<u>Topic 1:</u> ***Syntheses of mixed-valence inorganic/solid state compounds and their structural characterization***

Abstract:

The ternary compounds In_5Ch_5X (Ch = S, Se; X = Cl, Br) are synthesized by solid state methods in evacuated quartz ampoules. They represent new mixed valence solids with indium occurring simultaneously in three different oxidation states: In^+, In^{3+} and In^{2+}. Despite their similarity in the ionic formulation ($In_5Ch_5X = In^+ \, 2In^{3+} \, (In_2)^{4+} \, 5Ch^{2-} \, X^-$), which is the same for all compounds, they crystallize in two structure types (In_5Ch_5Cl-type: monoclinic, $P2_1/m$, Z = 2; In_5Ch_5Br-type: orthorhombic, $Pmn2_1$, Z = 2). Disregarding the distribution of the halogen atoms, the anionic partial structure is very similar in both structure types. The main difference is an exchange of (In^+) by $(In_2)^{4+}$ and vice versa on selected positions. This is possible due to the similar coordination of both ions (three-capped trigonal prisms). In contrast to the perfectly ordered crystals, HRTEM investigations show remarkable differences in the real structures of In_5Ch_5Cl and In_5Ch_5Br, where the chloride containing compounds revealed several structural defects atypical for the In_5Ch_5Br-type.

<u>Topic 2:</u> ***Thermoelectric and photoelectric properties of In_5Ch_5X (Ch = S, Se; X = Cl, Br) and their tuning by targeted substitutions***

Abstract:

The mixed valence compounds In_5S_5Br, $In_5S_3Se_2Br$, In_5SSe_4Br and In_5Se_5Br exhibit interesting thermoelectric properties. A continuous increase of the Seebeck potential is associated with an increase of the selenium content in the structure of In_5S_5Br. In_5S_5Br reveals low Seebeck potentials within the studied range (ΔT = 0 - 80K) and a maximum value of 0.34 mV for ΔT = 80K. It behaves as *p*-type semiconductor. The substitution of two sulphur species by selenium, as in $In_5S_3Se_2Br$, shows *n*-type conductivity and approx. -16.00 mV for the same ΔT. Further substitutions of sulphur in the structure maintain the *n*-type conductivity and increase dramatically the Seebeck potential to -225.26 mV (ΔT = 80K). Repeating cycles of Seebeck potential jump over time for In_5Se_5Br and In_5SSe_4Br, show differences in their potential and shape of maxima as well as in their recovery time.

I-U measurements on the individual micro needle-shaped crystals, of the ternary mixed valence compound In_5Se_5Cl, crystallizing in the monoclinic crystal system ($P2_1$/m), showed significant light sensitivities. Micro needles of In_5Se_5Cl “glued” on Si- and Cu- substrates were measured under five different wavelengths with various irradiation intensities to investigate their photo chromatic sensing behavior along with the substrate’s influence. In the measuring voltage range 0 – 3 V and maximal LED illumination intensity, current jumps above two orders of magnitude were observed for white light (4100 K; 200 lm), followed by the blue light (460 nm; 976 mW). The amber light (590 nm; 203 mW) exhibited the lowest response. Green- and blue light were selected to determine the substrate’s effect. The micro-needles chips prepared with Si-substrates displayed higher currents for the same voltages in comparison to those prepared with Cu-substrates. These differences decreased with the voltage increase for both employed wavelengths.

The mutual structural substitution of a selenium with sulfur, led to the compound In_5SSe_4Cl. The later crystallizes similarly to In_5Se_5Cl. Its I-U measurements recorded with green and blue light, on Cu-substrate chips within the voltage range 0 -3 V, revealed more pronounced photo chromatic sensorial for both wavelengths used. These differences increased with the voltage increase for both employed wavelengths. At 3 V, current increases up to 2.2 times and 2.4 times were observed for the green light and blue light respectively. Typically high and better distinguishable sensorial activity was observed for all the employed wavelengths using chips with In_5SSe_4Cl crystals on Cu-substrate, even at minimal irradiation LED power (0.25 %).