

## **RADIATIVE CENTERS FORMED BY HALOGEN MOLECULES INTERCALATED IN MoS<sub>2</sub> AND WS<sub>2</sub> LAYERED SEMICONDUCTORS**

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The study of the steady-state and time resolved photoluminescence of *2H-MoS<sub>2</sub>:Cl<sub>2</sub>* and *2H-WS<sub>2</sub>:Br<sub>2</sub>* crystals is presented. For both investigated materials two distinct spectral regions was identified: the excitonic region, located in the vicinity of the indirect band gap and consisting of several sharp zero-phonon lines and their phonon replica, and the vibronic broad band IR region, characteristic also for natural crystals without halogen impurities. The thermal quenching of the exciton emission at  $T > 60\text{K}$  was also observed. The strong sharp photoluminescence line of the indirect band gap semiconductors is attributed to the recombination of excitons bound on electron-attractive neutral centers, formed due to the intercalation of the halogen molecules in the van der Waals gap of the layered compound. In the framework of a kinetic model for a compensated semiconductor in thermal equilibrium, the temperature behaviour of the excitonic spectral line intensities, radiative decay time and the thermal quenching process of the bound exciton emission are described.

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### **1. Introduction**

Recently the first observation of the bound exciton luminescence of synthetic *2H-MoS<sub>2</sub>* crystals, intercalated with Cl<sub>2</sub> molecules, has been reported [1,2].

Due to the layered structure of the tungsten and molybdenum dichalcogenides, there is a good deal of interest at present in these materials and their intercalate complexes. Atoms within their layers are bound by strong covalent or ionic forces while individual layers are held together by relatively much weaker van der Waals type forces. Some contributions from covalent and ionic interaction with dichalcogenides layers are also possible, particularly in the intercalate complexes [3]. As a result of this type of structure, these compounds exhibit marked anisotropy in most of their physical properties that accounts for the great interest in this family of materials. So, for example, *MoS<sub>2</sub>* (also *WS<sub>2</sub>*) possesses very good antifriction properties, that, due to good adhesive characteristics and stability against moisture, make it to be extensively employed as solid lubricant. On the other hand, the weak interlayer forces also facilitate the intercalation of foreign ions, atoms or molecules between the layers. In this process intercalant species are inserted into the van der Waals gap, and in most cases they occupy the interstitial sites, and charge transfer between the intercalant species and the host layer generally accompanies the process. The interest for the optical and luminescent properties of these materials, especially of tungsten and molybdenum, becomes understandable if one takes into account the fact that transition metal dichalcogenides are very attractive semiconducting materials for use in photoelectrochemical energy conversion as electrodes, because they are not as susceptible to photodecomposition as are many other materials whose band gap are in the region of maximum solar energy efficiencies. Beside this, *2H-MoS<sub>2</sub>* and *2H-WS<sub>2</sub>* were the first compounds synthesized as inorganic fulleren-like material [4,5]. It was shown, that fulleren-like molybdenum and tungsten disulfides preserve the semiconducting properties of the layered crystals [6].

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Molybdenum and tungsten disulfides exist in two polymorphous types: two layer hexagonal form (2H) and three layer rhombohedral form (3R). Hexagonal  $2H-MoS_2$  and  $2H-WS_2$  (space group  $P6_3/mmc - D_{6h}^4$ ) consist of covalently bonded  $S-T-S$  layers (where  $T$  is transition metal) linked by weak van der Waals forces. The unit cell contains two layers; the sulfur atoms in one layer are directly above the molybdenum or tungsten atom in the next. All  $TX_2$  compounds are indirect band gap semiconductors [3,7,8]. This explains why, in spite of the large number of publications on optical studies, no radiative properties have been reported for the transition metal dichalcogenides until very recent reports on  $2H-WS_2$  and  $2H-WS_2e_2$  [1,2].

In this work we present the results of experimental investigations and modelling, for the temperatures domain  $2 \div 150 K$  and the energy range  $0.7 \div 1.4 eV$ , of the steady-state and time resolved photoluminescence of  $2H-MoS_2:Cl_2$  and  $2H-WS_2:Br_2$  crystals, compared with natural  $2H-MoS_2$  and  $2H-WS_2$  undoped crystals.

## 2. Experiment

The synthetic two layer hexagonal form (2H) of the transition metal dichalcogenides  $MoS_2$  and  $WS_2$  were obtained by chemical vapour transport method (CVT) using as transport agents halogens –  $Cl_2$  for molybdenite and  $Br_2$  for tungsten disulphide. The selection of transport agent for crystals growth were done from the point of view of close correspondence of the intramolecular distance between atoms in halogens molecules and the characteristic dimensions of their potential sites in the van der Waals gap. Indeed, as in other  $TX_2$  crystals, there are two adjacent tetrahedral coordinated interstitial sites in the interlayer gap of which distance between centres and dimensions are very close to those of the selected halogen molecules. In our opinion, the matching of the dimensions explains the phenomenon of inherent intercalation of these halogens in the interlayer gap, furthermore, this is the cause of the easiness of “capture” of these transport agents molecules compared with the cases of other intercalant with a mismatch of molecules dimensions to those of interstitial sites.

During the crystal growth of the synthetic crystals, the halogen molecules, used as a transport agent, can intercalate into the van der Waals gap. This phenomenon leads to some changes in electronic properties of the layered semiconductors. The first observation of the bound exciton luminescence of synthetic  $MoS_2$  crystals, intercalated with  $Cl_2$  molecules, has been already reported in [1,2]. Naturally grown samples were cut from natural bulk  $p$ -type molybdenum disulfide crystals and then cleaved to produce fresh clean surfaces.

The steady-state photoluminescence (PL) measurement were performed with a variable temperature optical cryostat, a grating monochromator coupled to a germanium detector using standard lock-in detection techniques. The luminescence excitation was provided by an  $Ar$ -ion laser or a diode-pumped cw solid-state  $532 nm$  laser.

## 3. Results

For both investigated materials two distinct spectral regions were identified (Fig. 1).

The first one is an excitonic region, located in the vicinity of the indirect band gap and consisting of several sharp zero-phonon lines and their vibronic replica. These lines appear due to recombination of excitons bound to halogen molecules, intercalated during the growth process. Alike to spectra of the natural crystals, these lines are present only for the spectra of the synthetic crystals doped with halogen molecules and thereby confirm the influence of the intercalated halogen molecules on the electronic properties of the layered semiconductors and can serve as index of halogen intercalation. The temperature dependence of the PL intensity in excitonic region of spectra, on the example of  $MoS_2$ , can be seen in Fig. 2.

The second spectral region is the IR vibronic broad band, characteristic also for natural  $MoS_2$  and  $WS_2$  crystals without halogen impurities, and associated with an intrinsic defect of the host lattice, which act as a shunt channel and contributes to the thermal quenching of the exciton emission at  $T > 60 K$  for  $MoS_2:Cl_2$  and  $WS_2:Br_2$ .

In contrast to the broad band, the intensity of which remains constant up to about  $100 K$ , the amplitudes of the sharp lines for the both investigated materials have a strong dependence on temperature. There were observed and identified at least three zero-phonon spectral lines: at

$E_A=1.174$  eV,  $E_B=1.176$  eV and  $E_C=1.186$  eV for MoS<sub>2</sub>:Cl<sub>2</sub> and at  $E_A=1.323$  eV,  $E_B=1.326$  eV and  $E_C=1.336$  eV for WS<sub>2</sub>:Br<sub>2</sub> respectively. For the both investigated materials, the 1-st line (marked in Fig. 2 with A) is manifested only at lowest temperature. The temperature increase leads to the redistribution of the PL intensity to the 2-nd and 3-rd lines (marked with B and C in Fig. 2). This is a extremely dependent on temperature process. For example, for MoS<sub>2</sub>:Cl<sub>2</sub>, already at  $T=6$  K the A-line can be observed just as a shoulder of the B-line; then the B-line amplitude is the highest in the whole emission spectra up to  $T\approx 50$ K, when the C-line became dominating and a fast thermal exponential quenching of the short wavelength emission occurs. At  $T>80$  K only the broad band luminescence is observed for both synthesized materials. The multiple phonon replicas of the A-C lines (peaks A<sup>Ph</sup> - C<sup>Ph</sup>) can be also observed.

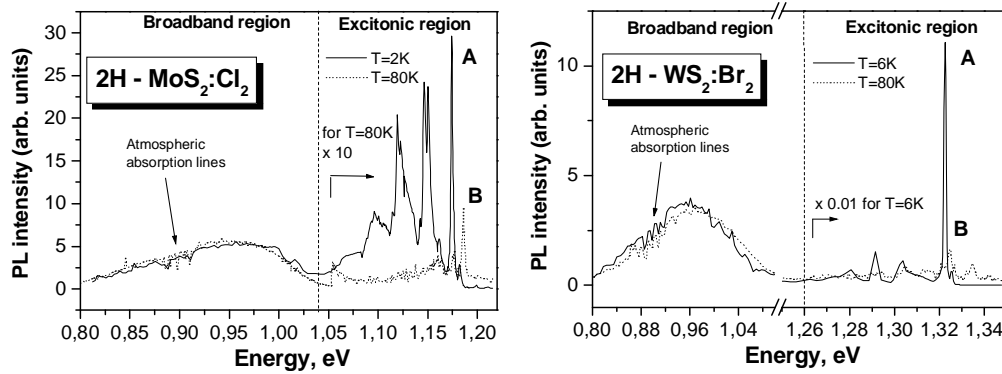


Fig. 1. Shapes of the PL spectra for MoS<sub>2</sub>:Cl<sub>2</sub> and WS<sub>2</sub>:Br<sub>2</sub> and their dependence on temperature.

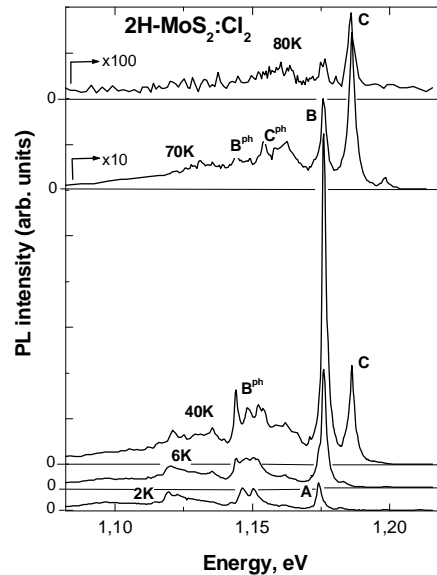


Fig. 2. The temperature dependence of the PL intensity in excitonic region of spectra

#### 4. Modelling

In order to describe the temperature behaviour of the excitonic spectral lines intensities, radiative decay time and the thermal quenching process of the bound exciton emission, a kinetic model for a *n*-type compensated semiconductor in thermal equilibrium similar to that developed in [9] was accepted (shown in Fig. 3), with a time of the excitonic-hole thermalization dependence on temperature expressed following [10]. In the modelling the kinetic model was applied.

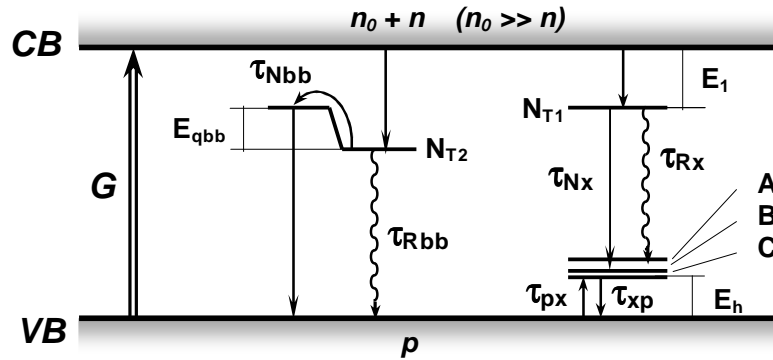


Fig. 3. Representation of zone diagram and proposed radiative and nonradiative processes.

In the model, the equations describing the population of levels were solved numerically as function of temperature and density of bound excitons and intrinsic deep host lattice defects participating in radiative and nonradiative recombination. The resulting theoretical curves compared with the experimental points for the temperature dependence of the quantum efficiencies of the broad-band emission  $\eta_{Rbb}(T)$  for  $MoS_2:Cl_2$  are presented in Fig. 4. Mismatches of these curves with experimental data, especially in the case of quantum efficiencies of the excitonic radiative recombination  $\eta_{Rx}(T)$ , can be caused also by the errors occurring during the data acquisition due to a small spectral resolution of the spectrometer compared with the peaks width. It can be seen that the phenomena of thermal appearing and quenching of excitonic lines are also described by this model. The compiled PL decay time for the excitonic lines and corresponding data for the  $WS_2:Br_2$  are presented in Fig. 5. One observes a narrow intense peak at  $\sim 6$  K and a large hump at  $\sim 50$  K. They could be due to the predominance of the transition on level A in the first case and on B and C for the second one.

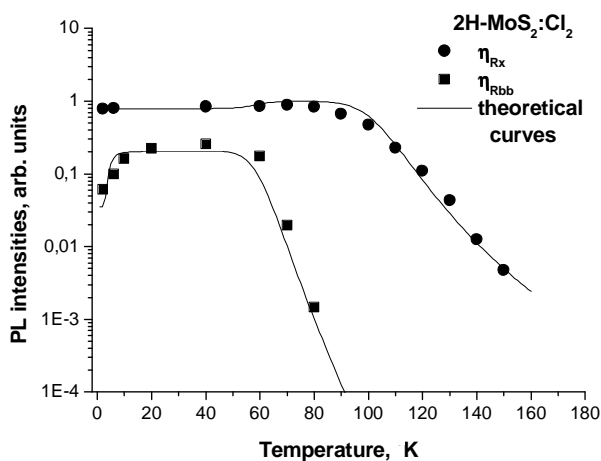


Fig. 4. Plots of theoretical (line) and experimental (scatter) PL intensities for  $MoS_2:Cl_2$ .

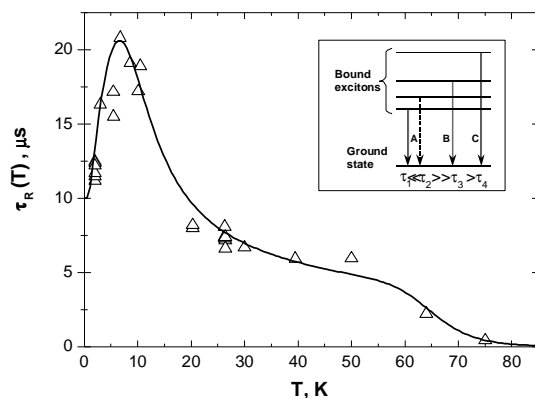


Fig. 5. PL decay time of the excitonic lines (A, B, C) for  $WS_2:Br_2$  as function of temperature. Solid line – theoretical curve, triangles – experimental data.

## 5. Conclusions

Halogen molecules, used as transport agents in single crystal growth, can intercalate between the layers of (2H) molybdenum and tungsten disulfides. This phenomenon is not restricted

to these materials but has also been observed in  $WSe_2$  and probably should be observed in other  $TX_2$  compounds, leading to a new class of near infrared emitters. The temperature behavior of the steady-state PL intensities of the  $A$  and  $B$  zero-phonon lines of the bound exciton are adequately described within the framework of a simple kinetic model applied to an  $n$ -type compensated semiconductor in thermal equilibrium.

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