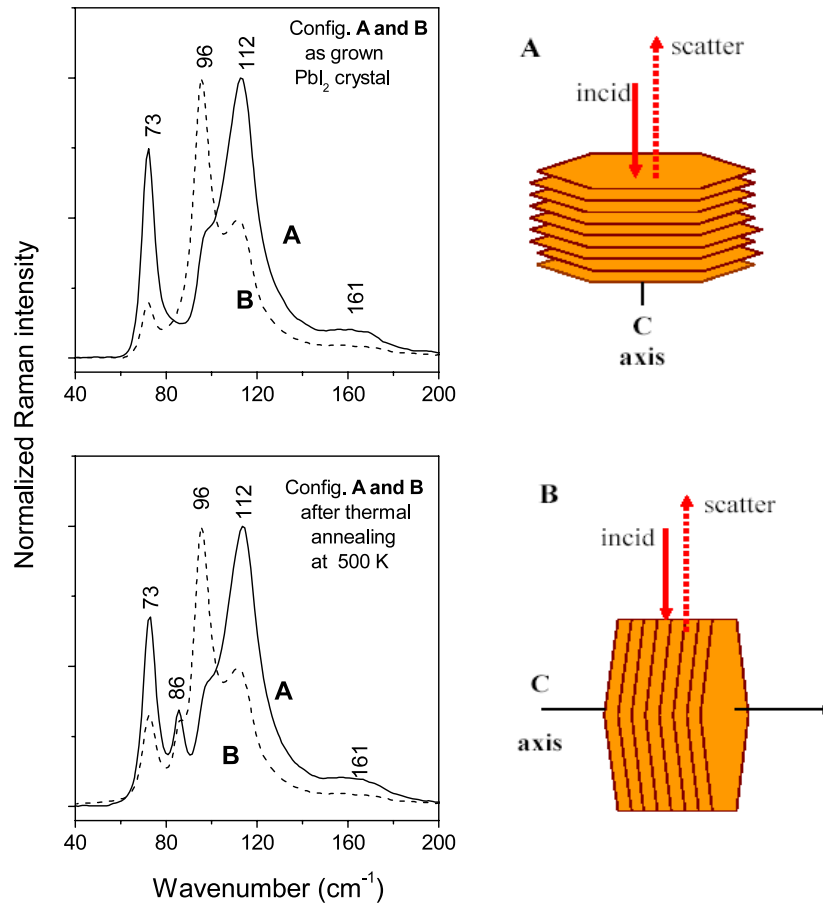


Figure 4. Raman spectrum anisotropy as a function of the polarized state of the incident light against direction of the *c* crystalline axis. Spectra were recorded in backscattering geometry at $\lambda_{exc} = 676.4$ nm on bulk as-grown PbI_2 previously subjected to vacuum thermal annealing at 500 K. At the top of the figure are shown the two back-scattering measuring configurations used.

Figure 6 demonstrates this. The Raman spectra of the PbI_2 crystal, before and after QTT, recorded at room temperature (RT) and LNT in two different measuring geometries under excitation by light of 676.4 and 514.5 nm, disclose significant and subtle modifications:

- (i) Figure 6(A) presents the Raman spectra at RT under *p* and *s* polarized excitation light (676.4 nm; 1.83 eV) using the two different measuring geometries shown at the top of the figure. As in figure 4, the spectra differed when the *p'* and (*p*; *s*) measuring geometries were used. As a marked feature we note that the Raman line at 95 cm^{-1} associated with breathing deformation along the *c* crystalline axis is easily visible in the (*p*; *s*) measuring geometries. Figure 6(A) illustrates a non-resonant Raman scattering process, which appears when the energy of the exciting light is smaller than the band gap.
- (ii) The same sample reveals a resonant Raman effect at RT under excitation with light of 514.5 nm (2.41 eV), which is close to the PbI_2 band gap energy (~ 2.5 eV), figure 6(B). The resonant Raman signature is given by the appearance of new lines, the most revealing being an overtone at 214 cm^{-1} . In this case, the Raman spectra become independent of the polarization of the exciting light; the black, red and green curves illustrating

- the spectra obtained in the *p'* and (*p*; *s*) measuring conditions practically coincide. Cooling the sample to LNT, the fundamental absorption edge increases so that the matching with the exciting light energy is no longer present and the Raman process becomes non-resonant. The fact is attested by the blue spectrum in which the additional band at 214 cm^{-1} is hardly observable.
- (iii) In this context, figure 6(C) supports the supposition that the thermal annealing of PbI_2 generates nanometric layered structures that include a varying number of I–Pb–I layers along the *c* crystalline axis. Such structures, behaving as quantum wells, are characterized by a shift of the fundamental absorption edge towards higher energies that in turn depends on the well thickness, i.e. how many I–Pb–I layers were bundled in a distinct formation. Figure 6(C) presents a subtle resonance Raman effect at RT observed under polarized excitation light of 514.5 nm. As in figure 6(B), the resonance must be confirmed by the intense overtone band at 214 cm^{-1} . In contrast to the case of PbI_2 subjected to thermal annealing is the appearance of the overtone band in equal intensity only in *p'* and *s* configurations. In the *p* configuration, achieved experimentally by the use of a half-wave plate that changes the polarization from *s* to *p*, the overtone

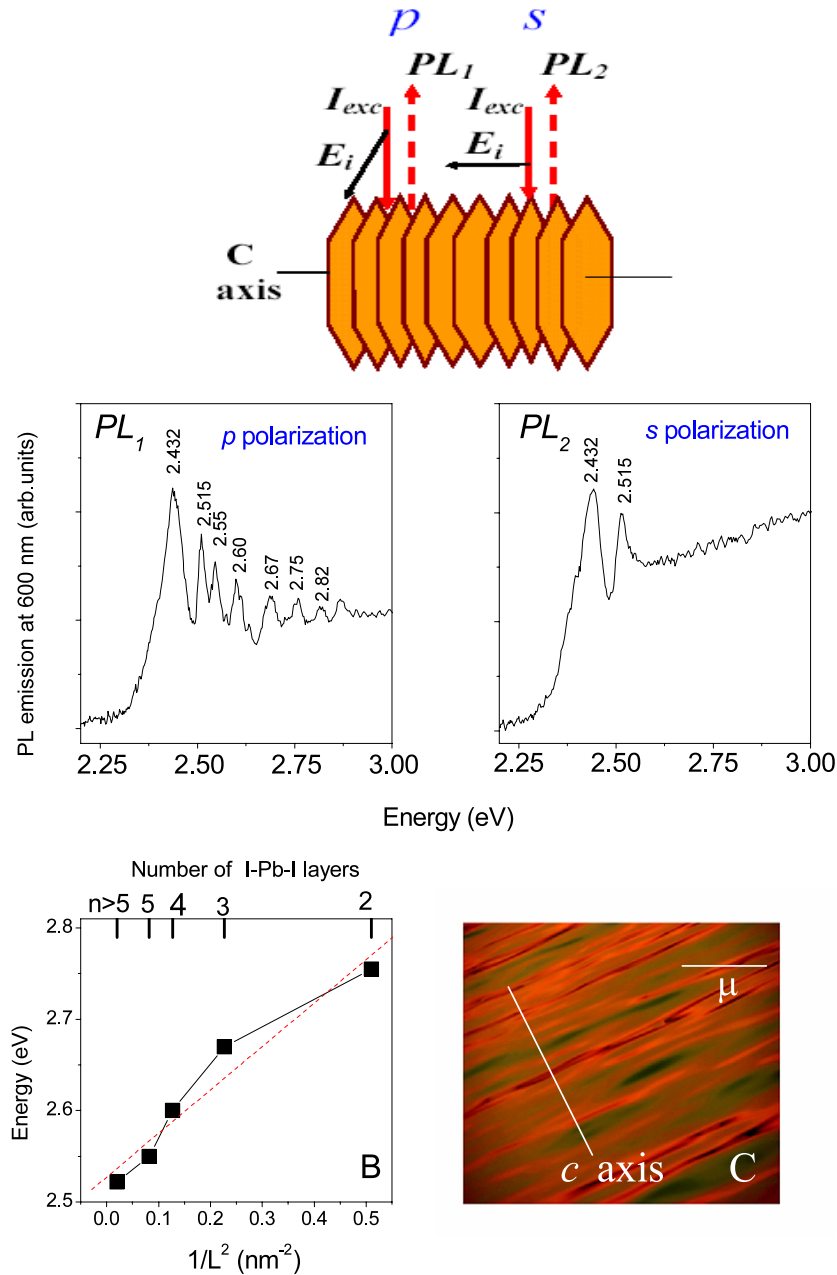


Figure 5. Polarized excitation spectra of the G emission band at LNT recorded on a vacuum thermal annealed (500 K) PbI_2 crystal. At the top of the figure the measuring configuration is depicted. The polarization states p and s refer to the excitation light with the electric field vector in the I–PbI–layer plane and perpendicular to the I–PbI–layer plane. In (B) are represented the peak energies of the excitation bands shown in PL_1 as a function of $1/L^2$. In (C) is illustrated microscopically the alternation of bundles of layers along the c crystalline axis.

band is less intense. This indicates a weaker resonance, so that matching of the exciting light with the band edge absorption is no longer given. The explanation is immediate: the PbI_2 structures resulting from thermal annealing are characterized by a wider band gap, so that p polarized excitation light of 514.5 nm no longer fulfils the resonance condition. The variation of the overtone band intensity is in the same sense as in the case when the as-grown PbI_2 crystal is cooled to LNT, when the band gap also increases (see the blue spectra in figures 6(B) and (C)).

4. Conclusions

Thermal annealing of PbI_2 crystals at 500 K followed by sudden cooling to liquid nitrogen temperature causes the continuity of the crystal along the c axis to be interrupted by the formation of stacking faults. These separate distinct layer structures of nanometric thickness in which varying numbers of I–Pb–I atomic layers are bundled. Such structures containing two, three, four, five etc I–Pb–I atomic layers behave as quantum wells of different widths.

The main signature of such effects is given by a gradual shift towards high energies of the fundamental absorption

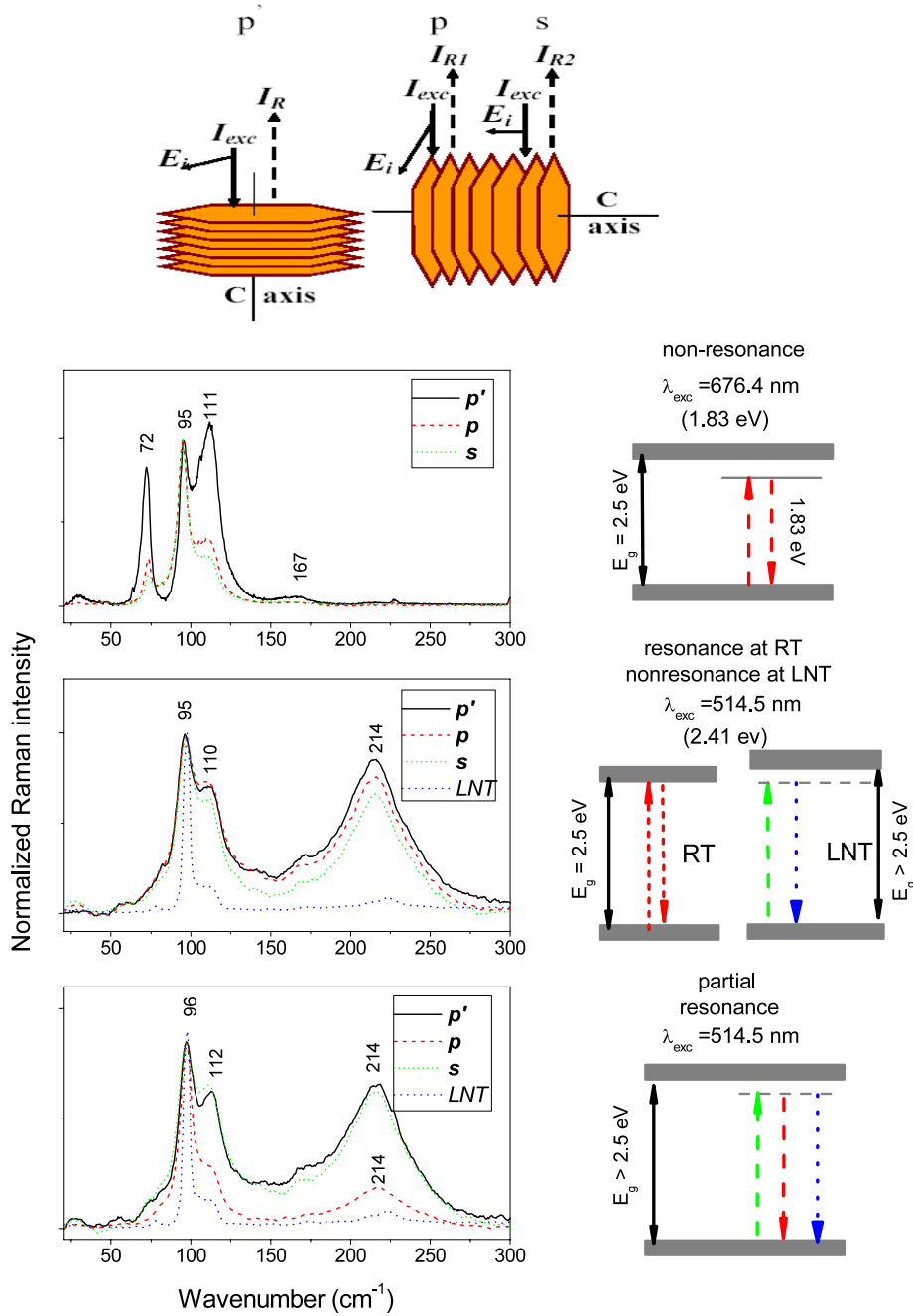


Figure 6. Raman spectrum anisotropy at $\lambda_{exc} = 676.4$ and $\lambda_{exc} = 514.5$ of an as-grown PbI_2 crystal ((A), (B)) and after vacuum thermal annealing at 500 K (C). At the top of figure are sketched the two back-scattering measuring configurations used (p' and p ; s) relative to the layer structure of the PbI_2 crystal and the meanings of the p and s polarized states. In (A) are presented the non-resonant Raman spectra $\lambda_{exc} = 676.4$ nm at the excitation wavelength of 676.4 nm. In (B) are presented the resonant Raman spectra at $\lambda_{exc} = 514.5$ nm. On cooling the sample to LNT, the fundamental absorption edge increases, so that the matching with the exciting light energy is eliminated and the Raman process becomes non-resonant (dotted spectrum). (C) shows the resonant Raman effect observed for the p polarized exciting light ($\lambda_{exc} = 514.5$ nm) on a PbI_2 crystal thermally annealed at 500 K. The departure from resonance occurs both when p polarized excitation light is used (dashed spectrum) and on cooling the sample (dotted spectrum) to LNT.

edge, which is revealed by specific anisotropy of the photoluminescence and Raman spectra. A novelty is the fact that such an effect is observed in bulk material, not only in nanometric thin films as was previously reported [7]. The quantum confining effect is revealed by specific variations of a wide extra-excitonic band (G) at 2.06 eV that originates in the radiative recombination of carriers (electrons and holes),

trapped on the surface defects. According to [7] the fine structure at 2.75, 2.64, 2.59 and 2.56 eV observed only for p polarized exciting light in the excitation spectrum of the G band is associated with the PbI_2 quantum wells including two, three, four and five I-Pb-I layers whose band gap energies are higher than the 2.52 eV that is the band gap of an as-grown crystal. A new and subtle supporting proof for quantum

wells behavior is found in the Raman spectra recorded with p polarized $\lambda_{\text{exc}} = 514.5$ nm. When the exciting light energy is close to the gap energy of PbI_2 , the Raman scattering has the character of a resonant process. It becomes non-resonant when the quantum well structures are generated inside the crystal because their band gap energies are higher than the energy of the exciting light. The role of surface defects in trapping the photo-generated carriers is demonstrated by the use of different samples: (i) crystalline slides cleaved from a PbI_2 crystal ingot with surface defects produced by mechanical scratching; (ii) microcrystalline powder and (iii) crystalline sample and microcrystalline powder subjected to thermal annealing at 500 K.

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