

EXCITONIC LUMINESCENCE OF THE TUNGSTEN DISULFIDE CRYSTALS INTERCALATED WITH HALOGEN MOLECULES

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The radiative recombination in the layered disulfide transition metal dichalcogenide compounds 2H-WS₂:I₂ and 2H-WS₂:Br₂ has been investigated. It is shown that the strong photoluminescence (PL) of these indirect band gap semiconductors is caused by recombination of excitons bound to neutral centres formed due to the intercalation of halogen molecules Br₂ and I₂ in the well defined sites of the van der Waals gap. These centres, located at energy $E_T \approx 0.1$ eV below the conduction band, display the same properties as the isoelectronic traps in GaP, providing the efficient radiative recombination. The temperature dependences of the quenching zero-phonon spectral line intensities are described by a simple expression for both types of crystals.

Key words: Layered compounds, Intercalation, Luminescence, Excitons.

INTRODUCTION

The hexagonal 2H-polytype of tungsten disulphide, WS₂, belongs to the class of transition metal dichalcogenides that exhibit many physical properties with a pronounced two-dimensional character [1]. The peculiar properties of these materials result from their layered structure ($P6_3/mmc - D_{6h}^4$), consisting of covalently-bonded S-W-S sheets linked by weak van der Waals forces. Within each sheet there is a trigonal prismatic coordination between the metal and chalcogenide atoms. Like the other transition metal dichalcogenide compounds, WS₂ is an indirect-gap semiconductor with the energy of the indirect band gap is $E_g = 1.35$ eV at room temperature [2] and 1.45 eV at T=80K.

In previous works was reported the first observation of the excitonic luminescence in tungsten dichalcogenides layered compounds 2H-WS₂, intercalated by Br₂ and I₂ molecules during the crystal growth processes. The halogen molecule placed in the adjacent tetrahedral sites of the gap gives rise to the neutral radiative center, with properties, similar to that of the isoelectronic impurities in GaP or Si, which provide the strong bound-exciton luminescence of the indirect band

gap semiconductor. Excitonic PL has been also observed in synthetic 2H-MoS₂ single crystals grown using chlorine Cl₂ as transport agent [3].

In this paper the results of the observed temperature evolution of the steady-state emission spectra and the fast thermal quenching of the excitonic luminescence of Br₂ and I₂ intercalated 2H-WS₂ single crystals are presented.

EXPERIMENTAL RESULTS

The PL spectra of 2H-WS₂:Br₂, as in the case of synthetic 2H-WS₂:I₂, consist of two parts: a short-wave excitonic region, which includes several sharp intense lines, and a relatively weak broad band. Fig. 1 shows the temperature evolution of the excitonic emission spectrum. At $T < 6\text{K}$ the spectra of the 2H-WS₂:Br₂ sample consist of only one sharp line A

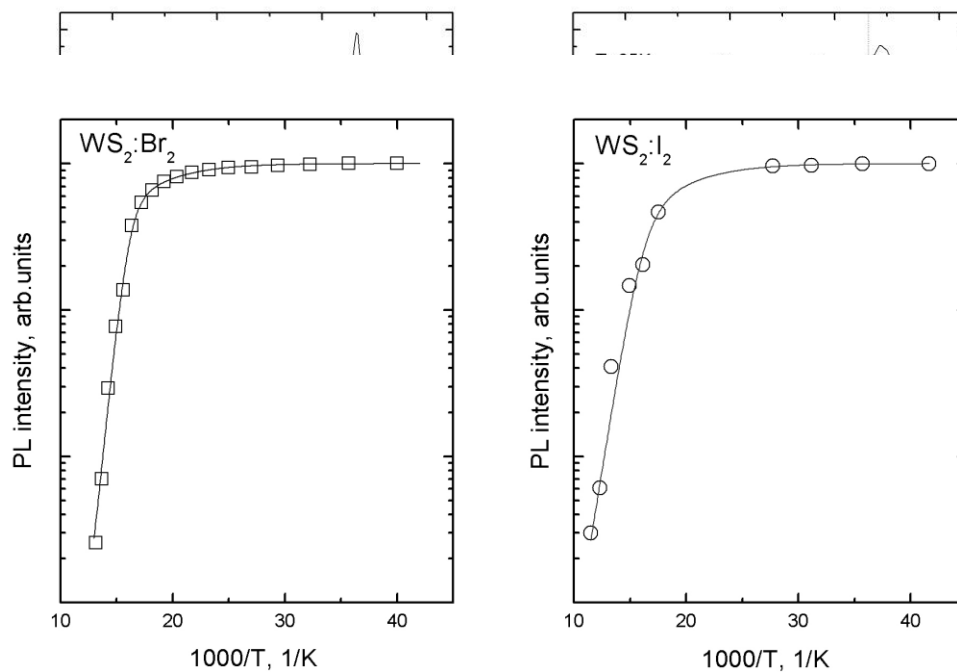


Fig. 2. Temperature dependence of the integrated intensity for the excitonic emission of 2H-WS₂:Br₂ (squares) and 2H-WS₂:I₂ (circles). The solid lines illustrate the fit of Eq. (1) to the thermal quenching behaviour.

($E_A=1.323\text{eV}$) and its vibronic side band. At temperature higher than 15K there is the second zero-phonon line B ($E_B=1.326\text{eV}$) which dominates the emission spectra. The energies of the A-B doublet peaks ($\delta=3.0\text{meV}$), are smaller by approximately 0.12eV than the indirect band gap energy of WS₂. With temperature increasing PL intensity is redistributed from the long wavelength peak A to the peak B, while the integral emission intensity remains constant up to 50K. The intensity of the third short wavelength peak C ($E_C=1.336\text{eV}$) becomes comparable to that of the main line only above this temperature. At $T > 60\text{K}$ a fast thermal exponential quenching of the PL emission occurs (Fig. 2

dots). The activation energy of this quenching is approximately 0.1eV. A similar spectral structure and temperature behavior is shown for 2H-WS₂:I₂ samples, but because of the relatively large width of the spectral components, the A-B doublet is not resolved. As compared to 2H-WS₂:Br₂ samples, the main peaks are shifted by 2.4meV to higher energies.

DISCUSSION

Fig. 2 shows the integral intensity of the doublet vs 1000/T in a semi-logarithmic plot. For excitonic luminescence the gradual decrease occurs so that the total quenching can be described by an expression

$$I(T)/I(0) = (1 + C_1 \exp(-E_1/kT) + C_2 \exp(-E_2/kT))^{-1}, \quad (1)$$

with activation energies E_1 and E_2 (C_1 and C_2 are constants; $C_2 \gg C_1$). The fit to the experimental values (Fig. 2) is noted by the solid line. There where obtained the activation energies values at $E_1=24\text{meV}$ and $E_2=150\text{meV}$ for 2H-WS₂:Br₂ and, respectively, 23meV and 96meV for 2H-WS₂:I₂.

As noted above, the short wavelength part of the emission spectra is caused by the recombination of excitons bound to the electron-attractive centres, formed by diatomic halogen

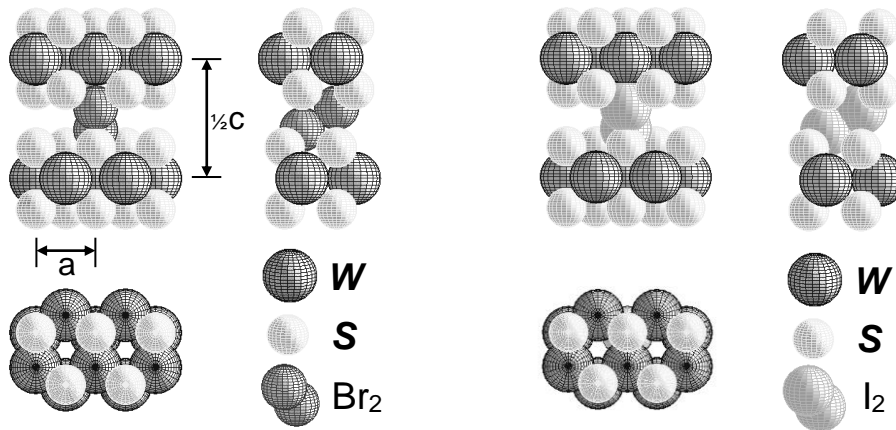


Fig. 3. Three projections of the 2H-WS₂ crystalline lattice fragment with a Br₂ and I₂ molecules positioned in the van der Waals gap. The atomic radius values are represented in the same scale as the lattice parameters and correspond to the atomic radius of the respective elements.

molecules unambiguously positioned within the van der Waals gap [3]. We wish to point out that in the case of 2H-WS₂, the Br₂ molecule dimensions have the best matching to the host crystalline lattice (Figure 3). There is a different situation in the WS₂:I₂ sample – the I₂ intramolecular distance is by about 20% bigger than the Br₂ intramolecular distance value. This discrepancy lead to the inhomogeneous distortion of the WS₂:I₂ host lattice induced by the intercalated iodine molecules. As a consequence of the distortion the width of the excitonic spectral lines, observed for WS₂:I₂ crystals, are almost of an order of magnitude larger than in the case of WS₂:Br₂.

CONCLUSIONS

Thus, the intercalation of transition metals dichalcogenides by halogens provides a new potential use of these layered materials: besides applications in such important areas as photovoltaic solar cells, solid lubricants, or intercalation batteries and references therein, the TX₂ compounds could be of interest as efficient luminescent materials in the near IR spectral region. It should be interesting to extend the excitonic PL study to TX₂ thin films and commercial powders having been submitted to an intercalation process in a halogen atmosphere.

REFERENCES

1. Wilson J. A. and Yoffe A. D.; (1969); Adv. Phys.; 18; 193-335.
2. Sourisseau C., Cruege F., Fouassier M., and Alba M.; (1991); Chem. Phys.; 150; 281-293.
3. Kulyuk L., Charron L. and Fortin E.; (2003); Phys. Rev. B; 68; 075314(1-5).