### HORIZON EUROPE PROGRAMME HORIZON-CL4-2023-DIGITAL-EMERGING-01-33

### GA No. 101135196

# Developing New 2D Materials and Heterostructures for Printed Digital Devices



## **2D-PRINTABLE - Deliverable report**

## D1.3 – Synthesis of exfoliable layered crystals





Deliverable No.	eliverable No. D1.3	
Related WP	WP 1	
Deliverable Title         Synthesis of exfoliable layered crystals		
Deliverable Date 30-3-2025		
Deliverable Type	REPORT	
Dissemination level	Public (PU)	
Author(s)	Zdenek Sofer (VSCHT)	2025-3-30
Checked by	Francesco Bonaccorso (BeD)	2025-4-10
Reviewed by	Claudia Bakes (UKa)	2025-4-10
	Joka Boha (BeD)	
Approved by	Jonathan Coleman (TCD) - Project Coordinator	2025-4-11
Status	Final	2025-4-11

#### **Document History**

Version	Date	Editing done by	Remarks
V1.0			
V1.1			
V2.0			
FINAL	11-04-2025	Zdenek Sofer	

#### **Project Scientific Abstract**

The 2D-PRINTABLE project aims to integrate sustainable large-scale liquid exfoliation techniques with theoretical modelling to efficiently produce a wide range of new 2D materials (2DMs), including conducting, semiconducting, and insulating nanosheets. The focus includes developing the printing and liquid phase deposition methods required to fabricate networks and multicomponent heterostructures, featuring layer-by-layer assembly of nanometre-thick 2DMs into ordered multilayers. The goal is to optimize these printed networks and heterostructures for digital systems, unlocking new properties and functionalities. The project also seeks to demonstrate various printed digital devices, including proof-of-principle, first-time demonstration of all-printed, all-nanosheet, heterostructures based light-emitting diodes (LEDs). In conclusion, 2D-PRINTABLE will prove 2D materials to be an indispensable material class in the field of printed electronics, capable of producing far-beyond-state-of-the-art devices that can act as a platform for the next generation of printed digital applications.



### Summary

Deliverable 1.3 focused on the development of a comprehensive library of 2D materials to serve as a foundation for fabricating inks and fully printed, nanosheet-based devices. A broad spectrum of 2D materials was successfully synthesized, and upscaling experiments were conducted on several selected compounds.

The library encompasses a wide range of semiconductors, including transition metal dichalcogenides (TMDs) and post-transition metal chalcogenides. Scalable synthesis procedures such as chemical vapor transport (CVT) and gradient flux solidification were developed, enabling batch production of over 25 g, with some compounds reaching 50 g and even 1 kg.

Solid solution formation in Mo and W dichalcogenides, particularly in the Mo-W-S-Se system and WTe<sub>2</sub> substituted with Mo and Se, was extensively explored. Controlled doping of MoS<sub>2</sub>, WS<sub>2</sub>, MoSe<sub>2</sub>, and WSe<sub>2</sub> was carried out to achieve both p-type and n-type behavior. Nb doping yielded consistent p-type characteristics, while V and Ta showed ambivalent behavior; Re doping resulted in pure n-type semiconductors.

Post-transition metal chalcogenides were synthesized via gradient freezing from flux in quartz ampoules, successfully producing chalcogenides of gallium, indium, tin, germanium, antimony, and bismuth. Selected compounds were also grown using the Bridgman method. Doping strategies led to the development of several p-type semiconductors, including Zn- and Cd-doped variants. Additionally, complex semiconductors such as low bandgap CuTIS and InTITe<sub>2</sub> were synthesized.

A series of metallic, conductive 2D materials were prepared, including V, Nb, Ta, and Ti dichalcogenides using the CVT method. Highly conductive 2D MXenes were also synthesized through chemical exfoliation of MAX phases, with multiple synthesis techniques employed.

For 2D insulators, materials such as hexagonal boron nitride (hBN) were grown from metal fluxes. Highk dielectric 2D materials, including rare-earth oxohalides (LaOBr, LaOCI) and bismuth-based compounds (e.g., Bi<sub>2</sub>SeO<sub>5</sub>, BiOCI), were also successfully prepared.

Ferroelectric materials included mixed MPX<sub>3</sub> compounds like  $CulnP_2S_6$  and others such as  $ln_2Se_3$ , AgCrS<sub>2</sub>, SnS, and SnSe. Multiferroic materials, including AgCrP<sub>2</sub>S<sub>6</sub> and AgVP<sub>2</sub>S<sub>6</sub>, were also developed.

A wide range of magnetic 2D materials was synthesized, including MPX<sub>3</sub> compounds like MnPS<sub>3</sub>, FePS<sub>3</sub>, NiPS<sub>3</sub>, MnPSe<sub>3</sub>, and their solid solutions. Additional magnetic materials included chalcogenhalogenides (e.g., CrSBr, CrOCI), as well as transition metal and rare earth tellurides and selenides (e.g., GdTe<sub>3</sub>, Cr<sub>2</sub>Ge<sub>2</sub>Te<sub>6</sub>, FeSe).

In conclusion, a comprehensive library of 2D materials and robust synthesis protocols has been successfully established, covering the complete spectrum of semiconducting, metallic, insulating, ferroelectric, and magnetic 2D materials.



## Contents

1	Intro	duction	5	
2	Meth	nods and core part of the report	6	
	2.1	Background	6	
	2.2	Procedures	6	
	2.3	Data Analysis	9	
3	Resu	Its & Discussion	9	
	3.1	Results	.1	
	3.2	Contribution to project (linked) Objectives1	.3	
	3.3	Contribution to major project exploitable result1	.3	
4	Conc	lusion and Recommendation1	.4	
5	Risks	and interconnections1	.5	
	5.1	Risks/problems encountered 1	.5	
	5.2	Interconnections with other deliverables1	.5	
6	Devia	ations from Annex 1 1	.6	
7	Refe	rences1	.7	
8	Acknowledgement			
9	Appendix A - Quality Assurance Review Form19			

List of Figures 5 Figures

List of Tables 1 Table.

## Abbreviations & Definitions

Abbreviation	Explanation
CVT	Chemical Vapor Transport
PVT	Physical Vapor Transport



### Introduction

Deliverable 1.3 focused on the creation of a comprehensive set of 2D materials to establish a robust library suitable for ink formulation and printed device fabrication. Over 100 distinct 2D materials were successfully synthesized, covering all fundamental components required for semiconducting devices. This includes materials with metallic conductivity, insulators, semiconductors with both p-type and n-type conductivity, as well as materials exhibiting other functional properties such as ferroelectricity, multiferroicity, superconductivity, magnetism, and non-linear optical activity. To achieve this broad range of materials, several synthesis techniques were employed, including chemical vapor transport (CVT), flux growth, melt growth, physical vapor transport (PVT), and hydrothermal methods. In addition to van der Waals-layered materials, the library was expanded to include chemically exfoliated layered compounds such as MXenes and layered perovskites.

For fine-tuning of bandgaps and other electronic properties, alloying strategies were applied, with a primary focus on solid solutions within the Mo-W-S-Se-Te system. Significant deviations between starting compositions and final crystal stoichiometry were observed, particularly when tungsten ditelluride was involved. These systems were also extensively explored for doping, successfully achieving both p-type and n-type behavior. Further doping experiments targeted Ga, In, Sn, and Ge chalcogenides, resulting in both p-type and n-type semiconductors. Additionally, low bandgap materials such as CuTIS and InTITe<sub>2</sub> were synthesized.

Metallic conductive materials included dichalcogenides of V, Nb, Ta, and Ti, synthesized via the CVT method in quartz ampoules. Other conductive materials were developed from the MXene family, including Ti<sub>3</sub>C<sub>2</sub>, Ti<sub>2</sub>C, Nb<sub>2</sub>C, Mo<sub>2</sub>TiC<sub>2</sub>, and V<sub>2</sub>C.The group of 2D insulators is represented by hexagonal boron nitride (hBN), grown from metal flux, and high-k dielectric materials such as rare-earth oxohalides and ternary compounds like Bi<sub>2</sub>SeO<sub>5</sub>, BiOCl, and CaAl<sub>2</sub>S<sub>4</sub>.Ferroelectric 2D materials such as CuInP<sub>2</sub>S<sub>6</sub> and In<sub>2</sub>Se<sub>3</sub> were successfully synthesized. Multiferroic materials, including AgCrP<sub>2</sub>S<sub>6</sub>, AgVP<sub>2</sub>S<sub>6</sub>, CuCrS<sub>2</sub>, and others, were also prepared. The 2D magnetic materials developed include antiferromagnetic thio-/selenophosphites like FePS<sub>3</sub>, FePSe<sub>3</sub>, NiPS<sub>3</sub>, and transition metal chalcogenides such as Cr<sub>2</sub>Ge<sub>2</sub>Te<sub>6</sub>, Fe<sub>3</sub>GeTe<sub>2</sub>, Fe<sub>5</sub>GeTe<sub>2</sub>, as well as rare-earth tellurides like GdTe<sub>3</sub>. A broad range of 2D halogenide magnets was also created, including Nil<sub>2</sub>, Crl<sub>3</sub>, FeBr<sub>3</sub>, and Gdl<sub>3</sub>.

Upscaling of synthesis was successfully performed for several material systems, achieving growth batches in the range of 10 g to 50 g, with selected materials scaled up to 1 kg. Chemical exfoliation methods were demonstrated for various compounds at scales of 10 g or more, including MXenes from MAX phases and silicene/germanene from Zintl phases. Multiple crystal growth techniques were adopted to build this extensive and diverse library of 2D materials.



## 1 Methods and core part of the report

### 1.1 Background

The primary aim of this deliverable is to prepare a fundamental set of 2D materials for ink formulation, enabling the fabrication of devices through heterostructure printing techniques. Extensive work was undertaken to develop reliable crystal growth protocols for a wide spectrum of 2D materials suitable for use in foundational electronic devices.

The material portfolio comprises over 100 different 2D materials, spanning categories such as semiconductors, insulators, metals, ferroelectrics, multiferroics, magnetic materials, and superconductors. For selected materials, protocols were also established for controlled doping and the formation of solid solutions to allow fine-tuning of their electronic properties.

Conductivity control was successfully demonstrated for several fundamental 2D semiconductors, including MoS<sub>2</sub>, WS<sub>2</sub>, MoSe<sub>2</sub>, WSe<sub>2</sub>, GaSe, InSe, SnSe, SnSe<sub>2</sub>, and Bi<sub>2</sub>O<sub>2</sub>Se. Additionally, chemical exfoliation techniques were developed for layered materials such as perovskites, MAX phases, and Zintl phases, expanding the library of exfoliable 2D materials for printed electronic applications.

### 1.2 Procedures

To enable the growth of single crystals of 2D materials, a broad portfolio of synthesis methods was developed, supported by the use of over 30 different types of furnaces. The most widely adopted technique was chemical vapor transport (CVT), which utilizes volatile species that either decompose at lower temperatures (exothermic) or require higher temperatures (endothermic) for reformation. This method is particularly effective for synthesizing chalcogenides, pnictides, and more complex mixed compounds such as transition metal chalcogen-halogenides.

Physical vapor transport (PVT) was primarily used for the growth of 2D halogenide compounds. In some cases, autotransport mechanisms (e.g., BiTel, FeBr<sub>3</sub>) were also observed. The process begins with filling quartz ampoules with precursors (typically elements) and sealing them under high vacuum, often with liquid nitrogen cooling for highly volatile components like bromine and iodine. The reaction to form the target compound is initiated by a controlled temperature gradient. Depending on the scale, this stage takes 3–10 days. The resulting bulk material is then subjected to CVT growth in a horizontal two-zone furnace.

Typical growth scales range from 10–25 g using ampoules of 200 mm length and 25–40 mm diameter. Larger-scale syntheses (40–250 g) utilize 250 mm long ampoules with 50–60 mm diameters. A demonstration of scalability was also achieved with a 1 kg growth experiment in a 100 × 600 mm ampoule using a three-zone furnace. Transport agents used included various halogens and halogenides such as  $I_2$ , SeCl<sub>4</sub>, SeBr<sub>4</sub>, TeCl<sub>4</sub>, TeBr<sub>4</sub>, and AlBr<sub>3</sub>.

![](_page_6_Picture_1.jpeg)

CVT was employed successfully for complex chalcogenides including  $ZnIn_2S_4$ , CdInGaS<sub>4</sub>,  $Ni_2TaS_5$ , and  $Ni_3GeTe_2$ , among others. The method was also extensively used for mixed chalcogen-halogenides (e.g., CrSBr), thiophosphites (MnPS<sub>3</sub>), and selenophosphites (MnPSe<sub>3</sub>), as well as for several magnetic (e.g., Fe<sub>3</sub>GeTe<sub>2</sub>, Fe<sub>5</sub>GeTe<sub>2</sub>), ferroelectric (e.g., CuInP<sub>2</sub>S<sub>6</sub>), and dielectric (e.g., Bi<sub>2</sub>SeO<sub>5</sub>) materials. Less common 2D compounds such as ScPS<sub>4</sub> and LuPS<sub>4</sub> were also successfully synthesized using this approach. The CVT technique proved particularly effective for producing intercalated transition metal dichalcogenides, such as  $Co_{1/3}NbSe_2$ ,  $Fe_{1/3}TaS_2$ , and  $Ge_{1/3}TaSe_2$ .

![](_page_6_Picture_3.jpeg)

Figure 1. Furnace configurations used for crystal growth: (A) Two-zone CVT furnaces; (B) Crucible furnaces for volatile precursor pre-reaction; (C) Bridgman furnace for melt growth.

Physical vapor transport and autotransport were primarily applied to halogen compounds, including lanthanide halides (e.g., Gdl<sub>3</sub>, LuBr<sub>3</sub>) and transition metal halides (e.g., NiCl<sub>2</sub>, Col<sub>2</sub>), as well as post-transition metal chalcogen-halides like BiTeI and BiSeBr. Over 20 different halides were grown using this technique. Due to their extreme sensitivity to moisture and oxygen, all manipulations were conducted in an inert-atmosphere glovebox.

Ceramic synthesis methods were used for layered niobates and tantalates, including the Bi<sub>2</sub>SrNan– $2NbnO_3n+3$  series (n = 2–5). This involves solid-state reactions of oxides and carbonates with excess carbonate to counteract evaporation losses during high-temperature synthesis (800–1400 °C). Selective etching of alkali metals (or other removable elements like Bi) from the layered structure using acids enabled exfoliation, followed by delamination with alkylammonium hydroxide to produce inks with flake sizes of approximately 1 micron.

![](_page_7_Picture_1.jpeg)

Melt growth was employed for compounds with congruent melting points, as well as some incongruent melting materials such as InSe and In<sub>4</sub>Se<sub>3</sub>, by using slightly off-stoichiometric flux compositions. Several post-transition metal chalcogenides were prepared this way, including GaSe, GaS, In<sub>2</sub>Se<sub>3</sub>, and chalcogenides of Sn, Ge, Pb, Sb, and Bi.

Crystalline growth of compounds containing glass-forming elements like As and Ge proved challenging; some complex systems like  $As_2Se_3$  did not yield crystalline products. Off-stoichiometric and chalcogenbased fluxes were tested for systems such as  $Cr_2Ge_2Te_6$  (using Te flux) and PtSe<sub>2</sub> (using Se flux). Separation of the product from flux was achieved through mechanical removal, high-temperature centrifugation, or sublimation, depending on the flux composition.

- Mechanical separation was used for Cr<sub>2</sub>Si<sub>2</sub>Te<sub>6</sub> and Cr<sub>2</sub>Ge<sub>2</sub>Te<sub>6</sub>, grown in a 2:2:10 composition (Cr:Si/Ge:Te) on a 50 g scale.
- Selenium sublimation was employed to isolate PtSe<sub>2</sub>.
- Centrifugation has not yet been implemented; a specialized crucible system is under development for compounds like TaIrTe<sub>4</sub> (grown from Te flux).

Halogenide flux methods were also applied, especially for lanthanide oxo-halides. Excess metal halide served as both solvent and reagent, enabling growth of compounds such as LaOBr and LaOI.

Chemical liquid transport (CLT) methods, using low-melting salt mixtures such as  $AICI_3$ -KCl and  $AICI_3$ -NaCl, allowed for gradient crystal growth of thermally sensitive compounds (e.g., FeSex,  $Cr_2Ge_2Te_6$ ) due to the high solubility of the flux.

Alkali metal halide fluxes were also explored for specific systems, such as rare-earth tritellurides (e.g., SmTe<sub>3</sub>), using eutectic mixtures of alkali chlorides, bromides, and iodides in sealed quartz ampoules.

High-temperature fluxes of transition metal sulfides (e.g., NiS, FeS, CoS) enabled the growth of sulfurbased MAX phases like Nb<sub>2</sub>SC, Nb<sub>2</sub>S<sub>2</sub>C, and intercalated transition metal sulfides such as Fe1/3NbS<sub>2</sub> and Ni1/3TaS<sub>2</sub>.

Finally, for thiophosphites, flux growth was carried out using  $P_2S_5$  as both a reagent and solvent. This enabled the successful synthesis of compounds such as  $CoPS_3$  and  $CuInP_2S_6$ .

![](_page_7_Picture_12.jpeg)

Figure 2. The results of various crystal growth experiments covering large scale boron nitride growth from metal flux in hydrogen/nitrogen atmosphere (Figure 2A), growth of cerium tritelluride from

![](_page_8_Picture_1.jpeg)

lithium and potassium iodide eutectic flux (Figure 2B), growth of  $CoPS_3$  from  $P_2S_5$  flux in thermal gradient (Figure 2C), growth of SnSe by gradient freeze solidification in ampoule (Figure 2D) and growth of insulating  $Bi_2SeO_5$  by CVT method in quartz ampoule (Figure 2E)

### 1.3 Data Analysis

The prepared materials were approved by X-ray diffraction and for several selected materials using also other methods like SEM combined with EDS, XPS and Raman spectroscopy. The electrical parameters of selected 2D semiconductors are shown in Table 1. The example of SEM and combined with EDS mapping is shown on Figure 3. Example of XRD of layered Bi2O2Se is shown on Figure 4.

![](_page_8_Figure_5.jpeg)

Figure 3. The SEM image and EDS mapping of mixed Mo-W diselenide.

![](_page_9_Picture_1.jpeg)

![](_page_9_Figure_2.jpeg)

Figure 4. The X-ray diffraction of Bi2O2Se for grinded powder (left figure) and single crystal flake (right flake).

Table 1.1 The list of doped TMDCH semiconductors with corresponding bulk carrier concentration, Hall voltage, free carrier	
mobility and its polarity.	

Material	Bulk Carrier	Hall Voltage	Mobility	Polarity
	density (/cm³)	(mV)	(cm2/V.s)	
MoS2 Re	2.70E+20	-0.05785	9.652305	n-type
$MoS_2$ Nb doped	1.51E+19	0.000106	4.027204	p-type
MoSe2 Nb	4.85E+19	0.0002	6.107663	p-type
MoSe2 Ta	2.08E+19	0.000525	5.132194	p-type
MoSe2 V	1.17E+19	0.000413	5.215592	p-type
WSe2 Nb	1.66E+19	0.000356	11.83195	p-type
WSe2 V	1.09E+19	0.000456	11.09485	p-type
WSe2 Ta	1.73E+19	0.000394	7.826144	p-type

![](_page_10_Picture_1.jpeg)

### 2 Results & Discussion

### 2.1 Results

In the first half of the project, a comprehensive base library of 2D materials was successfully established, including metals, semiconductors, insulators, and functional 2D materials such as superconductors, ferroelectrics, multiferroics, and magnets. In total, over 100 distinct 2D materials were synthesized.

#### Transition Metal Dichalcogenides:

The primary focus among semiconductors was on transition metal dichalcogenides (TMDs). Doping experiments were conducted on selected compounds to generate both p-type and n-type semiconductors. The most extensively studied materials were MoS<sub>2</sub>, WS<sub>2</sub>, MoSe<sub>2</sub>, and WSe<sub>2</sub>. Crystal growth of these materials was successfully upscaled, with 50 g batches of MoS<sub>2</sub> and WS<sub>2</sub>, 250 g batches of selenides, and even 1 kg of WSe<sub>2</sub> synthesized using a 5 L ampoule in a three-zone CVT furnace.

For large-scale growth, a controlled slow heating protocol was adopted to minimize rapid reactions between chalcogen and metal, thereby avoiding pressure buildup. Doping experiments on MoS<sub>2</sub> and WS<sub>2</sub> with niobium (Nb) and rhenium (Re) showed promising results—Re doping significantly increased electron concentration, while Nb doping enabled p-type behavior.

Doping of MoSe<sub>2</sub> and WSe<sub>2</sub> was explored with Nb at concentrations ranging from 0.01 to 1 at.%, successfully achieving p-type conductivity. Vanadium and tantalum doping yielded ambipolar behavior, while Re doping again resulted in pure n-type conductivity with high carrier concentrations. Current efforts include doping with Cr, Ti, Zr, and Hf, particularly for WSe<sub>2</sub> and MoSe<sub>2</sub>.

In the telluride system, Mo was substituted into  $WTe_2$ , and Se into Te, although the final crystal compositions differed from the initial stoichiometry due to varying transport behavior. This discrepancy was not observed for sulfides and selenides, and mixed compositions such as MoSSe, WSSe,  $Mo_xW_{1-x}Se_2$ , and  $Mo_x(W_{1-x})Se_2$  were successfully obtained.

All these dichalcogenides were synthesized using the CVT method. In parallel, efforts began on flux growth, including use of transition metal fluxes (e.g., FeS<sub>2</sub>) and high-pressure chalcogen fluxes (Se, Te). While these methods offer the advantage of reducing chalcogen vacancies, they present significant challenges due to the high pressure (>10 bar) required during synthesis. As an alternative, post-treatment of CVT-grown crystals with elemental selenium or tellurium is being explored. These methods will be evaluated using STM imaging (for direct defect observation) and low-temperature photoluminescence (PL) linewidth analysis. Demonstration of large scale (1 kg of WSe<sub>2</sub>) growth using CVT method in three-zone furnace on Figure 5.

![](_page_11_Picture_1.jpeg)

![](_page_11_Picture_2.jpeg)

Figure 5. Large scale growth of WSe<sub>2</sub> in three zone furnace (Figure 5A) and formed WSe<sub>2</sub> crystals (Figure 5B).

#### Post-Transition Metal Chalcogenides:

Several post-transition metal chalcogenides were also successfully grown as single crystals, including GaSe, GaS, GaTe, InSe, InTe, GeS, GeSe, GeS<sub>2</sub>, GeSe<sub>2</sub>, SnS, SnSe, SnS<sub>2</sub>, SnSe<sub>2</sub>, PbSnS<sub>2</sub>, and mixed chalcogenides of Bi and Sb, as well as Bi<sub>2</sub>O<sub>2</sub>Se.

Doping experiments were performed on GaSe, GaS, InSe, SnSe<sub>2</sub>, SnS, and Bi<sub>2</sub>O<sub>2</sub>Se using gradient freezing in quartz ampoules. While Zn doping of GaSe resulted in p-type conductivity, most dopants (Zn, Cd, Hg, Ge, Sn, P, As, Sb, Bi) led to semi-insulating or n-type behavior. Interestingly, thickness-dependent carrier concentration and conductivity type were also observed, which will be further studied to expand the library of p-type semiconductors. Initial experiments using the Bridgman method for crystal growth were also conducted.

#### Other Semiconductor Systems:

Low bandgap semiconductors such as CuTIS<sub>2</sub>, CuTISe<sub>2</sub>, AgBiP<sub>2</sub>Se<sub>6</sub>, and chalcogenides of Pt and Pd were prepared. Additionally, Zr and Hf dichalcogenides were synthesized using the CVT method. Monoelemental 2D materials included black phosphorus-arsenic alloys and hydrogenated/alkylated germanene, obtained through chemical exfoliation of CaGe<sub>2</sub>.

#### Metallic Conductors:

Metallic 2D materials explored included chalcogenides of Ti, V, Nb, and Ta. Growth conditions and phase behavior were studied, particularly for Nb and Ta systems, where mixed 2H and 3R phases were observed. Intercalation experiments with magnetic transition metals (Ti, V, Cr, Mn, Fe, Co, Ni) were performed for NbS<sub>2</sub>/NbSe<sub>2</sub> and TaS<sub>2</sub>/TaSe<sub>2</sub>, with high-quality crystals obtained via CVT using iodine.

MXenes were also investigated as 2D conductors. MAX phases such as  $Ti_3AlC_2$  and  $Mo_2TiAlC_2$  were synthesized at >100 g scale. Exfoliation methods included molten salt (CuCl<sub>2</sub>, CuBr<sub>2</sub>, CdCl<sub>2</sub>, CdBr<sub>2</sub>, EuCl<sub>3</sub>) and standard HF-based protocols (HF/HCl, LiF/HCl). New sulfur-based MAX phases and MXenes like Nb<sub>2</sub>SC and Nb<sub>2</sub>S<sub>2</sub>C were synthesized. Electrochemical exfoliation was tested for Nb<sub>2</sub>SC, while sulfur flux growth methods led to metal-intercalated Nb<sub>2</sub>S<sub>2</sub>C, which were subsequently de-intercalated via chemical etching.

![](_page_12_Picture_1.jpeg)

#### Insulating Materials:

Insulating 2D materials synthesized include hexagonal boron nitride (hBN) grown via metal flux, and mixed oxides such as Bi<sub>2</sub>SeO<sub>5</sub>, BiOCl, BiOBr, BiOI, prepared via CVT and flux growth. Mixed halides of Sr, Ba, Pb (e.g., PbClF, BaFBr) were also obtained. Rare earth oxo-halides were synthesized from mixed salt fluxes (NaCl-KCl, NaCl-MgCl<sub>2</sub>, NaBr-MgBr<sub>2</sub>).

#### Superconductors:

Superconducting 2D materials included Nb and Ta dichalcogenides, synthesized via CVT, and FeSe, grown using chemical liquid transport with AlCl<sub>3</sub>/NaCl flux under a thermal gradient.

Ferroelectric and Multiferroic Materials:

Ferroelectric materials such as  $In_2Se_3$  and SnSe were synthesized via flux growth. Mixed thiophosphites like  $CuInP_2S_6$  were grown using CVT, while multiferroic materials such as  $AgCrP_2S_6$ ,  $CuCrP_2S_6$ , and  $AgVP_2S_6$  were also successfully prepared.

### 2.2 Contribution to project (linked) Objectives

The deliverable focused on the fundamental synthesis of 2D materials forms the core foundation for subsequent research activities, as it ensures the availability of high-quality materials for exfoliation and device fabrication. A comprehensive library of 2D materials required for the following tasks has been successfully established, and the synthesis of many of these materials has been effectively upscaled to supply sufficient quantities for all downstream applications.

### 2.3 Contribution to major project exploitable result

This deliverable created fundamental base of materials to fabricate inks as well as fundamental study of exfoliated materials.

![](_page_13_Picture_1.jpeg)

### 3 Conclusion and Recommendation

A comprehensive library of 2D materials for ink fabrication has been successfully established, encompassing a wide range of material classes including **p-type and n-type semiconductors, metals, insulators**, and functional materials such as **ferroelectrics, multiferroics, superconductors**, and **magnetic 2D materials**. Several novel 2D compounds were also developed during the course of the project.

For selected 2D semiconductors, **reliable procedures for controlled p-type and n-type doping**, as well as **alloying techniques**, were implemented to enable precise tuning of electronic and physical properties. The majority of these materials were synthesized at scales exceeding **10 g per batch**, meeting the requirements for ink formulation and device prototyping. Key materials were successfully scaled up to **50 g or more**, with certain compounds grown in **100 g to 1 kg quantities**, demonstrating the scalability of the developed growth protocols.

The result is a robust and diverse 2D material library that provides a solid foundation for subsequent tasks involving **exfoliation**, **ink formulation**, **and device fabrication**, supporting further research and technological development.

![](_page_14_Picture_1.jpeg)

## 4 Risks and interconnections

### 4.1 Risks/problems encountered

None significant risk and problems were identified.

### 4.2 Interconnections with other deliverables

This deliverable providing materials for other deliverables focused on materials exfoliation, chemical functionalization and printed device fabrication. All main task of this deliverable were successfully fulfilled and complete library of 2D materials for device fabrication were created.

GA No. 101135196

![](_page_15_Picture_1.jpeg)

## 5 Deviations from Annex 1

None deviation from Annex 1 existing.

![](_page_16_Picture_1.jpeg)

## 6 References

![](_page_17_Picture_1.jpeg)

## 7 Acknowledgement

The author(s) would like to thank the partners in the project for their valuable comments on previous drafts and for performing the review.

# Partner		Partner Full Name		
short name				
1	TCD	TCD THE PROVOST, FELLOWS, FOUNDATION SCHOLARS		
		& THE OTHER MEMBERS OF BOARD, OF THE		
		COLLEGE OF THE HOLY & UNDIVIDED TRINITY OF		
		QUEEN ELIZABETH NEAR DUBLIN		
2	UNISTRA	UNIVERSITE DE STRASBOURG		
3	UKa	UNIVERSITAET KASSEL		
4	BED	BEDIMENSIONAL SPA		
5	TUD	TECHNISCHE UNIVERSITAET DRESDEN		
6	VSCHT	VYSOKA SKOLA CHEMICKO-TECHNOLOGICKA V PRAZE		
7	UNR	UNIRESEARCH BV		
8	UniBw M	UNIVERSITAET DER BUNDESWEHR MUENCHEN		
9	EPFL	ECOLE POLYTECHNIQUE FEDERALE DE LAUSANNE		

#### **Project partners:**

#### Disclaimer/ Acknowledgment

![](_page_17_Picture_7.jpeg)

Copyright ©, all rights reserved. This document or any part thereof may not be made public or disclosed, copied or otherwise reproduced or used in any form or by any means, without prior permission in writing from the 2D-PRINTABLE Consortium. Neither the 2D-PRINTABLE Consortium nor any of its members, their officers, employees or agents shall be liable or responsible, in negligence or otherwise, for any loss, damage

or expense whatever sustained by any person as a result of the use, in any manner or form, of any knowledge, information or data contained in this document, or due to any inaccuracy, omission or error therein contained.

All Intellectual Property Rights, know-how and information provided by and/or arising from this document, such as designs, documentation, as well as preparatory material in that regard, is and shall remain the exclusive property of the 2D-PRINTABLE Consortium and any of its members or its licensors. Nothing contained in this document shall give, or shall be construed as giving, any right, title, ownership, interest, license or any other right in or to any IP, know-how and information.

This project has received funding from the European Union's Horizon Europe research and innovation programme under grant agreement No 101135196. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union. Neither the European Union nor the granting authority can be held responsible for them.

![](_page_18_Picture_1.jpeg)

### 8 Appendix A - Quality Assurance Review Form

The following questions should be answered by all reviewers (WP Leader, reviewer, Project Coordinator) as part of the Quality Assurance procedure. Questions answered with NO should be motivated. The deliverable author will update the draft based on the comments. When all reviewers have answered all questions with YES, only then can the Deliverable be submitted to the EC.

NOTE: This Quality Assurance form will be removed from Deliverables with dissemination level "Public" before publication.

	Question	WP Leader	Reviewer	Project Coordinator
		Zdenek Sofer	Claudia Backes	Jonathan Coleman
1.	Do you accept this Deliverable as it is?	Yes	Yes	Yes
2.	<i>Is the Deliverable complete?</i> - All required chapters? - Use of relevant templates?	Yes	Yes	Yes
З.	Does the Deliverable correspond to the DoA? - All relevant actions preformed and reported?	Yes	Yes	Yes
4.	<i>Is the Deliverable in line with the 2D-PRINTABLE objectives? - WP objectives - Task Objectives</i>	Yes	Yes	Yes
5.	<ul> <li>Is the technical quality sufficient?</li> <li>Inputs and assumptions correct/clear?</li> <li>Data, calculations, and motivations correct/clear?</li> <li>Outputs and conclusions correct/clear?</li> </ul>	Yes	Yes	Yes
6.	<i>Is created and potential IP identified and are protection measures in place?</i>	Yes	Yes	Yes
7.	Is the Risk Procedure followed and reported?	Yes	Yes	Yes
8.	Is the reporting quality sufficient? - Clear language - Clear argumentation - Consistency - Structure	Yes	Yes	Yes