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Amorphous non-doped and Se, Cu, and Zn-doped Sb₂S₃ nanoparticles prepared by a hot-injection method: Bandgap tuning and possible observation of the quantum size effect

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Abstract

The modified hot-injection method was applied for the synthesis of amorphous non-doped and copper (Cu) and selenium (Se) doped antimony (III) sulfide (Sb2S3) nanoparticles with reduced sizes. Moreover, zinc (Zn) doped Sb2S3 nanoparticles were synthesized for the first time by the same approach. High-resolution transmission electron microscopy (HRTEM) and TEM of amorphous undoped and doped samples revealed small spherical nanoparticles of a few (1-4) nanometers aggregated into larger spherical clusters, while introducing different dopant ions into the Sb2S3 structure did neither influence the spherical morphology nor the sizes of samples. The presence of the basic elements (S and Sb) and dopants (Cu, Se, or Zn) was confirmed by EDX analysis and mapping. Additionally, field emission scanning electron microscopy (FE-SEM) was performed on the Zn-doped Sb2S3 sample, confirming spherical morphology as well as quantitative incorporation of Zn in the Sb2S3 lattice. X-ray powder diffraction (XRPD) results of the non-doped and doped samples revealed an amorphous structure. The crystalline Zn-doped Sb2S3 samples obtained by heating the amorphous ones revealed well-defined peaks from only the Sb2S3 phase, confirming a successful doping process. Diffuse reflectance spectroscopy (DRS) revealed high optical bandgap energies (2.03–2.12 eV) in comparison to the values (1.6–1.7 eV) obtained for large spherical non-doped and doped particles. It was demonstrated that there is not only a significant reduction in particle size compared to previously synthesized non-doped and doped amorphous nanoparticles of the same composition, but that there is also a significant increase in the bandgap values of 0.4-0.5 eV, which could be attributed to a quantum size effect. X-ray photoelectron spectroscopy (XPS) measurements revealed pure phase composition without any impurities for the undoped sample, and characteristic peaks for copper 2p, selenium, and zinc Auger peaks for the doped samples, respectively. The XPS valence band measurements were performed due to the weak Zn Auger peak, confirming a shift towards lower binding energy compared to the non-doped sample, demonstrating the doping of the observed sample. Photoluminescence (PL) measurements show that embedding Zn into the Sb2S3 host lattice suppresses the wide luminescence band with peaks at 1.7 eV, 2.0 eV, 2.2 eV, and 2.4 eV, which is related to intrinsic defects. Furthermore, the energy dependence of the light emission on the size of the synthesized nanoparticles suggests that the quantum confinement effect causes the light emission.

Keywords: energy nanomaterial, Sb₂S₃, amorphous material, quantum size effect;

1. INTRODUCTION

One of the most pressing issues in the materials science community is the use of a sustainable, renewable, and cost-effective energy source. The transition from fossil fuels to renewable technologies is an essential action that must be carried out as soon as possible. Solar energy is the most common renewable technology and requires the least amount of capital investment, with zero emissions of carbon dioxide. However, its use is still at an unsatisfactory level [1-5]. One of the factors limiting solar energy application is low solar cell power conversion efficiency (PCE) and high fabrication and installation costs. For these reasons, scientists are researching new low-cost materials, optimizing established device structures, and designing novel concepts [6-13].

Because of its abundant resources, nontoxicity, high stability, low cost, high absorption coefficient $(1.5 \cdot 10^5 \text{ cm}^{-1})$ [14], and suitable bandgap, the antimony sulfide (Sb_2S_3) semiconductor has piqued the interest of many researchers for use in solar cell devices. No impurity phase will be produced because this is a binary semiconductor compound with a single stable phase. However, the material is stable in its amorphous and crystalline form. This combination of favorable properties has driven an intensive effort to fabricate suitable synthesized materials or thin films for application in various solar devices [15-17].

In the last decade, we synthesized various non-doped and different-ion doped Sb_2S_3 nanomaterials in the form of powders and applied them to different solar device architectures [18-27]. In recent years, a wide range of doping elements and techniques have been experimentally applied to Sb_2S_3 semiconductors for use in thin films and solar cells [28-31], although synthesized non-doped and doped Sb_2S_3 nano-powders for solar device applications are still unknown to us. Doping strategies for the light-absorbing semiconductor Sb_2S_3 are crucial for bandgap engineering, carrier transport, improving conductivity, regulating film morphology, and enhancing stability.

Furthermore, in our case, films for use in solar cells were created through redispersion and deposition of synthesized nanoparticles. Because of this process, it is possible to combine modifications of the same material with different bandgaps and tunable electronic characteristics or combine this semiconductor with conductive polymers or dyes as absorption layer composites, thus expanding the range of useful photons by the absorbing layer [20, 21, 24, 27, 32, 33]. Furthermore, a tunable bandgap can greatly expand the semiconductor's applicability. The excitonic effect and the quantum confinement effect have been found to play an important role in the electronic structures and optical properties of Sb₂S₃ nanowires (NWs), indicating that optical anisotropy in Sb₂S₃ NWs is more pronounced than in the bulk. The optical absorption edge's blue-shift and red-shift indicate that these Sb₂S₃ NWs could be used in nanoscale light-emitting devices [34].

Up to now, there have only been a few reports concerning Zn and Cu-doped Sb_2S_3 , while Se-doped Sb_2S_3 is more prevalent [35-41]. It should be noted that all of those samples are doped in thin-film form and were obtained using different techniques. However, colloidally synthesized Cu and Se-doped Sb_2S_3 nanoparticles were reported rarely and mainly by our group [20, 22], while Zn-doped Sb_2S_3 nanoparticles are presented here for the first time.

In this manuscript, we present three new materials obtained by a modified hot-injection metallo-organic synthesis [18]: selenium-, and copper-doped Sb_2S_3 nanoparticles with significantly reduced nanoparticle sizes compared to earlier work, as well as amorphous Zn-doped Sb_2S_3 nanoparticles. The structural, morphological, electronic, optical, and photoluminescent properties of new materials based on non-doped and doped Sb_2S_3 have been investigated, characterized, and presented here. Many characterizations were performed, such as high-resolution transmission electron microscopy (HRTEM), transmission electron microscopy (TEM), field

emission scanning electron microscopy (FESEM), diffuse reflectance spectroscopy (DRS), X-ray powder diffraction (XRPD), X-ray photoelectron spectroscopy (XPS), as well as photoluminescence (PL) measurements, to show that the synthesis was successful and that we did get differently doped samples. It was demonstrated that the huge decrease in nanoparticle size observed compared to previous syntheses at higher temperatures (240 $^{\circ}$ C) [20, 22] than the present ones (150 °C) is accompanied by a significant increase in the energy bandgap, indicating a strong quantum size effect. However, bandgap values above 2.0 eV were already observed before by several authors for larger undoped amorphous Sb_2S_3 nanoparticles [42, 43] and also found by us for undoped nanoparticles prepared by the same procedure as in this work [18]. So far, this was mostly explained by differences in the bond lengths and angles of the amorphous material leading to a different mobility gap, not by a quantum size effect. In addition, it was revealed that as particle size decreases, new peaks appear in the PL measurements that are shifted towards higher energies. The additional high exciton energy discovered in the PL measurements, in conjunction with a possible quantum size effect, could be associated with novel electronic properties of synthesized non-doped and differently doped Sb₂S₃ nanoparticles.

2. EXPERIMENTAL

2.1.Materials and procedures for the synthesis of amorphous non-doped, Cu-doped, Se-doped, and Zn-doped Sb₂S₃ nanoparticles

All chemicals (antimony (III) chloride (SbCl₃) (99.0 % min), sulfur powder (S) (99.999 %), 2-ethylhexanoic acid (EHA) (99 %) (available from Alfa Aesar), oleylamine (tech.70% Sigma-Aldrich), copper (I) acetate, Se pellet, Zn acetate dihydrate as well as liquid paraffin (USP-NF,

BP, Ph. Eur.) pure, PanReac, hexane, isopropyl alcohol, methanol, and benzene (all purchased from J. T. Baker)) were of the highest purity available and used without further purification. All experiments were conducted in an argon atmosphere using standard glass equipment, including a Schlenk line. Before use, the reaction vessels were cleaned with nitric acid and repeatedly rinsed with deionized water.

Detailed experimental procedures, including synthesis of non-doped and doped Sb₂S₃ nanoparticles with different dopants, have been described in references 20 and 21. For this reason, we will not go into the details of the synthesis here but only point out that Zn-doped Sb₂S₃ nanoparticles were synthesized for the first time, using the same modified high-temperature method, which also was applied to obtain small Cu- and Se-doped nanoparticles [20-27]. In short, two precursor solutions were prepared. An S-oleylamine solution was created by dissolving 1.5 mmol of elemental sulfur in 6 mL of oleylamine. After that, 25 mL of paraffin oil was added, and the solution was heated to 150 °C while being stirred magnetically. After that, the Sb (III) complex solution was made by adding 1 mmol SbCl₃ to 5 mL of ethylhexanoic acid under magnetic stirring of the mixture and heating it to 90 °C in an oil bath. When both precursor solutions, and the reaction mixture was kept at 150 °C for 30 minutes under magnetic stirring. To stop the reaction, the heating mantle with an oil bath beneath the reaction vessel was removed, and hexane was injected into it.

Because copper and zinc replaced antimony, the antimony concentration was reduced at the expense of copper or zinc. At 90°C, Cu (I) and Zn (II) precursor solutions were made by dissolving 0.1 mmol of copper (I) acetate or Zn acetate dihydrate in 1 mL of 2-ethyl hexanoic acid and keeping them at 90°C. The Sb (III)-precursor solution was made by dissolving 0.9 mmol of SbCl₃ in 4 ml of 2-ethyl hexanoic acid in a flask and stirring it at 90 °C. As described above, the S-precursor solution was prepared in a separate flask and heated to 150 °C. The Sb (III)-complex precursor solution was injected rapidly and simultaneously with the Cu (I)-complex or Zn (II)-complex precursor solution into the S precursor solution. For 30 min, the temperature of the mixture was kept constant at 150 °C.

The synthesis of the Se-doped nanoparticles was performed as further described. After milling the Se pellet, 0.15 mmol of Se powder was dissolved in 2 ml of oleylamine and 5 mL of paraffin oil at 90 °C to make a Se-oleylamine solution. 1.35 mmol of S powder was dissolved in 4 mL of oleylamine and 20 mL of paraffin oil, which were kept at 150 °C under magnetic stirring. The Sb (III)-precursor solution was prepared in a separate flask by combining 1 mmol of SbCl₃ with 5 mL of 2-ethyl hexanoic acid and stirring at 90 °C. The solutions of the Se-and Sb-precursors were quickly poured into the S-precursor. For 30 min, the mixture was kept at 150 °C while being constantly stirred.

2.2. Characterization devices and measurements

The morphology of the samples was analyzed by high-resolution transmission electron microscopy (HRTEM) using a Talos F200X electron microscope from FEI Company, equipped with a CCD camera with a resolution of 4096×4096 pixels using the User Interface software package. The acceleration voltage was set at 200 kV. An energy-dispersive X-ray spectroscopy (EDs) system attached to the TEM operating in the scanning transmission (STEM) mode was used for elemental analysis, including surface chemical mapping of the samples. Additionally, a Zeiss EM 109 was used at an 80 kV acceleration voltage to record the TEM images.

Morphological and compositional properties were additionally investigated using field emission scanning electron microscopy (FESEM) on a FEI SCIOS 2 Dual Beam electron microscope with a 20 kV acceleration voltage. Energy dispersive spectrometry was used to determine the chemical composition (EDS).

The Zn:Se ratio was additionally determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The sample preparation was carried out by acidic digestion. 1.5 mg of the sample was dissolved in 1 mL aqua regia in an open glass vessel for 2 h. Subsequently, the solution was diluted with 9 mL ultrapure water and filtered with an 0.45 μ m syringe filter (regenerated cellulose, Macherey-Nagel). The instrument used was an Analytik Jena Plasma Quant MS Elite. Helium was used as collision gas, and indium was added as an internal standard. Optimization of instrumental conditions was performed using a tuning solution leading to sensitivities of ¹¹⁵In and ²³²Th of 1.4·10⁶ c/s and 1·10⁶ c/s, respectively, and oxide ratio (¹⁴⁰Ce¹⁶O/¹⁴⁰Ce) and doubly-charged ion ratio (138Ba++/138Ba+) of <2 %. The samples were diluted 250-fold in case of antimony and 20-fold in case of zinc before the measurement. The detection limit is 0.2 ppb for Zn and 0.3 ppb for Sb.

Diffuse reflectance measurements (DRS) were taken using an integrating sphere and a Cary 5000 UV–vis–NIR spectrometer (Agilent Technologies) with an internal DRA 2500. Particles were measured in special quartz cuvettes (type 26.715/Q/10/Z20; Starna) in the 400–800 nm range as a dispersion in isopropyl alcohol.

The X-ray powder diffraction (XRPD) measurements were carried out on a PHILIPS 1050 X-ray diffractometer with Ni-filtered Cu K radiation and Bragg-Brentano focusing geometry. The amorphous samples' patterns were taken in the 5–90° 2 θ range, with a step size of 0.05° 2 θ and an

exposure time of 5 s per step. The crystalline sample pattern was taken in the 10–90° 2 θ range, with a step size of 0.02° 2 θ and an exposure time of 12 s per step.

XPS spectra were recorded using a monochromatic Al K line (1486.74 eV) at 12.5 kV and 32 mA. The samples were analyzed using an XP50 M X-ray source for Focus 500 and a PHOIBOS 100/150 analyzer from SPECS Systems. The X-ray gun power was reduced to a minimum to minimize the binding energy shift, and a SPECS FG15/40 electron flood gun was used. All samples were pressed onto the copper foil to ensure a strong mechanical attachment and good electrical contact. Peak positions were calibrated using the C 1s line at 284.8 eV originating from adventitious carbon, according to the literature [44]. All survey XPS spectra (0–1300 eV binding energy) were recorded in the FAT mode with a constant pass energy of 40 eV, a step size of 0.5 eV, and a dwell time of 0.2 s, whereas detailed XPS spectra of corresponding lines were recorded in the FAT mode with a pass energy of 20 eV, a step size of 0.1 eV, and a dwell time of 2 s. Spectra were obtained at a pressure of 7×10^{-9} mbar. All spectra were collected using the manufacturer's SpecsLab data analysis software and analyzed using the CASA XPS software package [45]. After Shirley-type background subtraction, the best fits of the components (Cu 2p, Zn LMM, and Se Auger) were chosen using pseudo-Voigt profiles in the form of the product of Gaussian and Lorentzian lines with an intensity ratio of 70:30.

Photoluminescence (PL) and excitation spectra were recorded using the Horiba Fluorolog 3 spectrometer (Japan). Excitation of luminescence was performed in a stationary mode employing a xenon lamp of 460 W power. The input monochromator provided an excitation wavelength accuracy of less than 0.1 nm. A Synapse CCD camera was used to record emission spectra, which provides a signal-to-noise ratio of 20000/1. Excitation spectra were recorded based on registered 2D "excitation-luminescence" maps with a selection of the required luminescence wavelength. The study of the luminescence decay kinetics in the ps range was carried out using a laser diode (λ_{exc} = 410 nm), a multichannel PMT, and a photon-counting unit with specialized software. All measurements were carried out at room temperature.

3. RESULTS AND DISCUSSION

3.1. Non-doped and Cu-, Se-, and Zn-doped amorphous Sb₂S₃ nanoparticle morphology and elemental analysis

Figures 1-4 show HRTEM and TEM characterization of various synthesized samples, including amorphous non-doped and Cu, Se, and Zn-doped Sb₂S₃ nanoparticles observed at various high magnifications. The sizes and shapes of the nanoparticles can significantly influence their physical, electronic, optical, and structural properties, as well as some possible applications in many different fields [46-50]. So far, we have synthesized and applied many different non-doped and differently ion-doped Sb₂S₃ nanomaterials [18-27]. However, here, we used a modified method [18] at a comparably lower temperature (150°C), yielding reduced particle sizes where we can give strong indications of quantum size effects, which, as far as we are aware, have not been stated yet for amorphous Sb₂S₃ nanoparticles. From the HRTEM and TEM micrographs (Figures 1-4) of all the different samples, the same morphology was revealed: tiny nanoparticles, whose visibility depends on the sample, organized into larger nanoparticles. All the photographs of the synthesized non-doped and Cu, Se, and Zn-doped Sb₂S₃ nanoparticles were observed at high magnification only, and some of the photographs nicely confirm the presence of particles of a few nanometers, at least what is visible to us. It

should be emphasized here that limited visibility at higher magnification was due to enhanced degradation of the samples because of the damage to the samples by the electron beam [51].



Figure 1. HR-TEM micrographs of the synthesized amorphous, non-doped Sb₂S₃ nanoparticles. There are visible larger nanoparticles of around 50 nm in the micrographs, composed of tiny nanoparticles of just a few nanometers.



Figure 2. HR-TEM micrographs of the synthesized amorphous, Cu-doped Sb₂S₃ nanoparticles. In the micrographs, smaller nanoparticles of around 20 nm are visible, which are also built of very small nanoparticles of a few nm sizes.

Furthermore, as seen in the photographs, tiny particles aggregate into larger, mostly spherical formations. It should be emphasized that we checked the diluted solution of the non-doped sample on atomic force microscopy (AFM) and found separate nanoparticles of 1-4 nm.



Figure 3. HR-TEM micrographs of the synthesized amorphous, Se-doped Sb₂S₃ nanoparticles. There are visible tiny nanoparticles of a couple of nanometers.

For that, the expression "a few or a couple" nanometers were used in the paper. The EDX spectra of all the synthesized samples, together with the EDX mapping of the amorphous Cu-doped Sb_2S_3 sample, are presented in Figure 5. It is evident that the spectra indicate the presence of S and Sb as well as of the dopants Se and Zn in the doped samples.



Figure 4. HR-TEM and TEM micrographs of the synthesized amorphous, Zn-doped Sb₂S₃ nanoparticles. In the micrographs, there are also visible smaller nanoparticles with a diameter between 20 and 50 nm, which are also built of tiny nanoparticles of a couple of nanometers.

Since C and Cu are detected in the Cu-doped Sb_2S_3 sample because a carbon-covered Cu grid was used, an EDX mapping was performed. The homogenous distribution of Cu over all particles in the micrograph is evident. Furthermore, detectable oxygen (not shown in Figure 5) in the EDX



Figure 5. EDX spectra of amorphous non-doped, Zn-doped, and Se-doped Sb₂S₃ nanoparticles with distinct Sb, S, Zn, and Se peaks. Further, an EDS mapping of the Cu-doped Sb₂S₃ nanoparticles is present because of the presence of Cu in the grid. There is a visible, homogeneous distribution of Cu in the EDX mapping across all particles in the micrograph.

spectra of all investigated doped and non-doped nanoparticles could be attributed to impurities or oxidation of the nanoparticles during synthesis, cleaning, or preparation of the specimens [52].



Figure 6. FE-SEM micrographs of the synthesized Zn-doped Sb₂S₃ nanoparticles at lower resolution. The data of the extracted EDX spectrum (see Figure 5) is also provided, along with the weight and atomic percentage of all detected elements, Sb, S, and Zn.

Additional lower resolution FE-SEM micrographs were recorded only for the Zn-doped Sb_2S_3 nanoparticles, synthesized for the first time in this work. These images follow the same trend in the HRTEM micrographs, showing different agglomerations of nanoparticles, although the smallest nanoparticles are not visible in this case. However, the extracted EDX spectrum with the atomic and weight percentages of all detected elements, Sb, S, and Zn (presented in Figure 6) closely matches the expected element ratios of Sb and S. In the case of Zn, a doping degree around 25 times smaller than expected and in the range of the detection limit of EDX was found. For this reason, additional ICP-MS measurements were performed on the nanoparticles digested in aqua regia. These measurements revealed a molar Sb:Zn ratio of 2500 (\pm 100):1. This shows that Zn was incorporated, but the doping level is very low compared to the ratio during synthesis (molar ratio 10:1). The detection limit of ICP-MS is 0.2 ppb, which is 100 times lower than the concentration in the present measurements. The much higher sensitivity of ICP-MS compared to EDX explains the discrepancy in these data.

3.2. XRPD structural analysis of undoped and Cu-, Se- and Zn-doped amorphous Sb₂S₃ samples and annealed crystalline Zn-doped Sb₂S₃ sample

XRPD is a technique used to characterize the structural properties of the prepared samples in order to prove their purity, desired composition, and doping confirmation [53, 54]. The phase structure of the prepared amorphous non-doped, Cu, Se, and Zn-doped Sb₂S₃ samples, as well as a Zn-doped Sb₂S₃ sample which was additionally annealed for 15 min at 270 °C, was determined using X-ray powder diffraction, and the corresponding diffractograms are shown in Figure 7. All four non-doped and doped amorphous samples have similar diffraction patterns with broad peaks,



Figure 7. X-ray diffraction patterns of the amorphous non-doped, Cu, Se, and Zn-doped Sb₂S₃ nanoparticles confirm the amorphous nature of the synthesized samples. The last diffractogram represents the XRPD pattern of the Zn-doped Sb₂S₃ crystalline sample obtained by heating an amorphous sample at 270 °C is shown, where we prove the existence of the Sb₂S₃ phase as well as the absence of any

additional Zn compounds. There is also a slight amount of Sb₂O₃ developed by the heating process. Similar diffractograms were obtained for all other synthesized samples after an annealing process (not shown). demonstrating the amorphous structure of the measured samples [55, 56]. The XRPD pattern of the annealed crystalline Zn-doped Sb₂S₃ is shown in Figure 7. The initially amorphous samples crystallize in the stibnite Sb₂S₃ structure (COD 01-074-1046), and the absence of any separate zinc (Zn) phases indicates its incorporation into the stibnite lattice although that absence could be also related to low Zn dopant concentration (see further in the text). There is only a trace of the Sb₂O₃ phase present, which was formed during the heating process. Similar crystalline diffractograms were also obtained for the other non-doped and doped amorphous samples synthesized after a similar annealing process.

3.3. DRS spectra of undoped, Cu-, Se-, and Zn-doped synthesized amorphous Sb₂S₃ nanoparticles: Size dependences and bandgap values as potential consequences of the quantum size effect

The bandgap (Eg) energies of the amorphous non-doped, Cu, Se, and Zn-doped Sb₂S₃ synthesized samples were determined by performing DRS measurements and subsequent data analysis using the Tauc plot (see Figure 8). For this analysis: the absorption coefficient α is expressed by the Planck constant h, the photon's frequency v, a constant B, which Davis and Mott described as the magnitude of the optical absorption constant [57], and a transition factor γ which equals 2 for an indirect allowed transition:

$$(\alpha h\nu)^{1/\gamma} = B(h\nu - E_g) \tag{1}$$

We used the Kubelka-Munk function (Eq. 2) [58] to express α . $F(R_{\infty})$ is the quotient of the absorption coefficient *k* and the scattering coefficient *s*, which, in turn, is correlated to the reflectance of an infinitely thick specimen *R*.

$$F(R_{\infty}) = \frac{k}{s} = \frac{(1 - R_{\infty})^2}{2R_{\infty}}$$
(2)

We assume that the amorphous particles have an indirect bandgap, though several alternatives are available [59-61]. It should be emphasized that crystalline Sb_2S_3 has a direct bandgap with a value between 1.6 and 1.7 eV [62].



Figure 8. Reflectance spectra as well as the Kubelka-Munk method for bandgap (Eg) determination (values are given in the inset) of non-doped, Se-doped, Zn-doped, and Cu-doped Sb₂S₃ nanoparticles. The graphs are normalized to [0; 1].

This data analysis yields band gaps of 2.08 eV for the undoped, 2.07 eV for the Cu-doped, 2.03 eV for the Se-doped, and 2.12 eV for the Zn-doped Sb₂S₃. It should be emphasized that absorption measurements were also performed and the same values of the gaps were obtained (not shown). The results themselves can be used to draw two basic conclusions. One conclusion is that the differences in the bandgap values of non-doped and doped samples are insufficient to confirm doping. The second conclusion is that the bandgap energy values of the amorphous non-doped and

doped samples are large compared to the values of large amorphous non-doped and doped synthesized particles obtained so far by the hot injection synthesis [20, 22] as well as of crystalline Sb₂S₃. For undoped particles prepared by the same hot injection synthesis at a comparable lower



Figure 9. Scanning electron microscopy and field-emission scanning electron microscopy images of previously synthesized, larger amorphous non-doped, Cu-doped, and Se-doped Sb₂S₃ nanoparticles around 100 nm in size [20]. The corresponding reflectance spectra, as well as corresponding Tauc plots for bandgap determination (values shown in the figure), of non-doped, Se-doped, and Cu-doped Sb₂S₃ samples, are shown below.

temperature (150 °C), we found similar bandgap values after 30 min in an earlier work which demonstrates the high reproducibility of this approach [18], and even larger band gaps (2.18 eV and 2.12 eV) after shorter reaction times of 2 min and 5 min, respectively. In general, the energy bandgap in amorphous semiconductors can vary [64, 65].

Long-range disorder in amorphous nanoparticles disrupts the periodic arrangement of constituent atoms, which should be mentioned here. Because atom-atom distances and binding energies vary to some extent depending on their location in amorphous semiconductors, it appears that the band edge of amorphous semiconductors becomes indistinct, diffusing into the bandgap. As a result of the calculated differences, we must demonstrate and prove the evidence of sample doping using additional characterization methods. Concerning the second conclusion, for the purpose of better understanding, in Figure 9, SEM micrographs and DRS spectra with corresponding bandgap values for previously synthesized amorphous non-doped and Cu and Sedoped Sb_2S_3 nanoparticles with larger particle sizes [20] are given. All the presented samples, nondoped, Cu and Se-doped Sb_2S_3 nanoparticles are, at least partially, amorphous structures. It is clear from the preceding claim that doping amorphous nanoparticles can change their electronic properties and thus their energy bandgap. It is also obvious that there are differences in band gap values for different doped samples, which we do not see with the small nanoparticles obtained here (Figure 8). Further, as can be seen in Figure 9, the sizes of the synthesized nanoparticles were not smaller than 100 nm, which is quite larger than those obtained in the synthesis described in this manuscript and the bandgap of non-doped amorphous particles is different from the doped ones. Apparently, the doping process for larger amorphous nanoparticles causes changes in electronic properties, in particular, a decrease in the bandgap. For a better understanding, Figure 10 compares the SEM images of previous and current synthesis for a sample of Cu-doped Sb₂S₃ amorphous

nanoparticles, as well as bandgap values for all non-doped and doped samples with larger and reduced nanoparticle sizes. It should be stressed that large reductions in the nanoparticle sizes are present in all the synthesized non-doped and Cu and Se-doped Sb_2S_3 samples. As we have already explained, the Zn-doped Sb_2S_3 sample was synthesized for the first time, so we do not have comparison results. The large nanoparticle size reduction (from 100 nm to 1-4 nm) is followed by an increase in the values of the energy bandgap (~+0.4-0.6 eV), which is a strong characteristic of the quantum size effect [66-68].



Figure 10. One example of the field-emission SEM and high-resolution TEM images of the previously synthesized Cu-doped Sb_2S_3 with larger nanoparticles and the last synthesis of the same sample with smaller nanoparticles is shown. For comparison, below are given values of the bandgap for larger and smaller synthesized nanoparticles where the shift is caused by changing the nanoparticle size.

For instance, it has been observed that Zn-doping of Sb₂S₃ thin films causes bandgap reduction [36], the same trend observed in Figure 9 for Cu and Se-doped samples with larger nanoparticle sizes. In fact, the quantum size effect could be a real reason for not observing a difference in the bandgap values of the non-doped and doped Sb₂S₃ samples due to the fact that, generally, the bandgap energy is also affected by the composition of nanoparticle semiconductors. These compositions, to which impurities known as dopants belong, disrupt the band structures by generating local quantum states within the band gaps. Additionally, the optical band gap increases or decreases according to the density of localized states; the higher the localized state, the lower the optical gap, and the opposite. Using the theoretical calculations of the electronic structure (density functional theory), we calculated that the excitons in our system should be about 1 nm in radius to observe the quantum confinement (size) effect in one of our previous publications, where we combined experimental and theoretical results [62]. Additionally, the calculated size of excitons should be taken more as an order of particle sizes where the quantum size effect should be depicted and not the strict value due to the limitation of the single particle (one electron) approach in a many-particle system [62]. We are not aware of any similar work that has done similar calculations. Given the apparent size of nanoparticles of a few nanometers on HRTEM and the fact that even smaller particles are difficult to see for the reasons stated previously, it is clear that we have a strong indication of the quantum nanoparticle size effect.

3.4. X-ray photoelectron spectroscopy (XPS) for structural and electronic characterization of nondoped and Cu-, Se-, and Zn-doped amorphous Sb₂S₃ samples: purity, desired composition, as well as doping confirmation

The effect of Cu, Se, and Zn ion incorporation into the Sb_2S_3 lattice was studied by measuring the XPS spectra of the undoped, and doped powders. Survey spectra of amorphous non-

doped, Cu, Se, and Zn-doped Sb₂S₃ samples, as well as the valence band spectra of non-doped and Zn-doped Sb₂S₃ samples, are presented in Figure 11. A spectrum of amorphous non-doped Sb₂S₃ is provided for comparison, along with the spectra of all the doped samples, and a magnified section with the high-resolution characteristics of the Cu, Se, and Zn peaks are visible in the insets.



Figure 11. XPS survey spectra as confirmation of successful doping of amorphous non-doped, Se-doped, Cu-doped, and Zn-doped Sb_2S_3 samples are given. For all doped samples, the characteristic lines of the

dopants are found. For Se-doped and Zn-doped Sb₂S₃ samples, the Auger line is visible due to the fact that the Se and Zn lines overlap with the S and Sb lines. The last spectra present the XPS valence band of amorphous non-doped and Zn-doped Sb₂S₃ samples, where the expected shift of the doped sample to lower energy is visible.

It is possible to see the main photoelectron lines of Sb, S, Cu, Se, and Zn. It should be mentioned that all the peaks of Sb and S identified in non-doped samples are present in all doped Sb₂S₃ samples with the addition of dopant ions used in the synthesis. Furthermore, because the nanolayer is deposited on all types of samples, the C 1s peak is derived from the atmosphere [22]. As can be seen, copper is only detected in the powder of the Cu-doped Sb2S3 sample after the Cu-doping process (compared with the non-doped sample). An enlarged view of the Cu 2p lines taken from the sample is shown in the inset. Cu 2p3/2 and 2p1/2 lines situated at 932.1 eV and 951.9 eV can be attributed to the Cu ion [69, 70]. It should be emphasized here that the wide band in Cu 2p spectrum (see inset) at approximately 945.5 eV (near Cu 2p1/2 sub-band) is the Sb Auger line overlapped with the Sb 3s peak at 944 eV [70]. Furthermore, XPS survey spectra of Se-doped Sb_2S_3 are shown in Figure 11, with the characteristic line of Se shown in the inset at high resolution. Selenium in Se-doped samples is typically identified using Se 3d lines at 55.3 eV [72– 75]. In our case, the Se 3d line coincides with an inelastic contribution of the Sb 4d line, preventing it from being used for Se quantification. A similar situation is observed with the Se L₃M_{4,5}M_{4,5} Auger line, which overlaps with the inelastic contribution of the S 2p line and is the most intense line in the Se spectrum. Indeed, the only selenium line that does not overlap with any Sb or S line is the one corresponding to its L₂M_{4,5}M_{4,5} Auger transition (shown in the inset), which has a binding energy of 138.5 eV. Its position is slightly different in pure Se (137.8 eV [76]), most likely due to charging issues. The final and most challenging sample is Zn-doped Sb₂S₃, in which all zinc lines overlap with either the Sb or S lines. As far as we are aware, Zn-doped Sb₂S₃ nanoparticles have never been reported before. In one of the insets for the Zn-doped Sb₂S₃ sample, a Zn LMM reference Auger spectrum and shape for different Zn-containing compounds [77] are given. The

LMM spectrum of Zn has a very strong Poisson component (low statistics), and by using deconvolution, derivations of peak positions were made. In the second inset, a very weak Zn LMM Auger peak at a kinetic energy value of 989 eV is visible, corresponding to the Zn-S connection. Given that Zn as an ion should replace Sb in the lattice in a Zn-doped Sb₂S₃ sample, the Zn-S connection is something we expected. Due to the poor visibility of the Zn-LMM Auger line and thus the questioning of the identification of Zn in the sample, additional valence band measurements on the undoped and Zn-doped samples were performed and presented as the last spectra in Figure 11. The shape of the valence band in the Zn-doped sample differs significantly from that in the non-doped sample, with the latter clearly wider. In the case of Zn doping, the valence band maximum shift with respect to the reference sample was approximately 0.55 eV towards lower binding energies. The positions of the valence band maxima were calculated by intersecting the background tangent and the steepest slope of the valence band edge. The filling of the conduction band is expected to cause the valence bands in n-type semiconductors to shift towards higher binding energy, whereas the filling of the acceptor level is expected to cause the valence bands in p-type semiconductors to shift towards lower binding energy [78]. Additionally, it should be mentioned that according to Crist [71], the main valence band of Sb 5p is located at approximately 2.5 eV and the weak sub-band of Zn 3d at 9.7 eV (it is evident that the broader and additional peak in the recorded valence band spectra of the Zn-doped Sb₂S₃ sample appears). Also, no O 2p peak is seen in valence band measurements, nor an O 1s peak is seen in survey spectra, confirming that oxidation has not occurred in any of the synthesized samples.

3.5. Non-doped and Cu-, Se-, and Zn-doped amorphous Sb₂S₃ nanoparticle photoluminescence (PL) measurements: emission spectra, doping confirmation, and the energy dependence on the size of the synthesized nanoparticles due to a possible quantum size effect.

Photoluminescence measurements made earlier on crystalline Sb_2S_3 particles and larger amorphized Sb_2S_3 nanoparticles with a small crystalline fraction and a diameter around 100 nm [26], in the energy range of 2.4 to 1.5 eV, are shown in Figure 12a. The PL spectrum at room temperature is measured with an excitation of 2.48 eV (500 nm). The figure depicts the sharp and intense emission of the 1.65 eV peak in both samples. It should be noted that the



Figure 12. (a) Photoluminescence spectra and SEM images of partially amorphous and crystalline previously synthesized large Sb_2S_3 nanoparticles. (b) Photoluminescence spectra of non-doped and Zn-doped Sb_2S_3 newly synthesized small nanoparticles under $E_{exc} = 3$ eV. (c) Normalized excitation spectra

of emission at 1.67 eV (A-band), 2.02 eV (B-band), 2.22 eV (C-band) and 2.45 eV (D-band) for Zndoped Sb₂S₃ nanoparticles. (d) A schematic representation of the configuration diagram for the singlet ground states (S0) and excited states (S1) of A, B, C, and D excitons in Zn-doped Sb₂S₃ nanoparticles. In view of the very close excitation energies, the transitions $S_0 \rightarrow S_1$ are indicated by a single arrow for simplicity.

photoluminescence and excitation spectra of crystalline and amorphous chalcogenides are nearly identical. It has been found that photoluminescence is caused by well-defined defects similar to those found in the corresponding crystals [79, 80]. The bandgap energy determined by optical absorption measurements for amorphous and crystalline samples corresponds to the sharp and intense PL emission peaks (Figures 9 and 10).

Emission spectra of the non-doped Sb₂S₃ sample (Figure 12b) obtained using stationary excitation (xenon lamp) are represented as a wide band covering the visible range of the spectrum (from green to red) and relatively narrow peaks at 741 nm (1.7 eV), 613 nm (2.0 eV), 559 nm (2.2 eV) and 507 nm (2.4 eV). Broad emission bands for Sb₂S₃ nanoparticles, nanowires, and thin films were observed in some earlier works [81, 82] and are presumably associated with intrinsic defects of the matrix. Embedding of Zn into the Sb₂S₃ host leads to significant suppression of the wide luminescence band related to intrinsic defects. Zinc, penetrating into the cationic position of the matrix (Zn'_{sb}), affects the defects of the anionic sublattice primarily, stimulating the formation of sulfur vacancies ($V_s^{\bullet\bullet}$):

$$2Zn + Sb_2S_3 \rightarrow 2Zn_{\rm Sb} + V_S^{\bullet\bullet} \tag{1}$$

An increase in the concentration of vacancy defects induced by the embedding of zinc leads to the effect of concentration quenching of their emission (Figure 12, b). Although photoluminescence measurements of the Sb_2S_3 nanoparticles are rarely reported, four narrow bands with spectral

characteristics similar to our results were found in reference [83], which is devoted to the study of Sb_2S_3 single crystals. The authors of this work have shown theoretically and experimentally that four types of excitons (conventionally designated as A, B, C, and D) with slightly different spectral parameters of luminescence can exist in Sb₂S₃. The existence of four exciton types is due to the complex band structure (first of all, the structure of the valence band). These excitons are distinguished by their relatively high binding energy (100 meV), which is less than the thermal energy $k_BT = 26$ meV at T = 300 K. The excitons are stable at room temperature, we can observe their emission response in room-temperature spectra. Previously, we found by combining experimental and theoretical calculations that an additional difference (a part of the temperature difference, 300 K at which experiments were performed and 0 K, which theory gives) can be explained only by excitonic effects that cannot be neglected here due to the high calculated energy of an exciton (0.1 eV) [62]. Further, we emphasized that there are no scientific papers concerning doped Sb₂S₃ nanoparticles except for our results, and generally, for doped nanostructured Sb₂S₃ films photoluminescence measurements are rarely reported. We found that photoluminescence studies reported, for instance, for Zn-doped nanostructured Sb₂S₃ film [36] and reported emission peaks do not match our peaks, except for the peak at 715 nm (~1.7 eV) that we also observed in samples with larger and smaller non-doped and doped synthesized nanoparticles. The PL results confirming the possible quantum size effect should be highlighted here. If we compare Figures 12a and b, we can see that with the reduction of particle size, there is a blue shift of the peaks, i.e., peaks at higher energies appear in accordance with the change and value of bandgap with the particle size [84].

Figure 12c shows excitation spectra of narrow excitons-related emission bands at 1.67 eV (A-band), 2.02 eV (B-band), 2.22 eV (C-band) and 2.45 eV (D-band) for a Zn-doped Sb₂S₃ sample.

The observed excitation bands overlap with each other, and this overlapping indicates the similarity or very near origin of excitons. The maximum excitation band shifts towards higher energies with increasing luminescence energy (from A-band to D-band), indicating that the four types of excitons have slightly different energy level structures. The kinetics of emission for narrow bands was measured under pulsed laser excitation λ_{exc} = 405 nm (E_{exc} = 3 eV). The experimental results showed that the emission lifetime doesn't exceed the duration of the laser exciting pulse, which is about 100 ps. A very short lifetime is usually characteristic for mobile excitons, the relaxation of which is associated with singlet states. It can be assumed that the observed emission bands (A, B, C, and D) are associated with singlet excitons. Further, it was shown that the energy structure of excitons differs primarily in the position of the ground state level [83]. Based on the obtained spectroscopic data, we schematically depicted a system of configuration curves for the singlet ground states (S0) and the excited states (S1) of A, B, C, and D – excitons (Figure 12D). From Figure 12d, one can see a tendency to narrow the configuration curve of the ground S₀ state from D-exciton to A-exciton. Such a system of configuration curves explains the slight differences in the maximum of the excitation band of different excitons along with a more significant change in the Stokes shift.

4. CONCLUSION

Amorphous non-doped and Cu, Se, and Zn-doped Sb₂S₃ nanoparticles have been synthesized by a colloidal chemistry approach and characterized for potential use in solar cell devices. By using a hot-injection method at lower temperature (150°C) with a reduced reaction time, we significantly reduce the sizes of amorphous non-doped, Cu, and Se-doped nanoparticles previously obtained at a similar approach at 240°C. Moreover, amorphous Zn-doped nanoparticles were obtained for the first time. Additionally, due to the observed reduction in the amorphous nanoparticle sizes, we follow through the manuscript an inevitable increase in bandgap values as well as corresponding new blue-shifted photoluminescent emission peaks, which are possible due to a quantum size effect.

HRTEM and TEM were used to determine the morphology of the samples, as well as elemental analysis with EDX spectra, EDS mapping, and ICP-MS. The samples' micrographs revealed nanoparticles of a few nanometers organized into larger nanoparticles, and EDX spectra and EDS mapping confirmed the presence of the desired elements Sb and S, as well as dopants Cu, Se, and Zn. Furthermore, for a sample synthesized with Zn-doped Sb₂S₃, we perform FESEM measurements in conjunction with an extracted spectrum that includes the weight and atomic percentage of all detected elements, Sb, S, and Zn. ICP-MS confirmed the successful doping of the nanomaterial with Zn. DRS measurements and calculations were used to determine the values of the indirect bandgap of the amorphous non-doped and doped Sb_2S_3 samples, which is an essential electronic property of all semiconductor materials. The bandgap determination results were analyzed using a Tauc plot and assuming an indirect bandgap. High bandgap values were obtained, which are not typical for this semiconductor. We compared previously synthesized nondoped and doped amorphous nanoparticles of the same composition from a similar hot injection synthesis at a higher temperature (240 °C) with the newly obtained nanoparticles by using SEM, TEM, and reflectance measurements. This showed not only a drastic reduction in the size of the particles but also a strong increase in the bandgap values for $\sim+0.4$ -0.6 eV, which could be attributed to the quantum size effect. Furthermore, the differences in the bandgap values between the samples were insufficient to prove doping, so additional characterization methods were used. To verify the purity, desired phase composition, and doping of the samples, XRPD and XPS

characterization measurements were performed. XRPD measurements of amorphous samples produce diffraction patterns with broad peaks, confirming the samples' amorphous nature. Furthermore, to confirm that there are no other phases in the undoped and doped samples, as well as to prove doping, the Zn-doped sample was heated at 270 °C. For this sample, the XRPD measurements show a pure crystalline phase of Sb_2S_3 with no other phases (except for a small amount of Sb₂O₃ due to the heating in the presence of air) that could form the doping elements or foreign elements within the detection limit. Moreover, the XPS survey spectra of the amorphous non-doped and doped samples show characteristic peaks corresponding to the appropriate semiconductor and dopant elements, Sb and S, as well as either Cu, Se, or Zn. Because the corresponding Zn and Se peaks correspond to the S and Sb characteristic peaks, the Auger lines for Zn and Se were used as indications of doping. In addition, as rarely reported in the scientific literature, photoluminescence measurements as a characterization technique were performed on non-doped and Zn-doped Sb_2S_3 amorphous nanoparticles. The emission spectra of the Sb_2S_3 nanoparticle samples show wide band covering the visible range of the spectrum and relatively narrow peaks at 1.7 eV, 2.0 eV, 2.2 eV, and 2.4 eV, in contrast to previously synthesized larger nanoparticles where only one narrow band at 1.7 eV was observed. Embedding of Zn into the Sb₂S₃ host leads to significant suppression of the wide luminescence band related to intrinsic defects. Moreover, the dependence of the photoluminescence energy peaks, which are blue-shifted with the size of the synthesized nanoparticles, suggests the origin of the light emission could be due to a quantum confinement effect.

After trying many different dopant synthesis methods for colloidal Sb_2S_3 nanomaterials, including the newly synthesized Cu, Zn, and Se particles, further steps will be the application of the synthesized non-doped and doped Sb_2S_3 nanomaterials in variously designed solar devices. We

have prior experience dealing with this topic, which involves the fabrication and characterization of various types of solar cells. Finding the best material for solar devices in terms of structure, shape, electronic structure, and changed and tunable bandgap due to quantum size effect is difficult, especially given the general stringent requirements. However, it simultaneously enables different and broader designs for solar device applications and, at the same time, in other fields of electronics and optoelectronics.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The raw or processed data required to reproduce these findings are given as supplementary files.

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