Where No One Else Dares: Growing Bulk Sulfide Single Crystals

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As it was stated in famous Smet's review paper *"Luminescence in Sulfides: A Rich History and a Bright Future"*, sulfide-based luminescent materials have attracted a lot of attention for a wide range of photo-, cathodo- and electroluminescent applications [1]. They feature narrow band gaps and low phonon energy, and compared to their oxide counterparts, they exhibit greater covalency and atomic overlap due to the diffuse nature of sulfur's orbitals, which is, in part, attributed to its lower electronegativity. This leads to complementary properties, such as increased hole mobility and narrower electronic band gaps [1,2]. Another significant aspect of sulfides lies in their structural chemistry. The presence of larger sulfur ions, with a radius of 1.8 Å, stabilizes metal sulfides in lower symmetry structures with lower coordination numbers [3].

From the technological standpoint, sulfides have "the worst of both worlds" of halides and oxides. Similarly to halides, sulfides tend to react with oxygen and water at elevated temperatures to form very stable oxysulfides. Like oxides, sulfides often possess high melting points, but unlike oxides, they react with high melting metals used as crucible materials for oxide single crystal growth. This presents a significant limitation for growing high-quality sulfide crystals. However, our team possesses high-temperature annealing technology in a sulphonating atmosphere. The combination of the above-mentioned properties makes the growth of sulfide bulk crystals a challenging task.

In this presentation, a significant contribution to the sulfide crystal growth and research at the Institute of Physics of the Czech academy of sciences, will be acknowledged. Special attention will be given to crystalline platelets of ternary sulfide of general formula $ALnS_2$ (A = alkali metal, Ln = La, Gd, Lu, Y) [4] and single crystals of Pr^{3+}-doped Lu_2S_3 [5], as we are the only laboratory in the world carrying on systematic research of these highly interesting compounds. Special attention will be given to the ways of crystal preparation, followed by detailed characterization of their structural and luminescence properties, mainly by means of time-resolved luminescence spectroscopy. Applications mainly in the fields of fast-scintillators, white solid state LEDs or mid-infrared lasers will be addressed as well.

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