Optical spectroscopy of two-dimensional layered \((C_6H_5C_2H_4 - NH_3)_2 - PbI_4\) perovskite

K. Gauthron, J. S. Lauret, L. Doynette, G. Lanty, A. Al Choueiry, S. J. Zhang, A. Brehier, L. Largeau, O. Mauguin, J. Bloch, and E. Deleporte

1Laboratoire de Photonique et nanostructures, CNRS-UPR20, route de Nozay 91460 Marcoussis, France
2Laboratoire de Photonique Quantique et Moléculaire, École Normale Supérieure de Cachan, 61 avenue du président Wilson 94235 Cachan cedex, France

(Dated: August 30, 2009)

We report on optical spectroscopy (photoluminescence and photoluminescence excitation) on two-dimensional self-organized layers of \((C_6H_5C_2H_4 - NH_3)_2 PbI_4\) perovskite. Temperature and excitation power dependence of the optical spectra gives a new insight into the excitonic and phononic properties of this hybrid organic/inorganic semiconductor. In particular, exciton-phonon interaction is found to be more than one order of magnitude higher than in GaAs QWs. As a result, photoluminescence emission lines have to be interpreted in the framework of a polaron model.

PACS numbers: Valid PACS appear here

Optical properties of soft materials have attracted much attention for years thanks to their potential applications in optoelectronics devices. In particular, these last years, an increasing number of studies are dedicated on hybrid organic-inorganic materials[1], due to the possibility of combining the properties both of inorganic materials (high mobility, electrical pumping, band engineering) and of organic materials (low cost technology, high luminescence quantum yield at room temperature). In this context, organic-inorganic perovkites, having a chemical formula \(R(NH_3)_2 MX_4\) where \(R\) is an organic chain, \(M\) is a metal and \(X\) a halogen, represent a natural hybrid system. Such perovkites present a great flexibility in their optical properties: the spectral position of the excitonic transitions can be tailored by substituting different halides \(X\), the photoluminescence efficiency can be tailored by changing the organic part \(R\). This kind of perovkites has been studied both in the framework of fundamental studies \[2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24\] and of applications in optoelectronic as the active material in a distributed feedback laser for example \[25\]. Recently the strong coupling regime between the perovskite exciton and the optical mode of a Pétrot-Fabry microcavity has been demonstrated at room temperature in the UV range \[25\] and in the visible range \[26, 27\]. The physical properties of these new polaritons have now to be investigated. In particular, the demonstration of polariton-polariton interactions which lead to polariton scattering would be a breakthrough for the physics of these new devices in the context of the low threshold polariton lasers \[20, 27, 28\]. To evaluate these possibilities, a good knowledge of the perovskite material electronic properties is needed. As an example, the energy of the phonons and the strength of the electron-phonon coupling will indicate whether an efficient relaxation of perovskite polaritons is conceivable. Additionally, the origin of the different perovskite luminescence lines has to be clarified to improve the knowledge about the exciton which couples to the cavity mode.

In this paper, we report on the optical properties of a particular perovskite molecule, namely [bi-(phenethylammonium) tetraiodoplumbate]: \((C_6H_5C_2H_4 - NH_3)_2 PbI_4\) (named PEPI), absorbing and emitting in the green part of the visible range. Photoluminescence (PL) and photoluminescence excitation spectroscopy (PLE) are performed at various temperatures ranging from 10K to 300K. The origin of the different PL lines is discussed and an extensive study of the electron-phonon coupling is performed, for the first time to our knowledge in this kind of perovskite molecular crystal. A Longitudinal optical (LO) phonon energy of 14 meV and an electron-phonon coupling more than one order of magnitude higher than in GaAs quantum wells, have been estimated. PL and PLE experiments suggest that the PL signal at low temperature has to be interpreted in the framework of a polaron model.

FIG. 1: a) sketch of the perovskite structure. The blue points at the center of the octahedrons represent the Pb atoms while I atoms are displayed in green. The red symbols represents the organic chains. b) X-ray diffraction spectrum of a 50 nm \((C_6H_5C_2H_4 - NH_3)_2 PbI_4\) layer.
When a solution of $CgH5C2H4 - NH3I$ and PbI$_2$ dissolved in stoechiometric amounts in DMF (N,N-DiMethylFormamide) is deposited by spin-coating on a quartz substrate, a self-organization occurs, leading to the formation of a molecular crystal, consisting in an alternance of organic layers and inorganic layers (figure 7a). The self-organization occurs for thicknesses from 3 nm to 100 nm. The thickness of the perovskite layers can be controlled by changing the concentration of the solution, the speed and the acceleration of the spin-coater. AFM (Atomic Force Microscopy) measurements show that a high quality polycrystalline film is obtained, with a surface rugosity as small as 2 nm. X-ray diffraction has been used to characterize the ordering within the self-organized perovskite layers under study. Figure 1 shows an example of rocking curve measured on a 50 nm PEPI thin layer (obtained by spin-coating a solution of 10 wt% $CgH5C2H4 - NH3I$ and PbI$_2$ dissolved in stoechiometric amounts in DMF). The observation of numerous diffraction orders proves the high crystallinity of the thin layer and the very good periodicity of the stacking. Each satellite peak being regarded as a diffraction plane, it is seen that we can observe diffraction planes from (002) to (0022) beyond $\theta = 60^\circ$. As a consequence, a period of 16.4 Å can be accurately estimated. The inorganic layers, which consist of PbI$_{2-}$ octahedrons, having a lattice parameter of 6.4 Å, we deduce that the organic part has an extension of 10 Å along the growth direction. Identical results have been obtained from X-ray diffraction spectra on samples of different thicknesses.

Because of the very large energy difference between the band gap of the inorganic layer and the HOMO-LUMO of the organic layer, a multi quantum well electronic structure is formed in these self-organized perovskite structure with a strong 2D quantum confinement: the quantum wells are formed by the PbI$_{2-}$ octahedrons monolayers and the barriers by the organic alkylammonium layers. Moreover, the barrier and the well of these natural QW have very different dielectric constants ($\varepsilon_{\text{barrier}} \approx 2.1$; $\varepsilon_{\text{well}} \approx 6.1$)\cite{17}. Thanks to this high contrast in dielectric constants, the Coulomb interaction in the QW is hardly screened by the presence of the barrier: it is the well known dielectric confinement effect\cite{29,30}. Therefore, the electron-hole interaction within the exciton is strengthened, resulting in huge oscillator strengths and very large exciton binding energies (of a few hundred of meV).

PL and PLE experiments have been performed on a PEPI layer of thickness $\sim 5$ nm, containing 3 QWs: this thin layer has been obtained by spin-coating a solution of 1 wt% $CgH5C2H4 - NH3I$ and PbI$_2$ dissolved in stoechiometric amounts in DMF. The excitation source is a quartz-iode lamp spectrally filtered with a monochromator. The image of the exit slit of the monochromator is formed on the sample leading to a spot size of about 3 mm x 1 mm. PL experiments as a function of the excitation power are performed using a laser diode at 405 nm. The luminescence is then collected and dispersed in a 1 in double-spectrometer and detected with a photomultiplier. The sample can be placed either on the cold finger of a helium closed cycle cryostat (sample temperature between 10K and 300K) or in a bath of superfluid helium (2K).

Figure 2a exhibits the PL spectrum of the sample at 10K: two lines can be observed at 2.355 eV (S1) and 2.337 eV (S2). Similar optical spectra were already reported in the literature but interpreted in different ways\cite{10,15,17}. Fujisawa et al attribute the PL high energy line to the free excitons and the lower energy lines to bound excitons\cite{10}. Hong et al suggest the presence of free excitons, bound excitons and of phonon replica\cite{15} and Ishihara et al raise the possibility of the existence of three exciton lines named A,B and C as observed in GaN\cite{17}. In order to get more information about the two PL lines, PL spectra as a function of the excitation power (at 2K) have been performed (see fig. 2b). Excitation powers ranging between 3 µW and 4 mW have been explored, but results are presented only for excitation powers below 500 µW because the sample presents some photobleaching at higher powers. As evidenced on figure 2b, the two PL lines have the same behavior in this range of power. We can thus deduce that the satellite line S2 has an intrinsic origin and should not be attributed to excitons bound to defects (which would correspond to a sublinear dependance on the excitation power) nor to bi-excitons (surlinear behavior). Figure 2a shows also the PLE spectrum recorded at 10K with a detection energy tuned in resonance with the low energy PL emission line.
S2. The PLE spectrum recorded with a detection energy tuned in resonance with S1 is exactly similar: this again rules out an interpretation of S1 in terms of bi-exciton. Moreover the independence of the PLE spectra from the detection energy demonstrates that the two emission lines are connected to the same excited states. The PLE spectrum is composed of three lines at 2.365 eV, 2.398 eV and 2.436 eV, and of the 2D step around 2.565 eV which corresponds to the absorption edge of the uncorrelated electron-hole pair continuum. The energy difference between the first line and the 2D absorption step corresponds to an exciton binding energy of 200 meV, in good agreement with previous estimate deduced from optical absorption spectroscopy [15]. At 10 K, the Stokes shift between the PLE lower energy line and the PL line S1 is 10 meV. The origin of the Stokes shift will be further discussed in the following.

We now investigate the optical properties of this perovskite multi-layer sample for various temperatures. Figure 3 shows PL spectra measured for temperatures ranging from 10K to 295K: the energy of the high energy PL line increases with temperature. This is in contrast with other perovskites, for instance \((\text{C}_n\text{H}_{2n+1} - \text{N}_3\text{H})_2\text{PbI}_4\) for which the emission energy has been reported to decrease with temperature [17]. Our result shows the importance of the barrier nature for the understanding of the perovskite electronic structure. Indeed, depending on the exact composition of the barrier, the dielectric constant difference \(\epsilon_{\text{well}} - \epsilon_{\text{barrier}}\) between the barrier and the QW may increase or decrease with temperature. Moreover as detailed in ref. [13], the exciton energy in perovskite QWs is mainly determined by \(\epsilon_{\text{well}} - \epsilon_{\text{barrier}}\) through the dielectric confinement. As a result, changing the barrier composition may lead to opposite temperature behavior of the exciton transition energy. Additionally, the strain in the QW might be different depending on the nature of the barrier [4] and might also influence the exciton energy dependance on temperature. A detailed optical study of the temperature behaviour for several perovskites is under progress and should further clarify the exact role of the barrier composition.

Figure 4a summarizes the evolution with temperature of the integrated PL intensity measured on the S1 line. This emission intensity remains stable between 10 K and 100 K and decreases by 2 order of magnitude between 100 K and 300 K, approximately as \(\exp(E_a/kT)\) with \(E_a \sim 60\) meV. This value is quite different from the one measured by Hong et al [15]: in their paper, an activation energy of 230 meV is reported, quite similar to the exciton binding energy. For that reason, the decrease of the integrated PL intensity has been attributed by these authors to the partial ionization of the exciton. Nevertheless, the activation energy we measure here is far from the exciton binding energy.
binding energy. Performing similar measurements on several samples of same thickness but prepared at different days, $E_a$ is found to significantly vary from sample to sample between 30 meV and 80 meV. The strong dispersion in the measured value of $E_a$ demonstrates that the decrease of the integrated PL intensity should be related to an extrinsic non radiative mechanism.

As shown on fig. 4b, the measured full width at half maximum of the PL line $S_1$ continuously increases when increasing the sample temperature between 10 K and 300 K. We attribute this broadening to exciton interaction with phonons and describe it within a phenomenological model, often used for inorganic quantum wells [31]. The dashed line represents the fit of the exponential data with the function:

$$\Gamma = \Gamma_0 + a.T + \frac{\Gamma_{LO}}{\exp\left(\frac{\hbar \omega_{LO}}{kT}\right) - 1} + \Gamma_{imp}\exp\left(-\frac{E_a}{kT}\right)$$

(1)

In this model, $\Gamma_0$ is the linewidth at 0 K, $a.T$ represents the scattering of excitons with acoustic phonons. The third term corresponds to the interaction of excitons with optical phonons, where $\Gamma_{LO}$ is related to the strength of exciton-phonon coupling and $\hbar \omega_{LO}$ is the optical phonon energy. The last term corresponds to the exciton scattering on impurities with an activation energy $E_a = 60$ meV deduced from temperature dependant measurements. Some assumptions used in this model can be discussed in the case of organic-inorganic perovskite quantum wells. First, the model is valid within the framework of the envelope function [31], which requires that the variation of the excitonic wave function is smooth on several unit cells. In the perovskite molecular crystal, the exciton Bohr radius has been estimated to be 1.7 nm in the layers plane [15], that is to say 3 or 4 unit cells. Therefore, the limit of the envelope function approximation is reached in perovskite layers. Nevertheless, notice that perovskite layers present several features of 2D QW which are well described using the envelope function. Secondly, the thermal variation of optical phonons with temperature is neglected in our simple approach. However in soft material, this assumption could be too strong. In fact, the Van der Walls bounds which create the self-assembled QWs are weak as compared to covalent bounds in inorganic QW systems. As a consequence, a weak perturbation could strongly deform the structure and affect the phonon energies. Anyway, using this simple approach, we are able to give the first estimate of the phonon energy and of exciton phonon-interaction in this new system.

In order to extract physical values from the model, we have chosen to fix the optical phonon energy $\hbar \omega_{LO}$ to 13.7 meV (the value of optical phonons in PbI$_2$ [32]). A very good agreement between the experimental data and the theoretical model is then obtained providing some numerical values for the parameters $\Gamma_0$, $\Gamma_{LO}$ and $a$. A value of $\Gamma_0 = 17 \pm 1$ meV is deduced: it varies from a sample to another between 12 meV and 17 meV, as expected if $\Gamma_0$ is mainly dominated by inhomogeneous broadening. The parameter $a$ is equal to $0.03 \pm 0.01 meV.K^{-1}$. The uncertainty on this value is large because of the large inhomogeneous linewidth at 0 K. Nevertheless, the exciton interaction with acoustic phonons is found more than one order of magnitude higher than in GaAs QWs [31]. The coupling $\Gamma_{LO}$ with the optical phonons is estimated to ~ 70 meV which is also more than ten times higher than in inorganic quantum wells [31]. These values don’t depend on the sample, showing the intrinsic nature of these measurements.

To finish the discussion of the perovskite optical spectroscopy, we want to go further in the interpretation of the PL lines $S_1$ and $S_2$ and of the lines observed in the PLE spectrum. Figure 4c shows that the Stokes shift between $S_1$ and the lower energy PLE line does not depend on temperature. In inorganic quantum wells, the stokes shift is usually due to exciton localization in potential minima induced by disorder. The exciton trapping becomes less efficient as temperature is increased. As a result, the stokes shift decreases with temperature and eventually vanishes when the thermal energy $kT$ overcomes the trapping potential. The fact that in our Perovskite sample the 10 meV Stokes Shift is still observed when $kT$ is larger than 10 meV (above 115 K) strongly suggests that the energy difference between emission and absorption is not due to exciton localization in disorder potential. It has been reported that lead halides such as PbI$_2$, PbCl$_2$ or PbBr$_2$ exhibit a very strong excitons-phonon coupling leading to the existence of self-trapped excitons [33], and the Stokes Shift in PbI$_2$ amounts to 7.4 meV [34]. Moreover, note that the independence of the Stokes shift with temperature can also be observed in InGaN layers [35] and has been interpreted as an evidence of a polaron origin of the emission line. Since we have shown previously that the exciton-phonon coupling is very high in perovskite layers, the independence of the Stokes shift with the temperature strongly suggests that the mean emission line $S_1$ has to be described in a polaron model. Since the energy separation between $S_1$ and $S_2$ is 14 meV, which corresponds to the LO phonon energy we have determined in PEPI, $S_2$ may be a phonon replica of the main line $S_1$. Considering this context of high exciton-phonon coupling, the three lines observed in the PLE spectrum could also be related to phonon replica. Notice however that the energy separation between the PLE lines is superior to 30 meV (33 meV between the lower energy line and the middle one, 38 meV between the middle line and the higher energy one). This would mean that the vibration mode in the excited states is different from that in the fundamental state, as it is often observed in molecules or in molecular crystals where polaronic effect occurs [36]. Another interpretation of the low energy PL line could be related to the electronic structure of the conduction band: in PbI$_2$, the conduc-
tion band is three times degenerate, the crystal field and the spin-orbit coupling allowing the lift of the degeneracy. Therefore, the different lines observed in PL and PLE spectra could come from the different states of the conduction bands. Experiments as a function of the polarization of the incident light are under progress and should allow discriminating between the two interpretations.

To conclude, we have performed optical spectroscopy (photoluminescence and excitation of the photoluminescence) of $(C_6H_3(C_2H_4 - NH_2)_2PbI_4$ perovskite self-organized layers. For the first time an estimate of the optical phonon energy is obtained as well as of the exciton-phonon interaction. These results could be further confirmed using Raman spectroscopy and theoretical calculations of the Perovskite phonon structure. The exciton-phonon interaction is found to be more than one order of magnitude higher than in GaAs QWs, both for acoustic and optical phonons. This leads to an interpretation of the PL emission lines within the framework of a polaron model. The very strong exciton-phonon interaction in Perovskite QWs is very promising for the use of this material as an active medium in polaritonic systems such as microcavities operating in the strong coupling regime. It should allow efficient polariton relaxation, a key requirement to obtain polariton lasing.

Acknowledgments: Authors are grateful to M. Schott for helpful discussions. This work has been supported by the ANR grant "MICHRY", the CNRS "Région Ile de France" grant "MICROG" and the RTRA grant "MOSKITO". The Laboratoire de Photonique Quantique et Moléculaire de l’Ecole Normale Supérieure de Cachan is a Unité Mixte de Recherche associée au CNRS (UMR8537).

* Electronic address: lauret@lpqm.ens-cachan.fr

[1] D.B. Mitzi, K. Choudhuri and C.R. Kagan, IBM J. RES. & DEV., 45, 29 (2001).
[2] G.C. Papavassiliou and I.B. Koutselas, Synth. Met. 71, 1713 (1995).
[3] R. Parashkov, A. Bréchier, A. Georgiev, S. Bouchoule, X. Lafosse, J. S. Lauret, C. T. Nguyen, M. Leroux, and E. Deleporte, in Progress in Advanced Materials Research, edited by N. H. Volin Nova Science (2007).
[4] S. Zhang, G. Lanty, J.S. Lauret, E. Deleporte, P. Audebert, and Laurent Galmiche., Acta Materialia 57, 3301 (2009).
[5] G. Lanty, A. Bréchier, R. Parashkov, J.S. Lauret and E. Deleporte, New Journal of Physics 10, 065007 (2008).
[6] G. Lanty, J.S. Lauret, E. Deleporte, S. Bouchoule, and X. Lafosse, App. Phys. Lett. 93, 081101 (2008).
[7] A. Bréchier, R. Parashkov, J.S. Lauret, and E. Deleporte, App. Phys. Lett. 89, 171110 (2006).
[8] J. Wenus, R. Parashkov, S. Ceccarelli, A. Bréchier, J. S. Lauret, M. S. Skolnick, E. Deleporte, and D. G. Lidzey, Phys. Rev. B 74, 235212 (2006).
[9] J.I. Fujisawa, and T. Ishihara, Phys. Rev. B 70, 113203 (2004).
[10] J.I. Fujisawa, and T. Ishihara, Phys. Rev. B 70, 205330 (2004).
[11] M. Shimizu, and J.I. Fujisawa, J. of Lumin. 108, 189 (2004).
[12] T. Kondo, T. Azuma, T. Yuasa, and R. Ito, Solid state comm. 105, 253 (1998).
[13] K. Tanaka, F. Sano, T. Takahashi, T. Kondo, R. Ito, and K. Ema, Solid state comm. 122, 249 (2002).
[14] T. Hattori, T. Taira, M. Era, T. Tsutsui and S. Saito, Chem. Phys. Lett. 254, 103 (1996).
[15] X. Hong, T. Ishihara and A.V. Nurmiko, Phys. Rev. B 45, 6961 (1992).
[16] T. Ishihara, J. Takahashi and Takenari Goto, Solid State Comm. 69, 933 (1989).
[17] T. Ishihara, J. Takahashi and Takenari Goto, Phys. Rev. B 42, 11099 (1990).
[18] T. Ishihara, X. Hong, J. Ding and N.V. Nurmikko, Surface Science 267, 323 (1992).
[19] C.Q. Xu, H. Sakakura, T. Kondo, S. Takeyama, N. Miura, Y. Takahashi, K. Kumata and R. Ito, Solid state comm 79, 249 (1991).
[20] X. Hong, T. Ishihara and A.V. Nurmiko, Solid state comm 84, 657 (1992).
[21] C.Q. Xu, S. Fukuta, H. Sakakura, T. Kondo, R. Ito, Y. Takahashi, and K. Kumata, Solid state comm 77, 923 (1991).
[22] T. Katoaskia, T. Kondo, R. Ito, S. Sasaki, K. Uchida, and N. Miura, Phys. Rev. B 47, 2010 (1993).
[23] E.A. Muljarov, S.G. Tikhodeev, N.A. Gippius and Teruya Ishihara, Phys. Rev. B 51, 14370 (1995).
[24] M. Era, S. Morimoto, T. Tsutsui, and S. Saito, App. Phys. Lett. 65, 676 (1994).
[25] T. Fujita, Y. Sato, T. Kuitani, and T. Ishihara, Phys. Rev. B 57, 12428 (1998).
[26] A. Kavokin and G. Malpuech, Cavity Polaritons (Elsevier, Amsterdam, 2003).
[27] D. Bajoni, P. Senellart,E. Wertz, I. Sagnes, A. Miard, A. Lemaître, and J. Bloch, Phys. Rev. Lett. 100, 047401 (2008).
[28] S. Christopoulos and G. Baldassarri, H. von Hogersth, A. J. D. Grundy, P. G. Lagoudakis, A. V. Kavokin, J. J. Baumberg, G. Christmann, R. Butte, E. Feltin, J.-F. Carlin, and N. Grandjean, Phys. Rev. Lett. 98, 126405 (2007).
[29] L. V. Keldysh, JETP Lett. 29, 658 (1979).
[30] M. Kumagai, and T. Takagahara, Phys. Rev. B 40, 12359 (1989).
[31] J. Lee, E. S. Koteles, and M.O. Vassel, Phys. Rev. B 33, 5512 (1986).
[32] M.S. Skolnick, and D. Bimberg, Phys. Rev. B 47, 11099 (1993).
[33] V.G. Plekhanov, Progress in Materials Science 49, 787 (2004).
[34] T. Goto, and S. Saito, J. Of Lumin. 70, 435 (1996).
[35] H. Kudo, K. Murakami, H. Ishibashi, R. Zheng, Y. Yamada and T. Taguchi, Phys. Stat. Sol. (b) 228, 55 (2001).
[36] S. Jursenas, A. Gruodis, G. Kodis, M. Chachisvilis, V. Gulbinas, E.A. Silnish and L. Valkunas, J. Phys. Chem. B 102, 1086 (1998).
[37] I. Ch. Schlüter and M. Schlüter, Phys. Rev. B 9, 1652 (1974).