

Salient gas and photosensorial properties of new ternary and quaternary nano and micro mixed valence crystalline compounds

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The compounds $\text{In}_5\text{Ch}_5\text{X}$ (Ch = S, Se; X = Cl, Br) represent mixed valence solids with indium occurring simultaneously in three different oxidation states: In^+ , In^{3+} and In^{2+} . Despite the similar ionic formulation ($\text{In}_5\text{Ch}_5\text{X} = \text{In}^+ 2\text{In}^{3+} (\text{In}_2)^{4+} 5\text{Ch}^{2-} \text{X}^-$), they crystallise in two structure types ($\text{In}_5\text{Ch}_5\text{Cl}$ -type: monoclinic, $P2_1/m$; $\text{In}_5\text{Ch}_5\text{Br}$ -type: orthorhombic, $Pmn2_1$)[1]. The mixed valence character and their structural characteristics offer substitution possibilities on the cationic and anionic sites. The quaternary derivative of $\text{In}_5\text{Ch}_5\text{Cl}$, obtained by mutual substitution of one indium species by thallium, $\text{TlIn}_4\text{S}_5\text{Cl}$, synthesized in form of nanowires shows salient the resistivity sensitivity toward gaseous NO_2 and NH_3 in air [2]. Its resistivity can decrease by more than two orders of magnitude due to the adsorption of the NO_2 molecules. The $I-U$ measurements on the individual micro needle-shaped crystals, of the ternary and quaternary mixed valence compounds revealed significant light sensitivities. Within the potential range 0–3 V and maximal LED illumination intensity, current jumps of two orders of magnitude are observed for white light (4100 K; 200 lm), followed by the

blue light (460 nm; 976 mW) [3]. The mutual structural substitution of selenium by sulphur and bromine by chlorine, led to pronounced differences in the photochromatic sensorial properties. These differences increased with the applied potential increase. The increase of selenium content in $\text{In}_5\text{Ch}_5\text{Cl}$ (Ch = S, Se) shifts the optical band gap toward the higher wavelengths. The introduction of Thallium in the structure shows the opposite effect. These properties are supposed to be particularly important for future nanodevice applications.

Key words: Mixed valence, ternary and quaternary compounds, needle shape crystals, gas sensitivity, photochromatic sensitivity.

References

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