Raman and photoluminescence spectroscopy of atomically thin MoS_2, $MoSe_2$, and WSe_2

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Atomically thin molybdenum and tungsten dichalcogenides are of considerable interest due to their usability in fabricating electronic devices. Recently, photoluminescence (PL) of monolayer MoS_2 has been reported [1], which renders these materials also interesting for optical and optoelectronic applications. Light emission is due to the formation of a direct bandgap in monolayer material compared to an indirect bandgap of the bulk crystal.
We investigate photoluminescence, transmission, and vibrational properties of few- down to monolayer samples of MoS_2, $MoSe_2$ and WSe_2 [2], which are prepared by mechanical exfoliation from single crystals onto SiO_2/Si substrates. Raman spectroscopy shows that the energy, width, and amplitude of the vibrational modes strongly depend on the thickness of the flakes. As for MoS_2 we find for $MoSe_2$ that the Raman signal shows a characteristic softening (stiffening) of the A_{1g} (E^1_{2g}) mode with decreasing thickness of the material, respectively. Our high experimental resolution allows us to observe a Davydov splitting of the A_{1g} line for the first time. Starting from one Raman line for mono- and bilayer $MoSe_2$ it splits into two for three and four layer material. For five layers, three Raman lines appear. This effect is due to the presence of more than one $MoSe_2$ molecule in the unit cell. For $MoSe_2$ and WSe_2 we find that the B^1_{2g} mode, which is normally Raman inactive, becomes Raman active for a bilayer and is decreasing in intensity for thicker few-layer material.

PL emission of few- and monolayer $MoSe_2$, WSe_2, and MoS_2 is investigated with a confocal micro-PL setup. The observed PL intensity maxima for monolayer materials are in excellent agreement with the known direct A exciton in the corresponding bulk material. This observation corroborates recent model calculations for other transition metal dichalcogenides, which show that the indirect gap increases in energy, while the direct gap at the K point stays at about the same energy when decreasing the thickness from bulk to monolayer material. The PL intensity of monolayer $MoSe_2$ is 10 - 20 times stronger than that of the bilayer material. The emission intensity from the trilayer decreases again by one order of magnitude as compared to the bilayer. Interestingly, the PL intensity of the WSe_2 bilayer is only reduced by a factor of 4 compared to the monolayer. To gain insight into the efficiency of the PL emission process we investigate the role of absorption for each monolayer material. The retrieved values for A_{MX2} are similar for the three monolayer materials. In contrast, the PL emission is always brightest for WSe_2 and faintest for naturally grown MoS_2, differing by at least an order of magnitude, which might be due to a different quantum yield. This observation paves the way for optoelectronic devices based on this exceptional material.

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[2] P. Tonndorf, R. Schmidt, P. Böttger, X. Zhang, J. Börner, A. Liebig, M. Albrecht, C. Kloc, O. Gordan, D. R. T. Zahn, S. Michaelis de Vasconcellos, and R. Bratschitsch, Optics Express **4**, 4908-4916 (2013).