Luminescence and Optical Second Harmonic Generation in Atomically Thin Layered Transition Metal Dichalcogenides

Leonid Kulyuk (Culiuc)

Institute of Applied Physics, Academic str. 5, Chișinău, MD-2028, Republic of Moldova

Layered compounds involving transition metals and chalcogens are promising candidates for exploring atomically thin structures. Bulk crystals are semiconductors with an indirect gap in the near infrared spectral range. In contrast, monolayer dichalcogenides such as MoS_2, WS_2 or WSe_2 are 2D semiconductors with a direct gap in the visible spectral range [1 and references therein]. In their two-dimensional (2D) form the TX_2 compounds are promising building blocks for novel semiconductor heterostructures [2]. Moreover, owing to their layered structure, radiative properties of these indirect band gap bulk semiconductors can be provided by means of intercalation of halogen molecules into the van der Waals gap [3].

This work concerns the photoluminescence (PL) properties of 2H-WS_2, 2H-WSe_2, 2H- and 3R-MoS_2 bulk crystals and 2D flakes intercalated with halogen molecules, caused by direct gap emission with both neutral and charged exciton recombination, as well as by bound excitons recombination. The crystals were grown through the chemical-vapor method, using iodine, bromine or chlorine as transport agents. Single- and few-layer flakes of TX_2 samples have been obtained by mechanical exfoliation of bulk crystals.

Thin MoS_2 flakes of different thicknesses exfoliated on a silicon substrate have been studied using optical second harmonic generation (SHG) microscopy. A high SHG intensity was found not only for a countable number of atomic layers but also for thick flakes of up to 150 nm. Reduction of the SHG intensity was observed only for a small portion of flakes, for both very thin and quite thick ones. This was attributed to the presence of polytypism, i.e., of 3R non-centrosymmetric and 2H centrosymmetric polytypes, in a source bulk crystal. Absolute values of nonlinear susceptibility of flakes of different thicknesses were estimated.

The presence of two polytypes in the MoS_2 samples was confirmed by the spectral structure of the bound excitons luminescence observed in flakes at low temperature. It is shown, that this structure is unique and provides a robust experimental signature of crystal polytype investigated (2H- or 3R-MoS_2). This result is confirmed by X-ray diffraction analysis and DFT electronic band structure calculations. Thus, a quite simple optical technique for the reliable identification of the MoS_2 crystals polytype is proposed.

1. S. Das, J. A. Robinson, M. Dubey, H. Terrones, M. Terrones, *Annu. Rev. Mater. Res.*, **45,** 20.1-20.27 (2015).
2. A. K. Geim, I. V. Grigorieva *Nature*, **499**, 419-425 (2013).
3. L. Kulyuk, D. Dumchenko, E. Bucher, K. Friemelt, O. Shenker, L. Charron, E. Fortin, T. Dumouchel, *Phys. Rev.* ***B*****72**, 0075336(1-7) (2005).

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