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Scientific paper

PHOTO CHROMATIC SENSORS OF MULTINARY MIXED VALENCE INORGANIC MICRO NEEDLES

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Abstract

The recent 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 %). The micro-reflection measurements of both needle-shaped crystals displayed a substitution dependent band-gap. For In_5Se_5Cl the band gap was *estimated at 580 nm. Thickness interference oscillations strongly damped due to structural inhomogeneity or defect-related absorption suggest two possible band gaps for In_5SSe_4Cl; at 540 nm or at 620 nm.*

***Key words**: Photo chromatic sensors, micro needles, sensorial activity, substrate influence, substitution influence*

INTRODUCTION

Nano- and micro-crystals of several inorganic compounds are becoming very appealing in academic and industrial research due to their novel physical properties, i.e. electronic, optical, thermoelectric properties, for the construction of advanced functional nano- and micro-devices, such as field effect transistors [1,2], lasers [3], sensors [3-5], generators [6-8] and photodetectors [9,10]. The synthesis of nano- and micro-shaped materials with controlled structures and novel properties has been widely studied for their promising novel physical and chemical properties [11]. In particular, photo-detectors, known also as optical switches are essential elements in optical gating devices used for memory storage and logic circuits, and can be made with various 1D semiconductor nano-structures, such as InP nano-wires [12], ZnO nano-wires [13, 14], CdS nano-belts [15], CdSe and CdS nano-ribbons [16, 17], and Ge nanowires [18], etc.

Beside the wide use of binary sulfides and selenides for nano- and micro-photo-sensitive devices [15-17, 19-20] offering a specific and often discrete band gap, there is a group of ternary and quaternary sulfides-chlorides of indium such as In_5Ch_5Cl (Ch = S, Se) which offers tunable photosensitivity based on mutual elemental substitutions [21-23]. The mixed valence character of indium in them opens windows for oriented partial or complete substitutions of several ionic species. Parallel to indium substitutions, chalcogenes and halides can be substituted [21-24]. Earlier measurements of their nano- and micro-crystals under artificial polychromatic light illumination have revealed significant ionic substitution dependence of the photosensitivity of all synthesized derivatives. The *I-U* curves recorded in dark and upon three illumination levels of 0.08 mW/cm^2, 0.20 mW/cm^2 and 0.45 mW/cm^2 using two bias ranges of -2 to 2 V and -10 to 10 V have displayed pronounced light sensitivities for all indium-selenium-chloride-type structures [21]. Inspired from these earlier observations, we focused our recent research on the estimation and characterization of the photo-chromatic sensitivity of In_5Se_5Cl micro-crystals and its derivative In_5SSe_4Cl. Aiming in this way, the identification and evaluation of: (a) the proper influence of the electrode material (substrate), Si and Cu, on the photo-chromatic sensitivity of In_5Se_5Cl; and (b) the influence on the photo-chromatic response of a mutual substitution of one selenium position with sulfur in the structure of In_5Se_5Cl.

EXPERIMENTAL

Chemicals and Materials

The starting compounds for the synthesis of the ternary and quaternary mixed valence inorganic solids In_5Se_5Cl and In_5SSe_4Cl respectively, were obtained from commercial sources: In shot tear drop with a purity of 99.999 and Suflur Pieces < 7mm, 99.999%, Chempur GmbH, Germany, Selenium Shot 1-3 mm, 99.995% Fluka Chemie GmbH, Germany, $InCl_3$ powder, 99.999%, and the quartz ampoules were supplied by Heraeus, Germany.

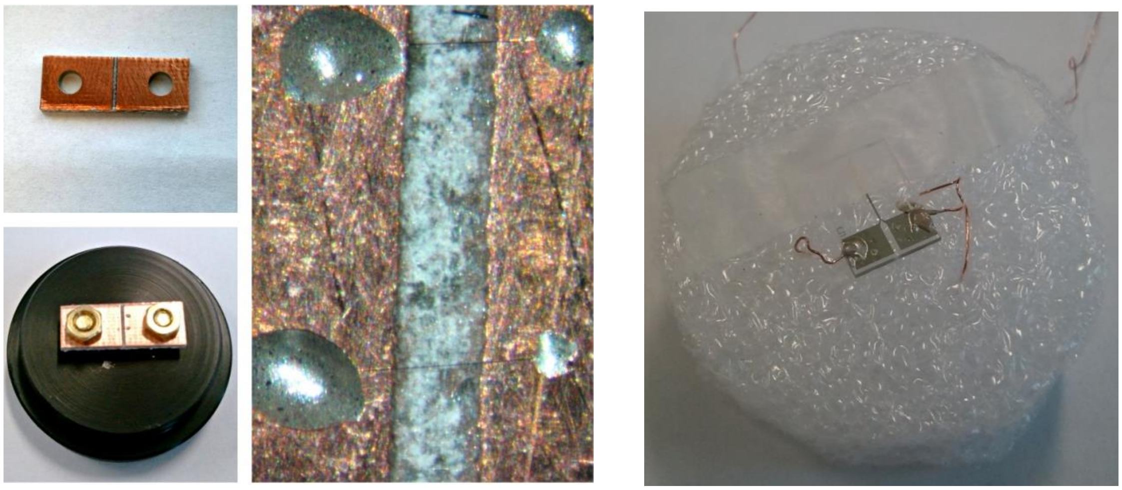
Syntheses and characterization of mixed valence compound In_5Se_5Cl and In_5SSe_4Cl

The multinary compounds In_5Se_5Cl, In_5SSe_4Cl were prepared from the elements and the binary compound $InCl_3$ in stoichiometric amounts in evacuated and sealed quartz ampoules placed in tubular ovens at 450°C for 2 weeks [24]. The determination of the samples morphology was performed with a CS44 SEM (Scanning Electron Microscope) delivered from the company CamScan (Cambridge) equipped with a Robinson BSE and SE detector. The qualitative elementary analyses were carried out with a WDX-3PC (Wavelength Dispersive X-ray Spectroscopy) system delivered from Microspec (Freemont). The X-Ray measurements for the characterization of the crystalline samples were performed with a powder diffraction device D5000 delivered from "SIEMENS" company (Karlsruhe). The device works with $CuK\alpha_1$-radiation in transmission mode. The diffraction patterns were recorded by means of a "Braun" Position Sensitive Detector (PSD-50M) with an angular increment of 0.015° and a measuring time varying from 0.5 - 10 hours.

Photoelectric measurements of the micro-crystals of In_5Se_5Cl and In_5SSe_4Cl

The electrical (current-voltage) measurements of single needles: In order to investigate their photo-electrical behavior and to determine the respective sensitivities at room temperature, the measurements were performed using pre-fabricated micro chips. Two individual needles were carefully selected using an electrical microscope and were aligned on the chip. Both ends of the individual needle were contacted to the microchip using Silver contacting epoxy (Fig. 1a). After that, the microchips were placed in a thermostat and thermally treated at 100°C for two hours. Prior to measurements, the chips (Si or Cu) were connected/tighten to a self prepared two electrode measuring cells (Fig. 1) The *I-U* measurements of the individual needles were performed on an

Electrochemical Interface & Impedance Analyser, "IVIUMSTAT" coupled with ModuLight module, which is a programmable polychromatic light source that has been specifically designed to investigate photo-electrical devices, such as solar cells.



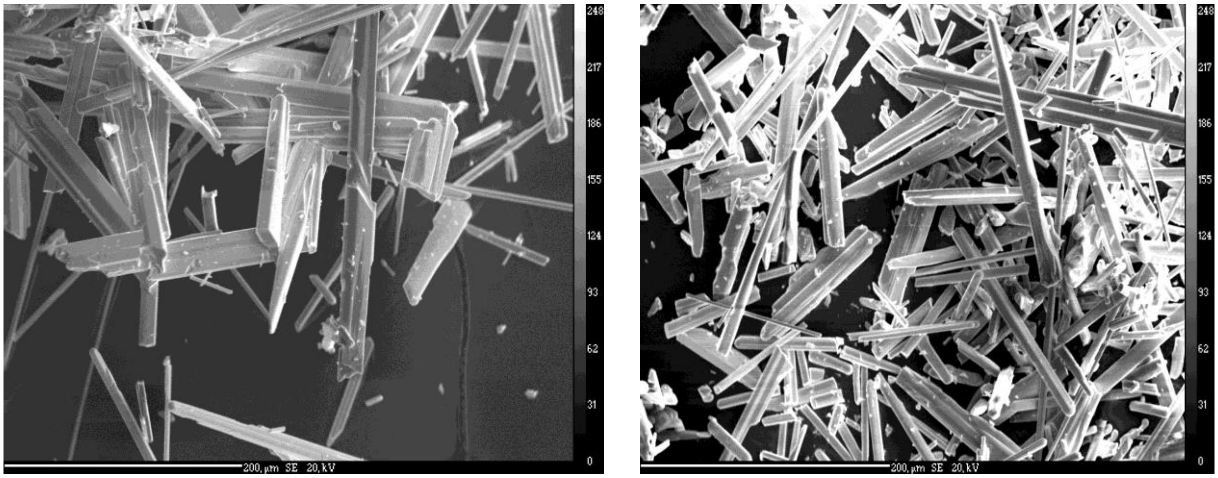
(a) **(b)**

Fig. 1. (a) Cu-substrate chip (top left), chip fixed on a self made 2 electrode cell (bottom left), two needle-shaped crystals contacted by silver contacting epoxy on a Cu-substrate chip, (b) Two needle-shaped crystals "glued" on a Si-substrate chip, contacted and fixed on a self made cell

DISCUSSION OF THE RESULTS

Morphological and symmetrical characteristics of the crystals

The classical solid state syntheses involving the elements of the 3rd, 6th and 7th main group such as In, Se, Cl, brought to light a group of mixed valence isostructural multinary *Me*-chalcogenide halides consisting of micro- wire needle-shaped crystals (Fig. 2 a,b) The *In*-chalcogenide-chlorides In_5Ch_5Cl (Ch = S, Se) crystallize in the monoclinic crystal system ($P2_1/m$), with two formula units in the unit cell and reveal several nanoscopic structural defects [24]. Due to the one dimensional preferential growth direction of their crystals, their powder diffraction patterns were strongly influenced by texture effects (Fig. 3). Besides the disadvantages, this morphology offers numerous of advantages associated with the high ratio of surface/volume. Parallel to this aspect, the mixed valence character of these compounds described as: $In_5Ch_5Cl = [In^+] [(In_2)^{4+}] 2[In^{3+}] 5[Ch^{2-}] [Cl^-]$ plays an important role in the properties of this compound. Oriented substitutions of indium, chalcogene and halides in them were strongly related to changes in physical properties, making them good candidates with tunable properties for various applications [21-23].



(a) **(b)**

Fig. 2. (a) TEM image of the micro crystals of (a) In_5Se_5Cl and (b) In_5SSe_4Cl

Parallel to the investigation of In_5Se_5Cl we considered in this study its mono-sulfur substitute derivative, namely In_5SSe_4Cl. It crystallizes similar to In_5Se_5Cl ($P2_1/m$), exhibiting micro- wire needle-shaped crystals (Fig. 2b). The similar crystallization symmetry of these crystals is shown in Fig. 3 by their measured powder patterns. The substitution of one selenium position in the structure of In_5Se_5Cl with sulfur, leads to a significant displacement of its reflections toward greater 2θ values, typical for In_5SSe_4Cl.

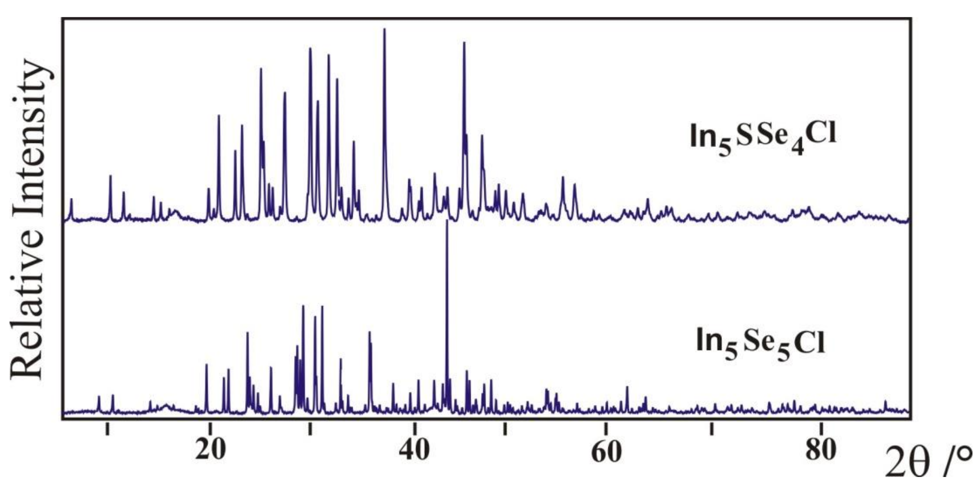
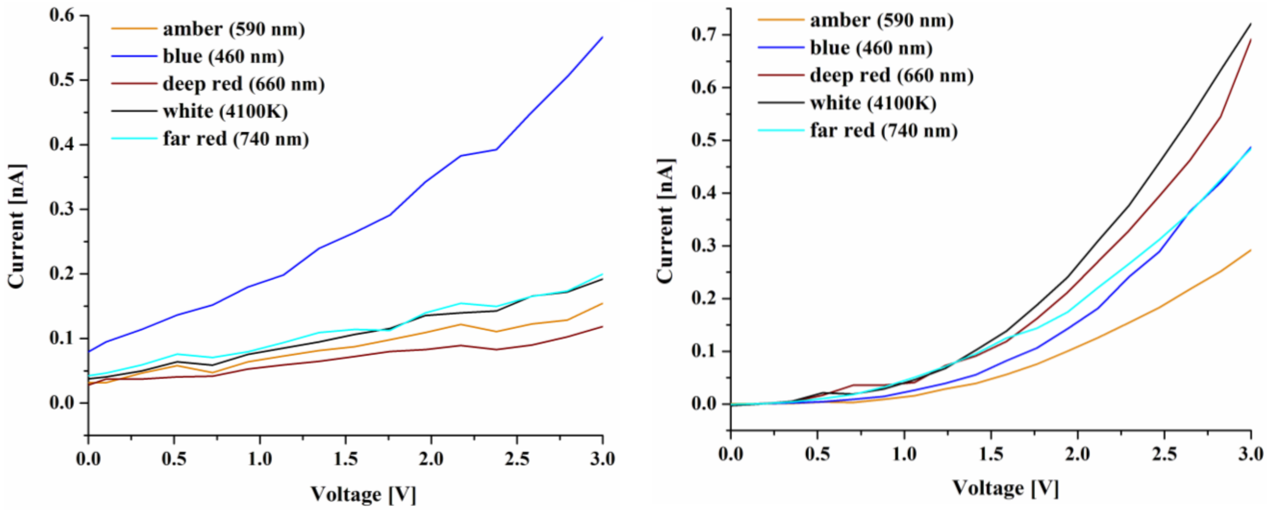


Fig. 3. Powder diffraction patterns of In_5Se_5Cl and In_5SSe_4Cl. Despite the same symmetry, the reflections of In_5SSe_4Cl are shifted to greater 2θ values

Light sensorial properties of In_5Se_5Cl

The substrate's influence

For the characterization of the influence electrodes substrate on the photo-sensitivity of the In_5Se_5Cl micro needles, selected crystals of In_5Se_5Cl were "glued" on Si- and Cu- substrates and measured under five different wavelengths, at room temperature (Fig. 4 a,b). For comparison reasons, the recorded *I-U* characteristics for amber light (590 nm), blue (460 nm), deep red (660 nm), white (4100 K) and far red (740 nm) are plotted in Fig. 4 a,b.



(a) **(b)**

Fig. 4. (a) I-U curves of In_5Se_5Cl micro-crystals (a) on Si-substrate, (b) on Cu-substrate, recorded at five wavelengths with the same illumination intensity, at room temperature, when applying a bias varying from 0 to 3 V

The In_5Se_5Cl crystals on Si-substrate different from them on Cu-substrate show a non-zero current even at zero voltage. For the blue light, the recorded current reaches up to 0.8 nA. At first sight, for low bias values the photo-response of the needles on Si-substrate seems higher than them on Cu-substrate. Anyway, in general the increase of bias leads to a more effective response of the crystals on Cu-Substrates than of them on Si-substrate. This ascertaining is true for all considered colors, except of the blue light. The response of In_5Se_5Cl on Si-substrate is higher than that on Cu-substrate for the whole bias range considered (Fig. 4 a,b).

Astonishing from these measurements is the response order of the same kind of crystals toward the chosen wavelengths. This observed dissimilarity might be related to the photo-conductivity contribution of their substrates. To study further the influence of the substrate on the photo electrical properties of In_5Se_5Cl, and to average the effect of individual needles, we built two photo-sensors using Si- and Cu-substrates, each containing two crystals of In_5Se_5Cl. The sensors were illuminated by green (525 nm) and blue (460 nm) light respectively. The recorded data from this experiment are presented in Fig. 5.

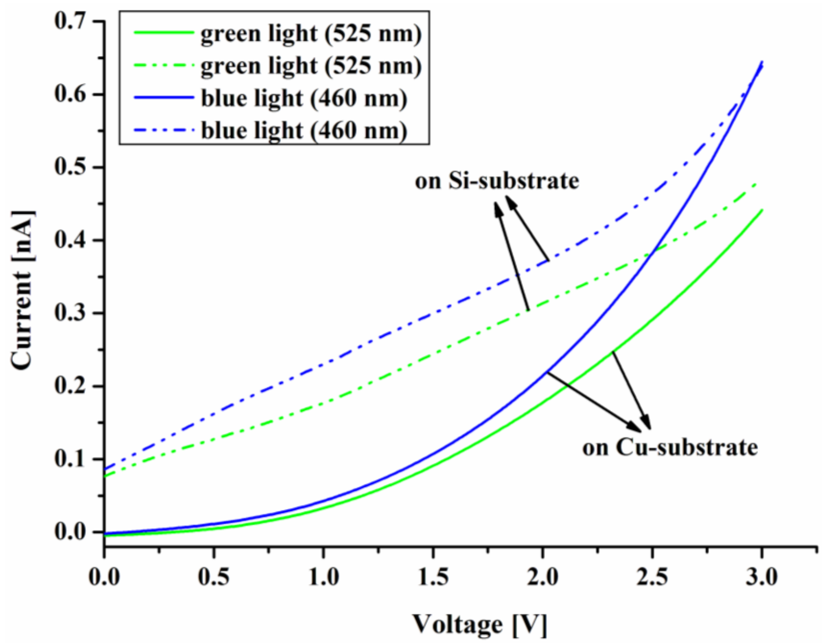


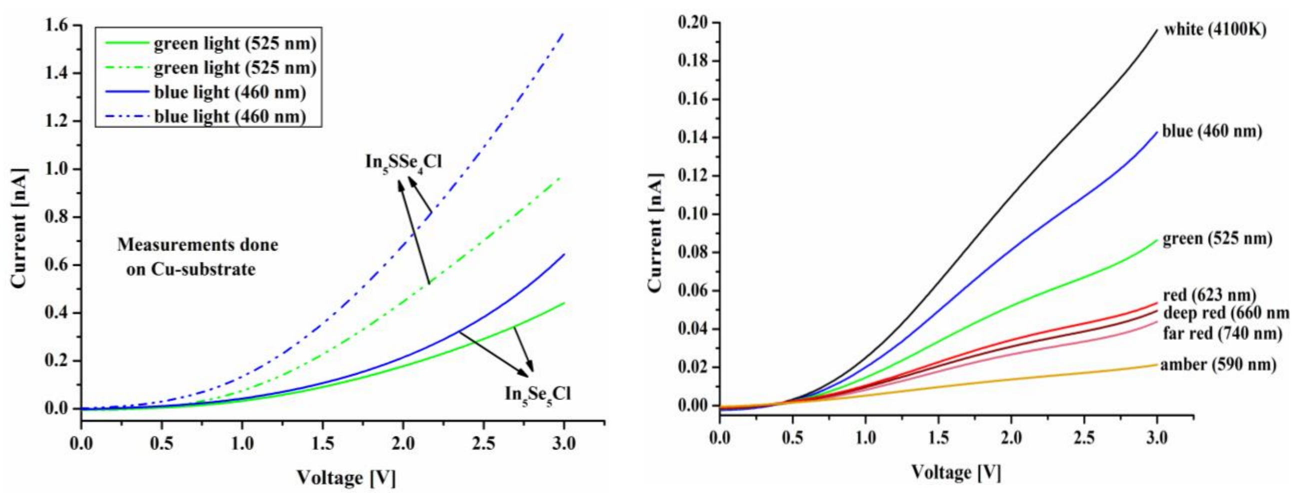
Fig. 5. I-U curves of In_5Se_5Cl crystals recorded for two wavelengths (green, blue), at room temperature

In spite of the illumination wavelength, 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 (Fig. 5). At 3V, the difference in the response of both chips for the green light is very small, and not significant for the blue light. These measurements emphasize the substrate's influence on the photo-sensitivity of the needles especially at low applied voltages.

The effect of mutual substitution of a Se position with S on the photo-sensitivity of In_5Se_5Cl

The mutual structural substitution of a selenium position with sulfur, led to the compound In_5SSe_4Cl. The later crystallizes similarly to In_5Se_5Cl, in the monoclinic space group ($P2_1/m$). For the characterization of the influence of structural substitution of one selenium position with sulfur on the photo electrical properties of In_5Se_5Cl, and to average the effect of individual needles, two photo-sensors using Cu-substrates built. Each of them contained two crystals of In_5Se_5Cl or In_5SSe_4Cl respectively. The sensors were illuminated by green (525 nm) and blue (460 nm) light respectively. The recorded data from this experiment are plotted in Fig. 6 a. *I-U* measurements recorded under green and blue light, on Cu-substrate chips containing In_5SSe_4Cl crystals, within the bias range 0-3 V, revealed distinguishingly higher photo-chromatic sensorial response for both wavelengths used, than In_5Se_5Cl crystals (Fig. 6 a).

In opposite to the substrate's influence, the differences in the light responses of both compounds increased in favor of In_5SSe_4Cl with the voltage increase for both employed wavelengths. At a bias of 3 V, current differences up to 2.2 times and 2.4 times were observed for the green light and blue light respectively for both compounds. In_5SSe_4Cl crystals on Cu-substrate show typically high and better distinguishable sensorial activity toward all the employed wavelengths, even at minimal illumination LED power of 0.25 % (Fig. 6 b). In spite of the low current response at such illumination power, the wavelength-dependent response is much better if compared to In_5Se_5Cl.



(a) **(b)**

Fig. 6. (a) the influence of the mutual substitution of Se with S in In_5Se_5Cl for two wavelengths (green, blue), (b) the photo-response of two In_5SSe_4Cl crystals on Cu-substrate toward minimal LED illumination power (0.25 %) for seven different wavelengths. All measurements are performed at room temperature

At these conditions, In_5SSe_4Cl shows the highest and the lowest sensitivity toward white and amber light respectively (Fig. 6). Earlier attempts for In_5Se_5Cl the optical band gap determination using spectroscopic ellipsometry failed due to the raw surface of measured crystals associated with diffuse (scattered) reflection. Later attempts using micro-reflectometry, resulted somehow promising. Micro-reflectometry measurements of In_5Se_5Cl yielded an optical band gap at 580 nm. For In_5SSe_4Cl, the band gap estimation wasn't that easy. Thickness interference oscillations strongly damped due to structural inhomogeneity or defect-related absorption, therefore two possible band gaps were suggested; at 540 nm or at 620 nm.

CONCLUSIONS

The characterization and the evaluation of the photo-chromatic sensitivity of micro-wire needle-shaped crystals of In_5Se_5Cl has been in the focus of this study. While performing photo-electric measurements of In_5Se_5Cl micro-needles on Si- and Cu-substrates, we found a significant influence of the substrate material on this property. Meanwhile, the substitution of one selenium position with sulfur in the structure of In_5Se_5Cl, yielding In_5SSe_4Cl, improved the photo-chromatic sensitivity of the micro-needles. In_5SSe_4Cl crystals on Cu-substrate showed a better and distinguishable sensorial activity toward all employed wavelengths, even at their minimal illumination power of 0.25 %.

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