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Treball Final de Grau

Colloidal synthesis of ternary semiconductor nanostructured materials with high NIR absorption. Síntesi col·loidal de materials semiconductors ternaris nanoestructurats amb elevada absorció en el NIR.

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"Comprender es el principio de aprobar." Baruch Spinoza

En primer lloc, vull expressar el meu agraïment al meu tutor, Albert Figuerola Silvestre, per la seva ajuda i suport en el meu treball. En tant poc temps, ha estat capaç de transmetre'm molts coneixements gràcies a la seva experiència i interès en el tema dels nanomaterials.

En segon lloc, agraeixo a tothom que ha fet que la meva experiència aquest semestre hagi estat molt agradable i profitosa. Gràcies als meus companys de laboratori, científics i tècnics de la institució, professors i estudiants del meu grup de recerca LM2N, especialment a Noelia Bornay. Estic contenta que hàgim compartit aquests moments d'aprenentatge, moments d'ajudar-nos mútuament i fins i tot moments d'estrès però sempre amb gràcia i somriures.



IDENTIFICATION AND REFLECTION ON THE SUSTAINABLE DEVELOPMENT GOALS (SDG)

The Sustainable Development Goals (SDGs) are 17 objectives defined in 2015 by the United Nation Organization (UN) to be accomplished before the year 2030. This is called the 2030 Agenda for Humanity which incorporates the social, economic and environmental challenges that will define the future development of humanity. The present 17 SDGs can be assigned into broad groups, called 5 Ps. This work in hand contributes to 3 of them, people, prosperity and the planet.

Goal number 3: Good health and well-being. Materials prepared in this project have a promising application in medicine. Nanostructured semiconductors with high NIR absorption can be employed in local disease detection and treatment. Main advantages of developing these materials are that IR radiation is not harmful, and nanoparticles can be biologically functionalized and travel in living beings. Obtaining proposed nanoparticles is one of the objectives in this work.

Goal number 7: Affordable and clean energy. Nanostructured semiconductors are prepared as great materials to produce low-cost and sustainable photovoltaic cells. Metals used are not as toxic as the usual products nowadays and they are more abundant.

Goal number 13: Climate action. Discovering synthetic routes to prepare this material open path into affordable and sustainable solar energy, which should be well developed and highly effective to substitute contaminant energy sources.



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1. SUMMARY

Nanoscience is an expansive and rapidly evolving field with diverse applications across multiple disciplines. Over the past 50 years, advancements in nanomaterials have significantly impacted areas such as physics, chemistry, biology, and engineering, leading to innovations in electronics, medicine, and environmental science.

This project focuses on the development of ternary semiconductor Wittichenite (Cu₃ BiS₃) nanoparticles. These nanoparticles are a promising alternative to the currently dominant light-absorbing materials in thin-film solar cells, such as Copper Indium Gallium Selenide (CIGS), Copper Indium Selenide (CIS), and Cadmium Telluride (CdTe). The primary advantages of using Cu₃ BiS₃ lie in the abundance and lower toxicity of its constituent elements, copper and bismuth. Additionally, binary sulfides like Bi_2S_3 and Cu_2S already demonstrate suitable bandgaps (ranging from 1.2 to 1.5 eV) and high absorption coefficients for the solar spectrum, encompassing visible, ultraviolet (UV), and infrared (IR) light.

The ternary compound Cu₃BiS₃ is expected to exhibit enhanced properties, such as improved stability, homogeneity, an optimal bandgap, and efficient near-infrared (NIR) absorption, making it a viable candidate for next-generation solar cell materials.

The synthesis method employed in this project follows a bottom-up approach, which is generally simpler and more straightforward than top-down methods for nanoparticle preparation. Specifically, colloidal thermal decomposition, a solution-based technique, is used due to its superior versatility and precise control over the nanoparticle size, shape, and phase. This method facilitates the production of high-quality nanoparticles that meet the desired criteria for advanced photovoltaic applications.

Keywords: Nanoparticles, Cu₃BiS₃, ternary semiconductor, thermal decomposition

2. Resum

La nanotecnologia és un camp ampli i en ràpida evolució amb diverses aplicacions en múltiples disciplines. Durant els darrers 50 anys, els avenços en els nanomaterials han impactat significativament àrees com la física, la química, la biologia i l'enginyeria, donant lloc a innovacions en l'electrònica, la medicina i la ciència ambiental.

Aquest projecte se centra en el desenvolupament de nanopartícules de Wittichenita (Cu₃BiS₃), un semiconductor ternari. Aquestes nanopartícules presenten una alternativa prometedora als materials absorbents de llum actualment dominants en cèl·lules solars de pel·lícula fina, com el Seleniur de Coure, Indi i Gal·li (CIGS), el Seleniur de Coure i Indi (CIS) i el Tel·lurur de Cadmi (CdTe). Els principals avantatges de l'ús de Cu₃BiS₃ resideixen en l'abundància i menor toxicitat dels seus elements constituents, el coure i el bismut. A més, els sulfuris binaris com Bi₂S₃ i Cu₂S ja demostren bandgaps adequats (entre 1,2 i 1,5 eV) i alts coeficients d'absorció per a l'espectre solar, incloent la llum visible, ultraviolada (UV) i infraroja (IR).

S'espera que el compost ternari Cu₃BiS₃ exhibeixi propietats millorades, com una estabilitat millorada, homogeneïtat, un bandgap òptim i una absorció eficient de l'infraroig proper (NIR), fent-lo un candidat viable per als materials de les cèl·lules solars de nova generació.

El mètode de síntesi emprat en aquest projecte segueix un enfocament de baix a dalt, que generalment és més simple i directe que els mètodes de dalt a baix per a la preparació de nanopartícules. Concretament, es fa servir la descomposició tèrmica col·loidal, una tècnica basada en solucions, a causa de la seva versatilitat superior i control precís sobre la mida, forma i fase de les nanopartícules. Aquest mètode facilita la producció de nanopartícules d'alta qualitat que compleixen els criteris desitjats per a aplicacions fotovoltaiques avançades.

Paraules clau: Nanopartícules, Cu₃BiS₃, semiconductor ternari, descomposició tèrmica

3. INTRODUCTION

Many of modern technologies are invested in nanoscience research since this field has become foundational power of their growth. Whereas scientists have the possibility to manipulate and visualize individual atoms and molecules, nanoscience emerged as a distinct field and opened the gates to numerous studies and their potential applications.

Nanomaterials range from 1 to 100 nanometers of at least one of its dimensions and present physical and chemical properties that differ from pertinent bulk materials. The properties of nanocrystals are determined by its size, shape, composition, and structure. Mainly because of the small size of nanoparticles, which concludes in an increased area/volume ratio, quantum mechanics, surface and dimensional effects become increasingly important. This means that precise synthesis of nanomaterials permits to manipulate the electronic, optical, and magnetic properties of a solid material. ^[1]

Nanoscience encloses a wide range of disciplines like physics, chemistry, biology and engineering. Research specialists in these areas continuously exploring nanomaterials during the last 50 years have made possible the rapid advance of humanity in electronics, medicine and environmental science. Nanomaterials have the potential to revolutionize numerous fields. For example, in medicine, they can be used for targeted drug delivery, imaging, and diagnostics. In electronics, they can be used to develop smaller and more efficient devices. In energy, they can improve the efficiency of solar cells and batteries. Nanomaterials hold promise for addressing some of the most pressing societal challenges, including healthcare, environmental sustainability, and energy production.

3.1. NANOMATERIALS: RESEARH AND APPLICATIONS

Nanoparticles can be tailored via different synthetic methods into multifaceted forms including nanotubes, nanowires, nanoparticles or nanosheets, each with its own properties and conceivable applications. The versatility of nanomaterial structures and composition challenges

scientists to design reproducible methods to synthetize homogenous nanoparticles which is important so that physical and chemical properties can be related securely to its structure. To approach these studies thoroughly, interdisciplinary collaboration is often needed. Therefore, diverse fabrication techniques of nanomaterials exist which may be classified and studied as chemical or physical techniques or both.

Semiconductor materials exhibit electrical conductivity intermediate between a conductor and an insulator. They can conduct electricity under certain conditions but not as effectively as conductors. Its conductivity is explained by the electron energy band structure. Semiconductors have a valence band, that is fully occupied by electrons at low energy levels, and a conduction band, which is empty at high energy levels. The energy gap between these bands is called the bandgap, parameter that defines a semiconductor. It determines the electrical conductivity of the semiconductor because it indicates the energy required to move an electron from valence band to the conduction band. The movement of electrons is temperature dependent so at higher temperatures the semiconductor conductivity increases.^[4]

One interesting application of nanoscience studies lies in renewable energy technologies. Nanomaterials engineered for solar energy conversion, such as multicrystalline silicon wafers, cadmium telluride or Culn_(1-x)Ga_xSe₂ known as CIGS are now the available options for photovoltaic devices. ^[2,3]

Solar cells, also known as photovoltaic cells, are devices that convert sunlight directly into electricity. Photon absorption frees electrons to flow and consequently semiconductor material resistance decreases. For this conversion to be effective under solar wavelength spectrum including visible, ultra-violet and infra-red light, semiconductor bandgap should range from 1.2 - 1.5 eV. Also, high absorption coefficient and photocarrier efficiency are determining.

When a semiconductor structure is at nanoscale, electrons behave more like waves than particles and it must be considered to explain its unusual properties. This phenomenon is referred to as quantum confinement effect. In bulk materials, electrons exhibit continuous energy bands but nanomaterials have discontinuous energy levels. As the size of the nanoparticle decreases, the energy levels become increasingly discrete, resulting in a quantized energy spectrum instead of a band (Figure1). And it also alters the band gap.^[2] The separation between the highest energy level of the valence band and the lowest one of the conduction bands, which are the equivalents to HOMO and LUMO in molecules, increase. This leads to changes in the material's optical and electronic properties. ^[5,6]



Figure 1: Representation of semiconductor electron energy bands of bulk and nanomaterial.

3.2. BISMUTH AND COPPER SULPHIDES

Both Bi₂S₃ and Cu₂S are semiconductor materials reported in numerous research papers, articles, and patents devoted to their synthesis, characterization, properties, and applications. These materials gained significant interest due to their electronic, optical, and chemical properties, making them suitable for photovoltaics, photocatalysis, sensors, and optoelectronic devices.

Bismuth (III) Sulphide is a crystalline p-type semiconductor that belongs to the same metal chalcogenides group as Antimony and Arsenic but advantageously it is a non-toxic material. Its band gap value varies between 1.3 and 1.7eV which makes it active in visible range of the solar spectrum. Moreover, it presents a high absorption coefficient (10⁴-10⁵cm⁻¹) and usually possesses sulphur vacancies, so its carrier mobility and electron concentration are high. ^[7,8] These properties all combined make Bi₂S₃ very attractive material for energy storage and photovoltaic applications. Bi₂S₃ is structured of a lamellar arrangement of Bi³⁺ and S²⁻ in alternating infinite chains that often crystallizes into orthorhombic system. Numerous groups fabricated bismuth sulphide of different morphologies as nanospheres, nanorods, nanoflowers and hexagonal nanostructures. ^[9]

Copper Sulphide is a p-type semiconducting material with bandgaps of 1.2 and 1.5eV depending on the phase, since Copper sulphides present variable stoichiometry and crystallographic phases.^[10] Mineral chalcocite Cu₂S, covellite CuS or digenite Cu₂S are all copper sulphides, in general Cu_(2-x)S, that present high solid-state ionic mobility and can exhibit localized surface plasmon resonance (LSPR), meaning that at specific wavelengths, depending on the size and shape of the nanoparticles, conduction electrons oscillate with the electromagnetic radiation. This property finds application in sensing and detection, photothermal therapy and optoelectronics. ^[11, 12] To make the most of this material, it is crucial to synthetize monodisperse nanoparticles with defined size and shape distribution control.

3.3. TERNARY SEMICONDUCTOR Cu₃BiS₃

Previously it was said that for optoelectronic applications, a semiconductor needs to have a suitable bandgap, high absorption coefficient and good carrier mobility. Many of fitting binary compounds exist, but most of them contain toxic heavy metals like Cd, Pb or Hg. Previously introduced Copper and Bismuth Sulphides are more sustainable alternatives but not the only possibility.

Ternary and quaternary compounds also permit tuning bandgap value without employing toxic metals. For example, CuInS₂, CuInSe₂ or Cu(In,Ga)Se₂ also known as CIS and CIGSe having 1.53, 1.05 and 1.3eV bandgap values. Being these more complex compounds, it is challenging to control composition and structure in synthesis, but the topic has been actively investigated since 2008. ^[13]

For the last few decades, light-absorbing materials based on CIGS, CIS and CdTe have dominated the research in thin-film solar cells. But to fabricate large-scale solar cells from these materials, problems may arise due to limited availability of Se, In, Cd, and Te. ^[14]

Mineral Wittichenite (Cu₃BiS₃) is an efficient semiconductor, with high optical absorption coefficient and electrical conductivity. Its bulk bandgap equals to 1.5eV, capable of absorbing visible and near-infrared (NIR) radiation of the electromagnetic spectrum. Considering that copper, bismuth and Sulphur are earth-abundant, less toxic species, in addition to Wittichenite being a potential optoelectronic and plasmonic material, it is fair to dedicate time and efforts into its synthetic research. ^[15] Various studies were published that obtain nanoparticles ^[16], rods and stars of wittichenite ^[17,18] by solvothermal method with large structures of 252, 150 and 558nm respectfully. Only two studies described a colloidal thermal decomposition method that produced nanostructures of 5-15 and 10nm average diameter. ^[19,20] The bandgap determined for these wittichenite nanoparticles is the lowest for macrostars being 1.40eV ^[18] And the largest bandgap of 1.59eV being determined in 5nm nanoparticles ^[19]. Because this value is related to the optoelectronic characteristics of the material, and when the size of the particles is small, larger bandgaps are shown, it would be interesting to define easy synthetic methods for small and homogeneous Cu₃BiS₃ nanoparticles.

3.4. SYNTHETIC METHODS

Researchers studying nanoparticles commonly employ various synthetic methods. As it was mentioned previously some of the techniques are chemical vapor deposition (commonly used to produce semiconductor thin-films by self-assembly and deposition on a substrate ^[21]), sol-gel method (a popular industrial method for metal oxides and ceramics ^[22]), thermal decomposition, etc.

The choice of synthesis method depends on factors such as desired nanoparticle properties, scalability, cost-effectiveness, and compatibility with the targeted application. Considering the complexity of the materials of interest, solution-phase synthesis is more powerful and versatile than vapor-based methods. Vapor-phase synthesis require finding ideal precursors with good volatility, stability during evaporation and similar decomposition temperature. Vapor reactivities are difficult to control, and gas-phase reactions may occur.

In solution-based methods, solvents must possess high boiling points, high chemical and thermal stability. Then, the capping agents, which are usually amines, carboxylic acids, alcohols or thiols, contribute to precursors solubility in organic medium, and regulate particle growth, shape and size distribution. Due to the ligating atoms (N, O or S), capping agents or surfactants form complexes with metals at intermediate temperatures and control the equilibrium between dissolved species.^[9] Named parameters are controllable in thermal decomposition method of metallic precursors, where crystallization depends on equilibrium condition, although the growth kinetics can be modulated through the action of capping ligands and solvents. ^[1] Thus, this technique permits to alter the characteristics and obtain different types of nano and micro structured materials.

3.4.1. Hot Injection Method

In the hot injection method, while one precursor is dissolved in the reaction flask, the second precursor solution is rapidly injected at high temperature into the reaction mixture under vigorous stirring as it is shown in Figure 2. The rapid injection of the precursor solution momentarily leads to nucleation burst and subsequent growth of nanoparticles, ideally improving the homogeneity of the particles obtained. Typically, the reaction mixture is

maintained at a high temperature throughout the synthesis process to facilitate the formation of nanoparticles. This method allows precise control over nanoparticle size, size distribution, and shape by adjusting reaction parameters like injection and reaction temperatures, reaction time, precursors, solvent and surfactant. ^[23]



Figure 2: Hot injection setup scheme

3.4.2 Heat-Up Method

In the heat-up method, solution containing all precursors needed is heated gradually over time to initiate nanoparticle formation. Firstly, the solution is heated to a lower temperature to dissolve the precursors and promote the formation of reaction intermediates. As the reaction progresses, the temperature of the reaction mixture is gradually increased to induce nucleation and growth of nanoparticles. The gradual increase in temperature facilitates the growth of larger, more crystalline nanoparticles but it has no noticeable operation to control size uniformity. This technique also has the flexibility to adjust reaction parameters such as temperature ramping, precursors, solvents and surfactants.^[23]

3.5. NANOSCIENCE RESEARCH AND ENABLING TECHNOLOGIES

Nanoscale research is heavily assisted by current advanced technical and instrumental resolutions. Without present-day technological progress possibilities of nanoscience research would be very low to zero.

Characterization techniques play a crucial role in understanding the microstructure, properties and behaviour of nanocrystals. Some commonly used characterization techniques for nanocrystals are scanning and transmission electron microscopy (SEM and TEM), X-ray diffraction (XRD) and Electron energy loss spectroscopy (EELS).

3.5.1. TEM

Transmission Electron Microscopy (TEM) is a powerful microscopy technique that enables high-resolution imaging and analysis of materials at the nanoscale. Simplifying, TEM uses a focused beam of electrons transmitted through a thin sample layer, the interaction of electrons with the sample crystals is converted to an image.

TEMs are equipped with an electron source, electromagnetic lenses, sample holder, an objective lens and camera or detector. The electron gun typically consists of a heated filament (such as tungsten or lanthanum hexaboride) that emits electrons when heated to high temperatures. Emitted electrons need to be focused and aligned into a coherent beam by a series of electromagnetic lenses. The nanoparticle-based sample preparation consists of depositing nanomaterials on thin support film made of amorphous carbon attached to a copper rack. The deposition is often done by drop-casting. The focused electron beam passes through the specimen, interacting with the atoms and electrons within the material. The interaction between the incident electrons, and the specimen generates several signals, including transmitted electrons, scattered electrons, and emitted electrons. The transmitted electrons pass through the sample and are collected by an objective lens located below. The objective lens forms a magnified image of the sample on a fluorescent screen or a digital camera detector. The resulting image is a projection of the nanostructures as the interaction of electrons with the particles generates contrast in the TEM image based on electron density, thickness of the sampled substance and its crystallinity.

Overall, TEM characterization provides detailed information about the structure, morphology, and crystallinity of materials at the atomic and nanoscale. ^[24,25]

3.5.2. X-ray diffraction

X-ray diffraction (XRD) is a technique used to analyse the crystal structure; it provides information about the arrangement of atoms within a crystalline sample.

XRD equipment use a source of X-rays which can be a sealed tube of copper or cobalt target. Samples for XRD analysis must be crystalline, meaning that their atoms are arranged in a regular and repeating three-dimensional pattern. Before the measurement it is needed to ground crystals into a fine powder to ensure a random orientation of crystal grains. This is necessary for obtaining a representative diffraction pattern. The X-ray beam is directed onto the sample, where it interacts with the electrons within the crystal lattice. When X-rays strike the atoms in the sample, they are scattered in different directions and some of them follow the Bragg's law of diffraction. The diffracted X-rays produce a diffraction pattern, which consists of a series of discrete spots or peaks on a detector screen. Each peak corresponds to a specific set of crystal planes within the sample that diffract X-rays at a particular angle, according to Bragg's law.

By measuring the angles and intensities of the diffraction peaks, information about the crystal structure and lattice parameters of the sample can be obtained using software to identify and interpret the diffraction peaks. The positions and intensities of the peaks are compared to known reference patterns or databases of crystal structures to determine the phase composition and crystallographic features of the sample. From the diffraction pattern, various crystallographic parameters can be extracted, including lattice constants, crystal symmetry, grain size, texture, and preferred orientation. ^[24,25]

3.5.3. EELS

Electron energy loss spectroscopy (EELS) is a local atomic analysis technique that functions by measuring the energy lost by electrons directed at the sample and is performed in a TEM microscope. High-energy electrons from the beam interact and excite atomic electrons from inner orbitals which are less affected by the outer structure. The energy lost by the electron

beam in this inelastic interaction is characteristic to atoms and its oxidation state, so by observing the energy loss spectrum generated from at a localized spot on the sample explains its elemental composition.

4. OBJECTIVES

The general objective of this project is to optimize conditions of colloidal synthesis of Wittichenite (Cu₃BiS₃) ternary semiconductor and obtain homogeneous nanostructures. To achieve the main goal, we propound the following intermediate objectives:

- Prepare Bi₂S₃ and Cu2S nanostructures through colloidal thermal decomposition method.
- Study the effect of parameters like solvent, surfactant, reaction temperature and time on the synthesis of ternary Cu₃BiS₃ nanomaterial by thermal decomposition method.
- Determine if heteroattachment of Bi₂S₃ and Cu₂S can be an alternative strategy to direct synthesis of Wittichenite.
- Characterize synthetized nanoparticles by X-ray Diffraction and Transmission Electron Microscopy.
- Determine the absorption properties of Bi₂S₃, Cu₂S and Cu₃BiS₃ nanoparticles in dispersion.

5. RESULTS AND DISCUSSION

5.1. Bi₂S₃ AND Cu₂S NANOPARTICLES

In the first place, preparation of binary Bi_2S_3 and Cu_2S nanoparticles will be discussed. Preparation of Bismuth (III) Sulfide nanoparticles described in section 6.2 was taken from a reported article describing a facile colloidal synthesis of Bi_2S_3 nanorods. ^[26] This synthesis has been executed by hot-injection method previously explained in the introduction and is known to produce homogeneous samples of Bi_2S_3 nanorods of different lengths depending on the carbon-chain length of the amines employed. On the other hand, for Cu₂S preparation various synthetic experiments were tested before discovering the best option described in the experimental section 6.3. This synthesis extracted from an article discussing diverse Copper Sulfide Nanocrystals generates homogeneous nanodots of Cu₂S using Copper (II) Nitrate precursor, octadecene solvent and triphenylphosphine caping ligand. ^[11]

5.1.1 Bi₂S₃ nanorods synthesis

The protocol (section 6.2) was performed twice (samples named M1, M2) aiming to learn the proper technique of Sulfur injection, get used to manipulating the Schlenk line and adjust cleaning procedures. These experiments additionally demonstrated the reproducibility of the method, providing neat X-ray diffraction patterns (Figure 3) and TEM micrographs (Figure 4).



Figure 3: XRD patterns of prepared Bi_2S_3 (both samples M1 and M2) with Bismuthinite reference pattern

XRD pattern of prepared Bi₂S₃ nanoparticles completely repeat Bismuthinite bulk reference pattern, no other phase is detected. TEM micrograph (Figure 4) reveals; Bi₂S₃ samples are composed of homogeneous nanobelts of 139 nm long with standard deviation 10.2 and 11.6 nm

wide, standard deviation 3.6.



Figure 4: TEM micrograph of Bi₂S₃ nanorods

As it was noticed in the first experiments, the injection of the second precursor makes a drastic color change in the solution, from orange to black, and then no further transformation is observed. Considering this observation and knowing the dynamics of other similar materials synthesis, it is worth studying the rate of growth of the Bi_2S_3 nanorods. Sample M3 was prepared following the same procedure but after the injection, small aliquots at 5, 10, 20 and 30 minutes were taken from the solution with caution to not alter the reaction system excessively.

Resulting TEM micrographs of the aliquots illustrate that at 5 minutes (Figure 5a) of reaction time abundant nanorods of mean dimensions 127nm long/9.7nm wide are already produced. At 10 minutes rods have 139nm length/9.9nm width (Figure 5b); 20 minutes rods are 146nm x

10nm and at 30 minutes rods are 147nm/11nm.

These results bring us to the conclusion that the formation of nanorods is very rapid, within



Figure 5: TEM micrographs of Bi_2S_3 nanorods extracted at (a) 5minutes, (b) 10 minutes, (c) 20 minutes and (d) 30 minutes.

5 minutes or less homogeneous NRs are formed, demonstrating a great saving in terms of time and energy compared to the original synthesis which is reported to last 1 hour. It is also observed that very poor Ostwald ripening is operating during the reaction, since between 30 and 60 minutes of reaction there are no rods that grow larger taking reactive species from other rods being dissolved. Diffraction patterns were not possible to obtain in the aliquots because of little amount extracted but diffractogram of the Bi_2S_3 NRs after 1 hour coincide with and bismuthinite reference.

5.1.2. Cu₂S nanoplates synthesis

This synthesis is on the edge to be called a heat-up method because the reaction starts long after heating all the precursors. The final product contains very small, homogeneous nanoplates that present great colloidal stability in Toluene (Figure 6). Analysis of different TEM images with ImageJ software shows that Cu₂S nanoplates have an average diameter of 5.16nm with standard deviation 0.7.



Figure 6: TEM micrograph of Cu₂S nanoplates synthetized

XRD pattern collected for this sample (Figure 7) shows very broad peaks due to the small particle size. Crystals at nanodimensions, may show some irregularities in XRD patterns; wider peaks, different relative intensities or notorious 2theta displacements. Even though, in this case,

reference pattern of orthorhombic Chalchocite (Cu₂S) acurately allows to confirm the desired structure of the product synthetized.



Figure 7: XRD pattern collected of Cu₂S nanoplates prepared

5.2. Cu₃BiS₃ NANOPARTICLES

Searching optimal experimental conditions to synthetize Cu₃BiS₃ nanoparticles, multiple experiments were performed. Parameters like solvent, capping ligand, reaction temperature and time are decisive on the produced nanocrystal size and form. Table 1 summarizes the most important experimental data.

Exp	Cu:Bi:S ratio	solvent	surfactant
(*)1	3:1:12	OLAm	OLAm
2	3:1:3,5	OLAm	1-DDT
3	3:1:3,5	ODC	1-DDT
4	3:1:3,5	TOPO	1-DDT

Table 1: Conditions of precursor ratio, solvents and surfactant in Cu₃BiS₃ preparations.

It is usual ^[27] to add an excess of the second precursor, S in this case, to the reaction solution to secure the rapid integration of the reactive species to the flask. However, XRD diffraction (Appendix 1) of the 1st experiment prepared, as in Table 1, entry 1 it is described,

reveals an important amount of amorphous material, presumably S, that covers Cu₃BiS₃ obtained XRD pattern.

Study of different solvent/surfactant combinations determined that dodecanthiol (1-DDT) improves crystallinity of the product. Then, another experiment was defined with correspondent proportions and surfactant (Table 1, entry 2). Micrographs of this sample (Figure 8a) present large and polyhedric crystals of 200nm which guarantee the observation of a well-defined X-Ray Diffraction pattern (Figure 8b).



Figure 8: (a) TEM micrograph of experiment Nº2, (b) XRD pattern

Wittichenite phase is clearly identified with the reference pattern but some of the peaks (27, 38 and 40 2theta values) represent planes of metallic Bismuth impurity in the sample. Round particles from 100 to 150nm have been observed in various samples, which corresponding XRD diffractograms always indicated the presence of Bismuth with more or less quantity. Based on this observation, without atomic analysis of the sample, marked particles can be identified as Bi impurities.

Another research published mentions how Bismuth chloride precursor yielded significant elementary Bi in comparison to Bismuth (III) nitrate. ^[28] Additionally, the reducing character of OLAM, used as solvent in both previous experiments, might also trigger the nucleation of the metallic undesired phase.

 Cu_3BiS_3 crystals synthetized until this moment were not pure phase nor homogeneous Wittichenite nanoparticles, so further modifications into experiments N°3 and 4 (Table 1) are required.

5.2.1. Growth of Wittichenite nanoparticles

Prepared Cu₃BiS₃ crystals in experiments 1 and 2 barely stay stable in Toluene, without physical agitation these particles precipitate easily due to their size. Shortening reaction time of the experiment is one of the options to control the growth. Next experiment was designed to monitor the reaction after Sulfur precursor injection through aliquot extraction at 2, 5, 10, 20, 40 and 60 minutes of reaction time.

As it is observed in Figure, nanosheets of Wittichenite grow from 10 to 100nm long in 40 minutes and self-pack accordingly. An interesting observation is that at the very beginning of the reaction, rods are visible, but they redissolve in 5 minutes. Very fast formation of similar structures was observed in Bi_2S_3 synthesis (Figure 9a), so it is suspected to be bismuth sulfide without any characterization.

Chang Yan and others' article at Nanoscale mentions that the Cu_3BiS_3 phase produced in the initial stage contains both CuS (covellite) and Bi_2S_3 (bismuthinite).^[28] It suggests CuS and Bi_2S_3 are intermediates for this synthesis. In general, it can be assured that, during this synthesis, Wittichenite crystals do not nucleate as such from the very beginning.



Figure 9: TEM micrographs of Cu_3BiS_3 synthesis at (a) 2 minutes, (b) 5 minutes, (c) 10 minutes, (d) 20 minutes, (e) 40 minutes and (f) 60 minutes.

5.2.2. Size, shape and phase control

Changing the solvent affects precursor solubility and regulates reactive species interaction. Two more synthetic options are to employ a nonpolar octadecene solvent (ODE) or a more polar triphenylphosphine oxide (TOPO), which are experiments 3 and 4 described in Table1. Both succeed to produce phase pure nanocrystals of Wittichenite without Bi impurities.

Nanoparticles synthetized in octadecene are initially very small (6nm diameter, SD 1.5), spherical and uniform (Figura 10a). However, after 30 minutes of reaction, the sample shows the simultaneous presence of a lot of long strands (Figure 10b) that were determined by HRTEM and EELS as the same Cu3BiS3 phase as the one found in small round particles. (Figure 12a,b)



Figure 10: TEM micrographs of Cu_3BiS_3 prepared in ODE at (a) 5 minutes and (b) 30 minutes

Using TOPO solvent, the result is very different. Small nuclei grow fast into nanosheets (Figure 11a) which average width is 152 nm (SD 13) and longitude 114nm long wit 22 SD. These gradually become more uniform and self-stack into 8nm thick crystals according to their shape (Figure 11b). The diffraction of this sample shows clear correspondence with the Wittichenite reference pattern with slightly wider peaks due to the thin feature of the crystals (Appendix 2). XRD pattern confirms the purity of the ternary phase.



Figure 11: TEM micrographs of Cu_3BiS_3 prepared in TOPO at (a) 5 minutes and (b) 30 minutes.

HRTEM analysis (Figure 12) verified that both experiments 3 and 4 from Table 1 produced phase pure Wittichenite even though synthesis in ODE present two morphologies; nanoparticles (Figure 12a) and macrobelts that grow in [100] direction (Figure 12b).

Cu₃BiS₃ synthetized in TOPO is also verified phase pure Wittichenite nanocrystals (Figure 12c).



Figure 12: HRTEM micrographs Cu_3BiS_3 in ODE (a,b) and TOPO (c).

5.3 Bi₂S₃ AND Cu₂S NANOPARTICLES HETEROATTACHMENT

Selected samples of Cu₂S and Bi₂S₃ had Cu and Bi concentration analyzed by ICP. The resulting concentration of each metal permits us to estimate the particle concentration through a rough estimation of their volume by analyzing TEM images. Bi₂S₃ nanorods have an average length of 149nm and width of 11nm. To calculate the mean volume, we assume nanorods to have a regular cylindrical shape. Knowing the density of this material is 6.88g/cm³ we conclude that the Bi₂S₃ nanorods solution has a concentration of 5.8 µmols of nanorods /L.

Analogous calculations were performed on a Cu₂S nanocrystal sample. Mean diameter of Cu₂S nanosheets is 5.15nm and the thickness of them is assumed to be 1nm. Resulting concentration is 594,3 μ mols of nanoparticles/L.

Ехр	Bi2S3	Cu2S	ratio	Toluene	T(°C)	Time (h)
1	517µL	25µL	1:5	458µL	50	4
2	517µL	126µL	1:25	357µL	50	4
3	517µL	25µL	1:5	458µL	25	24
4	517µL	126µL	1:25	357µL	25	24

Table 2: Experimental conditions of heteroattachment synthesis. All samples have a total volume of 1mL.

Well-known copper (II) sulphide and bismuth (III) sulphide were investigated for optoelectronic applications, but few reported heterojunctions combining of these two. Hybrid combination is simple and easy to control ternary compounds preparation.^[29] Nanoparticle synthesis permits tuning size, shape and phase of binary products but heteroattachment products combine properties and often surpass precursors individual capacities.

Bi₂S₃ nanorods and CuS nanoplates heterostructure formation have been reported by Yu-Qiao Zhang and others. ^[30] It suggests that nanoplates get attached on the long facetes of rods and presented good visible absorption.

Experiments from 1 to 4 in Table 2 do not present any visible Wittichenite phase in collected XRD patterns (Appendix 3) nor in TEM micrographs any attachment was observed. Due to large

difference in sizes, it was impossible to determine certainly if Cu₂S were attached to nanorods or not without applying HRTEM. On the other hand, XRD pattern previously collected of Cu₂S (Figure 7) has already shown that these particles present very narrow and low intensity diffraction peaks.

Lastly, for further studies, an idea to improve the quality of results higher reaction temperature should be considered, like 120-150°C. ^[29, 30]

5.4 OPTICAL PROPERTIES

All semiconductor nanomaterials synthetized have had their Absorbance measured as it is described in section 8.4.3.

Bi₂S₃ nanorods have an absorption band at 850nm wavelength, observation that concords with a published article that evaluates how different morphology, size and concentration affect optical properties, where Bi₂S₃ nanoparticles absorbance band fluctuates between 600 and 650nm depending on synthesis conditions.^[9]

Cu₂S nanoplates has shown band at 350nm and 1550nm wavelengths, which is the visible color and the plasmon bands respectively. Absorption spectra of these particles is similar to previously synthesized and published nanorod Cu₂S. ^[10,11] Colloidal stability of these particles have been stood up once more; during few seconds that the instrumental changes the detector time for the full range scan, only this spectra do not present a fall of intensity at 750nm approximately. Less stable sample precipitate during this seconds notoriously, matter observed as a vertical fall on the spectra collected.

Cu₃BiS₃ nanoparticles both products of 3rd and 4th experiments (Table 2) were analyzed but none have demonstrated expectable NIR plasmon band. These samples were the most challenging to maintain in colloidal dispersion during the measurement. Concentrated samples rapidly precipitated without possibility of measuring the desired spectra (250-2500nm) and the diluted samples presents high diffusion effects during the measurements. Due to these difficulties the result of absorption measurements in colloidal dispersion is not reliable. Tree measurement were taken from Wittichenite prepared in TOPO of different concentrations in decreasing order. For more accurate characterization, reflectance measurements in solid state of these particles should be considered (Appendix 4).

6. EXPERIMENTAL SECTION

6.1. MATERIALS AND METHODS

Chemicals. **Sigma-Aldrich**: Copper (II) chloride 97%, Trioctylphosphine oxide 90%, Oleylamine 70%, 1-Dodecanthiol 98%, Dodecylamine 98%, i-Octadecene 90% and Supelco Chloroform for analysis. **STREM CHEMICALS**: Sulfur powder 99%, Bismuth (III) Chloride 99%, Copper (II) Chloride anhydrous 99.99%, Copper (I) Chloride anhydrous 99.99%. **PanReac**: Copper (II) Nitrate 3-hydrate, Toluene 99.5%, Tetrachloroethylene purissimum **LABKEM**: Nitric acid 69% Analytical grade. **FisherScientific**: Ethanol, Methanol Analytical grade

Physical Measurements.

Rutinary morphological characterization was performed in a JEOL JEM 1010 Transmission electron microscope (TEM) operating at 80 kV. And local HRTEM observations were performed in a Jeol JEM-2100 operating at 200kV. Samples were prepared at room temperature, nanomaterials dispersed in toluene were diluted and deposited on copper grids for TEM or niquel grids for HRTEM. Prepared dilutions are sonicated for a minute before the drop casting on the amorphous carbon side of the grid to obtain better isolated particles in the micrographs. ImageJ and Digital micrograph software were used for image analysis of TEM and HR-TEM respectively.

X-Ray Diffraction (XRD) data were collected using a PANalytical X'Pert PRO MPD Alpha1 powder diffractometer in Bragg Brentano $\theta/2\theta$ geometry of 240 millimeters of radius, Cu Ka radiation: $\lambda = 1.5406$ Å and work power: 45 kV – 40 mA. Samples were prepared by drop casting chloroform solutions of nanocrystals onto a glass substrate (approximately 20mm diameter) and allowing the solvent to evaporate in air. Scans in the range $2\theta = 4-100^{\circ}$ were run at a step size of $2\theta = 0.017^{\circ}$ and 100 s per step. The data were treated with X'Pert HighScore Plus software.

To determine the concentration of NPs in solutions by Inductively Coupled Plasma–Atomic Emission Spectroscopy (ICP–AES). For Bi_2S_3 and Cu_2S solutions, 50μ L were precipitated in MeOH in a 4mL vial. The supernatant was discarded, the precipitate re-dispersed with 1mL of CHCl₃, and subject overnight to 90 °C in an oven for evaporation. 2.5 mL HNO₃ 69% were added to the precipitate and vials were left at room temperature until complete dissolution was reached. The resulting solutions were transferred to 25mL volumetric flasks and diluted with milliQ water.

Absorption measurements were performed using a Cary 5000 UV-VIS-NIR spectrophotometer, in Tetrachloroethylene solution on a glass cuvette of 1 cm optical path.

6.2. PREPARATION OF BISMUTH (III) SULPHIDE

A known synthetic method of bismuth (III) sulfide (Bi2S3) [26] which is known to produce homogeneous nanorods becomes the starting point of this experimental section. Precursors of Bismith and Sulfur are solids stored in the glove box under Nitrogen flow. In independent 4mL glass vials, 96 mg of S (3.0 mmols) and 157 mg of BiCl₃ (0.5 mmols) are weighted on an analytical scale, Sulfur is dissolved in 0,9mL of degassed Oleylamine (OLAm) and both vials are sealed under N_2 with a plastic tap with and without septum respectfully. Sulfur powder may not dissolve completely in OLAm at room temperature, so the use of a heating gun and a vortex is required to obtain a proper solution to be later injected into the reaction mixture, as explained later. In a 25mL three neck round bottom flask, weighted BiCl₃ powder, 1g of Dodecylamine (DDCAm) and 8mL of OLAm are mixed. The solution is degassed at 120°C during 30 minutes under vacuum. Then, the solution needs to be conditioned from vacuum to N_2 inert atmosphere. Manipulating the Schlenk line in an orderly manner requires 3 cycles of vacuum/N₂ onto the setup. After piercing one side of the flask the temperature sensor is introduced into the solution without disturbing the magnetic stirring bar. The solution is heated up to 170°C. At that moment the injection of the sulfur precursor solution is performed. The injection of the orange sulfur solution into the flask must be rapid but cautious. Immediate color change from yellow to black is observed after injection, and the solution is kept on 170°C for 1 hour.

Black product dispersion is poured from the round bottom flask into a 10 mL glass vial. To clean the product from unreacted precursors, excess surfactant and solvent, the solution is

precipitated with EtOH in the centrifuge (3000rpm for 10minutes) and redispersed in Toluene. This process can be repeated various times, but it was further determined that to stabilize the resulting nanoparticles it is better to perform only one cycle of EtOH cleaning. That way, enough surfactant rests in the vial to maintain nanoparticles in relative stable suspension. More exhaustive cleaning was performed only to aliquots destined for characterization.

6.3. PREPARATION OF COPPER (I) SULPHIDE

The most successful synthetic method of Cu₂S nanoparticles performed in this work was extracted from You Zhai and Moonsub Shim article that contains rich discussion on different copper precursor reactivity and Cu₂S nanoparticle shapes. ^[11]

A solution of 124mg (0.51 mmols) of Cu(NO₃)₂ precursor and 1g of capping ligand TOPO was degassed at 120°C for 30 min and then heated to 230 °C under N₂. 1-DDT was added to the reaction mixture at 120 °C. Around 227°C the color of the solution changed from orange to red and brown gradually. At 230°C the solution is left to react for 10 minutes. Upon completion, the reaction mixture was cooled to room temperature. The product of the reaction mixture was precipitated with ethanol and then redispersed in toluene. An aliquot for further characterization had the precipitation/redispersion process repeated three times.

6.4. PREPARATION OF HOMOGENEOUS WITTICHENITE NANOPARTICLES

6.4.1. Synthesis in non-polar and polar solvents (ODE / TOPO)

In 4mL glass vials, 14.6 mg of S (0.455 mmols) and 40 mg of BiCl₃ (0.127 mmols) are weighted on an analytical scale. Sulfur powder is dissolved in 0,9mL of degassed Oleylamine (OLAm) and both vials are sealed under N₂ atmosphere in the glove box with a plastic tap with and without septum respectively. In a 25mL three-neck round bottom flask, weighted BiCl₃ powder, 50.5mg (0.376 mmol) of CuCl₂, 2.4g of 1-DDT and corresponding amount of solvent (3.8mL if ODE or 4.0g if TOPO) are mixed. The solution is degassed at 120°C for 30 minutes under vacuum. Then, the solution is conditioned from vacuum to N₂ inert atmosphere, and it is heated up to 170°C. Meanwhile the solution is heating, the Sulfur solution-containing vial is also conditioned under N₂ atmosphere. After the injection of the orange sulfur solution into the flask, immediate color change from orange to black is observed, and the solution is kept at 170° C during 5 or 30minutes for better crystallinity.

Black product dispersion is poured from the round bottom flask into a 10 mL glass vial. Cleaning procedures vary depending on the solvent used. To clean the product from excess precursors, ODE and surfactants, the solution is precipitated with MetOH/Acetonitrile (3:1) in the centrifuge (3000rpm for 10minutes) and redispersed in Toluene. This process may be repeated twice. In the case of TOPO solvent, it suffices to precipitate with EtOH and redisperse in Toluene once. At room temperature, TOPO solidifies in the reaction mixture, but heating the mixture up to 60°C, or adding 2 mL of toluene to the mixture before complete cooling, is enough to transfer the product from the flask to a vial in the liquid phase.

6.4.2. Heteroattechment synthesis

The experiments in Table 2 were designed considering the available volume of precursors to test ratio, temperature and time effects. After agitation and sonicating, using micropipette, indicated volumes of precursors were mixed in a 4mL vial each. To a total volume of 1mL, the remaining Toluene was added. Experiments 1 and 2 were heated on a water bath and stirred with a magnetic bar for 4 hours. Experiments 3 and 4 were performed at room temperature on an orbital vial vortex for 24 hours.

For TEM samples preparation no procedure is needed except dilution to not saturate the sample substrate. Before XRD samples preparation all vials were centrifugated at 4000rpm for 10minutes and redispersed in chloroform.

7. CONCLUSIONS

Cu₃BiS₃ nanocrystals have been successfully synthesized via the thermal decomposition method of metal salt precursors. The synthesis conditions were optimized by studying various parameters such as surfactant type, temperature, time, and solvent.

 Bi_2S_3 nanorods and Cu_2S nanodiscs were prepared, and their structure and homogeneity were determined using TEM, XRD, and spectroscopy characterization. These particles were used as precursors to test the possibility of heteroattachment between them to form Cu_3BiS_3 at the interface of Bi_2S_3 and Cu_2S . However, XRD patterns did not reveal the presence of the Wittichenite phase, and TEM micrographs did not show any possible heteroattachment between the nanorods and nanosheets.

All three nanomaterials were dispersed in TCL, and their UV-VIS-NIR absorbance was measured. Despite issues with coagulation and precipitation, Bi₂S₃ and Cu₂S exhibited characteristic absorbance. In contrast, Cu₃BiS₃ did not meet the expectations of wide VIS-NIR absorbance bands.

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9. ACRONYMS

NPs: nanoparticles NRs: nanorods TEM: Electron Transmission Microscopy HRTEM: High Resolution TEM XRD: X-ray Diffraction OLAm: Oleylamine DDCAm: Dodecylamine

1-DDT: 1-dodecanthiol

ODE: octadecene

TOPO: tryoctylphosphine oxide

APPENDICES

APPENDIX 1: CU₃BIS₃ FIRST PRODUCT XRD PATTERN



APPENDIX 2: XRD PATTERN OF CU₃BIS₃ PREPARED IN TOPO



APPENDIX 3: COLLECTED XRD PATTERNS FROM HETEROATTACHMENT EXPERIMENTS



APPENDIX 4: COLLECTED ABSORBANCE SPECTRA OF CU_3BIS_3 , BI_2S_3 and CU_2S

