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Title: Electrodeposition of Indium on W and Cu electrodes in the Deep Eutectic Solvent choline chloride- ethylene glycol (1:2)

Article Type: Research paper

Keywords: Deep eutectic solvents, indium, disproportionation, diffusion coefficient, Cu-In intermetallic compounds.

Corresponding Author: Dr. Enrique Barrado, PhD

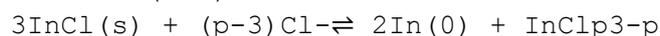
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Manuscript Region of Origin: SPAIN

Abstract: A procedure for drying the deep eutectic solvent (DES) choline chloride - ethylene glycol, ChCl-EG (1:2), based on the use of molecular sieves has been developed, being the final water content of the electrolyte  $145 \pm 5$  ppm. In this dried DES, the stability of InCl and InCl<sub>3</sub> as well as the electrochemical behaviour of their solutions have been investigated using electrochemical techniques, X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM). Experiments performed under a N<sub>2</sub> atmosphere show that InCl<sub>3</sub>, dissolved in the rich chloride media as InClp<sub>3-p</sub>, is reduced on a tungsten electrode to indium metal via only one electrochemical step. Conversely, InCl undergoes the following disproportionation reaction when dissolved in the eutectic ChCl-EG (1:2)



generating In(0) and giving place to identical electrochemical signals as those obtained after the addition of InCl<sub>3</sub> to the DES.

On a tungsten electrode, nucleation and crystal growth of In plays an important role in the electrodeposition process. Chronoamperometric results were consistent with instantaneous three dimensional nucleation on a finite number of active sites with diffusion controlled growth of the nuclei, whatever the applied overpotential and temperature. Mass transport towards the electrode is a diffusion process, and the following empirical expression for the temperature dependence of the diffusion coefficient was calculated

$$\ln D = -(3.58 \pm 0.22) - (3665 \pm 76) T^{-1}$$

The electro-reduction of In(III) solutions was also investigated at a copper substrate. The resulting cyclic voltammograms evidenced the formation of In-Cu intermetallic compounds. Hence, In-Cu alloy films were obtained by continuous potentiostatic electrolysis and intensiostatic pulse electrolysis. The obtained samples, characterized by XRD and SEM, revealed the formation of the metastable CuIn phase that could be transformed into Cu<sub>11</sub>In<sub>9</sub> by thermal annealing.





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Spain

Ms. No.:

Valladolid 30<sup>th</sup> May 2018

Dear Prof. Feliu,

We are submitting the revised version of the paper entitled "Electrodeposition of Indium on W and Cu electrodes in the Deep Eutectic Solvent choline chloride-ethylene glycol (1:2)", whose authors are: Y. Castrillejo, S. García, J.A. Rodriguez, E. Barrado

We would like to thank the reviewers for their careful revision, permitting us to correct the errors appearing in the original manuscript. All changes made are discussed in the response of reviewers.

We feel that these changes have certainly helped to improve the description of our work and hope they will clear the way for publication in **JOURNAL OF ELECTROANALYTICAL CHEMISTRY**. Please do not hesitate to contact me should you require any further information concerning our manuscript.

Yours sincerely

Enrique Barrado

## Research Highlights

Molecular sieves have been used to reduce water content in  $\text{ChCl-EG}$  (1:2)

$\text{InCl}$  undergoes a disproportionation reaction giving  $\text{In}(0)$  and  $\text{InCl}_p^{3-p}$

Electrodeposition of  $\text{In}$  onto  $\text{W}$  involves instantaneous three dimensional nucleation

Electroreduction of  $\text{In(III)}$  at  $\text{Cu}$  substrate generates  $\text{In-Cu}$  intermetallic compounds

Metastable  $\text{CuIn}$  phase can be transformed into  $\text{Cu}_{11}\text{In}_9$  by thermal annealing.

**Reviewer 1**

**Report manuscript number JELECHEM-D-18-00513**

We are very grateful to the reviewer for his/her comments on the paper, according to which we have changed and rewritten some parts of the article.

**Excellent paper. All the experimental details are given without too much explanations and the text is very pleasant to read. The electrochemical curves reflect the accuracy of the measurements and the care brought to the preparation of the media (very hard to study due to its high hygroscopicity).**

**The determination of diffusion coefficient if In(III) is done using several techniques and leads to the determination of activation energy.**

**An important point concerns the identification of Cl<sub>2</sub> gas at the anodic limit of the solvent.**

**About deposition of In, it was shown the great interest of using pulse current to obtain a non porous solid deposition.**

**One small detail could be improved on Figure 11: it is difficult to distinguish the experimental measurements and the calculated curve for instantaneous nucleation: may be another color could be used.**

Taken into account the reviewer's suggestion Figure 11 has been modified accordingly.

**This paper reflects the rigor and the great mastery brought by reseachers both in the experimental measurements and in the results exploitation.**

**Reviewer #2:**

We are very grateful to the reviewer for his/her comments on the paper, according to which we have changed and rewritten some parts of the article.

**General comments**

The manuscript titled "Electrodeposition of Indium on W and Cu electrodes in the Deep Eutectic Solvent choline chloride-2 ethylene glycol" reports interesting results about the application of a deep eutectic solvent in the study of the electrochemical behaviour of Indium on different electrodes. I would recommend publication of this work, although a number of issues should be addressed:

**Specific Comments:**

**1) I would like to suggest a change in the way of naming of deep eutectic solvent. In the manuscript, authors name the used DES as "ChCl:2EG". I suggest naming it as ChCl:EG (1:2) since it is the generalized form used by most authors in the bibliography.**

Taken into account the reviewer's comment ChCl-2EG has been changed to ChCl-EG (1:2) in the new version of the manuscript.

**2) In my opinion, units of the diffusion coefficient and temperature are not necessary in the abstract due to this information is properly given in the manuscript. Abstract is a brief information about the study presented in the reported work without the need for additional details.**

Taken into account the reviewer's comment, ( $D_{in}$ :  $\text{cm}^2 \text{s}^{-1}$  and T: K) has been eliminated in the abstract.

**3) Regarding to molecular sieves activation section, I have some doubts. From my knowledge, the described process in the manuscript is a drying process. It is true that a drying process is convenient in order to ensure the maximum elimination of water from the compound to use, DES in this case. However, authors do not give any information about the type of the used molecular sieves, therefore I do not know if it is a drying or an activation process. Please, could you explain to me what exactly is the activation process described in section 2.1.?**

In our experiments we have used molecular sieves with channel sizes 4A, as it is indicated in the text.

Taken into account the reviewer's comment, the following sentence has been included:

*Before using molecular sieves as a drying agent, they must be "activated" by removing all traces of water and other volatile compounds. Therefore, the appropriate amount of molecular sieve 4A was added to a dry flask and heated in a microwave for 2 minutes at 500 W....*

**4) In solvent preparation section, it is said that: "The dried solvent can be used after 10 days". I would like you to explain to me why this time is necessary to use the solvent.**

Once the container with the DES was hermetically closed with a Septum, the water content of the DES was analysed every 2 days by means of the Karl-Fischer titration. The water content decreases exponentially with time, achieving a constant value of 145 ppm after 10 days.

Taken into account the reviewer's comment, the following sentence has been included.

*"The dried solvent can be used after 10 days (i.e. when the water content remains constant)"*

**5) In the abstract and conclusions, the reported water content is of 145 ppm but in the manuscript the reported water content is of 150 ppm. Please, revise these data.**

Thank you very much for this comment. The water content is  $145 \pm 5$  ppm

**6) Density and viscosity data of the used solvent are described by two equations in the solvent preparation section. Please, include more information about these equations in the manuscript. By**

**this I mean that the type of equation used for fitting the density and viscosity data is mentioned (lineal equation, Vogel-Fucher-Tamman equation, Arrhenius-like law...) in the manuscript.**

Taking into account the reviewer's comments, the following paragraphs have been included:

*"The experimentally measured density of ChCl-EG (1:2) is found to vary lineally with the absolute temperature and was fitted to the following equation:"*

$$\rho(\text{g cm}^{-3}) = (1.2835 \pm 0.0008) - (5.529 \pm 0.024) \times 10^{-4} \times T \quad (1)$$

*"Although the measured viscosity of ChCl-EG (1:2) may be described by the simplest Arrhenius model over the temperature range studied (293-373 K), the Vogel-Fulcher-Tamman (VFT) model appears to more satisfactorily describe the viscosity as follows":*

$$\eta(\text{mPa}\cdot\text{s}) = (0.07614) \exp \frac{1046.22}{[T-137]} \quad (2)$$

**7) In section 2.3, the uncertainty in the temperature measurement is not given in the manuscript. Please, include this data in the text.**

Following the reviewer's comment the following sentence has been rewritten:

*The cell was connected to a TAMPSON TC6B thermostat in order to control the temperature to  $\pm 1\text{K}$*

**8) In page 6, an analysis by UV-Vis is reported. Please, include information about the spectrophotometer used in the manuscript.**

Taken into account the reviewer's comment the following sentence has been included in the new version of the manuscript.

*"The presence of  $\text{Cl}_3^-$  in the solution used in the macro-electrolysis experiments was also tested by UV-Vis using a Hewlett Packard 8453 (G1103A) Diode-Array Spectrophotometer".*

**9) In my opinion, in the legend of Figure 4, it is necessary to indicate that dotted pink line corresponds to the electrochemical window on W electrode in order to avoid confusions.**

Taken into account the reviewer's comment the legend of Figure 4 has been modified accordingly

**10) In Figure 7, different cyclic voltammograms are depicted. Although, no information about the differences between them is reported in any part of the manuscript. Please, include more information about them either in the legend or in the manuscript. The same suggestion is made for the legend of Figure 15. Which is the different between the showed CVs in the figures?. Please, legends of figures should show about all the relevant information of the depicted figures.**

Following the reviewer's suggestion, legends of figures 7 and 15 have been modified as follows:

Fig.7.- Cyclic voltammograms recorded at different inversion potentials on a tungsten electrode at  $100 \text{ mV s}^{-1}$  and  $343 \text{ K}$  after the addition of anhydrous  $\text{InCl}$  to  $\text{ChCl-EG (1:2)}$ .

Fig. 15.- Cyclic voltammograms obtained at different potential limits ( $-0.76$ ;  $-0.78$ ;  $-0.79$ ;  $-0.80$ ;  $-0.85$ ; and  $-0.90 \text{ V}$  vs  $\text{Ag(I)/Ag}$ ) with a  $\text{In(III)}$  solution ( $C_0 = 7.29 \times 10^{-5} \text{ mol cm}^{-3}$ ) at a  $\text{W}$  electrode (grey line) and a  $\text{Cu}$  electrode (dotted lines) at  $343 \text{ K}$ . Scan rate:  $10 \text{ mV s}^{-1}$ .

**11) In the results obtained with addition of  $\text{InCl(s)}$  section, I would suggest that it will be mentioned that the solid analysed by XRD was formed at the bottom of the cell in the manuscript and not only in the legend of Figure 9.**

Taken into account the reviewer's comment, the following sentence has been included

*In order to endorse the disproportionation of  $\text{InCl}$ , the solid formed at the bottom of the cell was analysed by XRD*

**12) I would suggest that authors indicate the different potentials applied in the chronoamperograms showed in Figure 10 in its corresponding legend in the same way as they did in Figure 11. I do the same suggestion for the different currents applied in the legend of Figure 12.**

Following the reviewer's suggestion the legends of Figures 10 and 12 have been modified accordingly.

**13) Please, check the manuscript in order to correct some errata, as for example, abbreviation of DES both for the singular or the plural form; It is indicated that Figure 6 is formed by 6 (a-c) in the text but I only find Fig. 6 (a) and Fig. 6 (b); When W or GC electrodes are mentioned by the first time, please inform that they are tungsten or glassy carbon electrodes in the manuscript; Unify the style of references according to the requirements of the journal...**

Thank you for the comments. The errata have been corrected in the new version of the manuscript

**14) Finally, conclusions are clear and reflect the result obtained in the study.**

**Electrodeposition of Indium on W and Cu electrodes in the Deep Eutectic Solvent **choline chloride-ethylene glycol (1:2)****

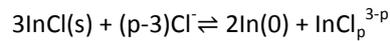
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## ABSTRACT

A procedure for drying the deep eutectic solvent (DES) choline chloride - ethylene glycol, **ChCl-EG (1:2)**, based on the use of molecular sieves has been developed, being the final water content of the electrolyte  $145 \pm 5$  ppm. In this dried DES, the stability of  $\text{InCl}$  and  $\text{InCl}_3$  as well as the electrochemical behaviour of their solutions have been investigated using electrochemical techniques, X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM). Experiments performed under a  $\text{N}_2$  atmosphere show that  $\text{InCl}_3$ , dissolved in the rich chloride media as  $\text{InCl}_p^{3-p}$ , is reduced on a tungsten electrode to indium metal via only one electrochemical step. Conversely,  $\text{InCl}$  undergoes the following disproportionation reaction when dissolved in the eutectic **ChCl-EG (1:2)**



generating  $\text{In(0)}$  and giving place to identical electrochemical signals as those obtained after the addition of  $\text{InCl}_3$  to the DES.

On a tungsten electrode, nucleation and crystal growth of  $\text{In}$  plays an important role in the electrodeposition process. Chronoamperometric results were consistent with instantaneous three dimensional nucleation on a finite number of active sites with diffusion controlled growth of the nuclei, whatever the applied overpotential and temperature. Mass transport towards the electrode is a diffusion process, and the following empirical expression for the temperature dependence of the diffusion coefficient was calculated

$$\ln D = -(3.58 \pm 0.22) - (3665 \pm 76) T^{-1}$$

The electro-reduction of  $\text{In(III)}$  solutions was also investigated at a copper substrate. The resulting cyclic voltammograms evidenced the formation of  $\text{In-Cu}$  intermetallic compounds. Hence,  $\text{In-Cu}$  alloy films were obtained by continuous potentiostatic electrolysis and intensiostatic pulse electrolysis. The obtained samples, characterized by XRD and SEM, revealed the formation of the metastable  $\text{CuIn}$  phase that could be transformed into  $\text{Cu}_{11}\text{In}_9$  by thermal annealing.

*Keywords: Deep eutectic solvents, indium, disproportionation, diffusion coefficient, Cu-In intermetallic compounds.*

## 1.- INTRODUCTION

Indium and its alloys are suitable materials for producing semiconductor compounds such as the binaries (InP, InSb, InAs), ternaries (InGaP, GaInAs, CuInSe<sub>2</sub>) and quaternaries (CuInSSe and Cu(In,Ga)Se<sub>2</sub>) which are widely used in electronic and optoelectronic technology [1-3]. In this context, polycrystalline thin films of the chalcopyrite materials CuInSe<sub>2</sub> and Cu(In,Ga)Se<sub>2</sub> are proposed as absorbent materials for photovoltaic solar cells, due to their high optical absorption coefficient of approximately  $10^{-5}$ , and p-i-n-type electrical conductivity with band gaps of 1.0 eV for CuInSe<sub>2</sub> and 1.09 eV for Cu(In,Ga)Se<sub>2</sub> respectively, [2,3].

Electrosynthesis is an attractive option to prepare advanced materials under the form of coatings or thin layers, due to its many advantages: i) economics (e.g. low investment is required for an easy composition control, with large coverage areas and high deposition rates), and ii) ecologic (no product loss, and efficient use of raw materials) [3, 4]. The processes to prepare chalcopyrite absorber layers involve electrodeposition of precursor films of Cu-In alloy, CuInSe<sub>2</sub>, Cu(In,Ga)Se<sub>2</sub> followed by recrystallization by thermal annealing at high temperature in selenium atmosphere [2]. The most usual approach to electrodeposit metal and alloys takes place in aqueous solutions. Nevertheless, aqueous electrolysis presents an important shortcoming; the hydrogen discharge that hinders the electrodeposition of very electronegative elements such as Ga and In, reduces the plating efficiency, and has destructive impacts on the thin film quality causing the appearance of pinholes and dendritic morphologies [5].

An alternative to aqueous electroplating solutions is to use as electrolytes low cost room temperature ionic liquids, as the deep eutectic solvents (DES) based on combinations of choline chloride with urea or ethylene glycol. DES exhibit important properties, including high conductivity, relatively wide potential range of electrochemical stability, low vapor pressure, and ability to solvate many metal salts [6]. All these properties make DES good candidates to be used as electrolytes for the electrodeposition of metals [7, 8], alloys [9] and semiconductors [2, 5].

Electrodeposition of precursor films of Cu-In alloy, CuInSe<sub>2</sub>, Cu(In,Ga)Se<sub>2</sub> deals with the electrochemical behaviour of several elements, each of them with specific electrochemical properties, making the overall system very complex. Therefore, the electrochemical production of precursor films can **only** be rationally conceived via a deep understanding of the chemistry and electrochemistry of the elements in the selected electrolytic bath. In this context, the present work examined the feasibility of using the mixture choline chloride (ChCl)-ethylene glycol (EG) in the eutectic composition, ChCl-**EG (1:2)**, for the electrodeposition of In on different substrates: i) W, as an inert material, and ii) Cu, a metal with possibility of alloy formation. The electrochemical behaviour of InCl<sub>3</sub> and InCl solutions on the W substrate have been studied, to our knowledge for the first time, by using electrochemical techniques, including cyclic voltammetry, chronoamperometry and chronopotentiometry. The electrodeposition of Cu-In alloys is also reported, being the obtained electrodeposits analysed by X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX).

## 2. EXPERIMENTAL.

### 2.1.- Molecular sieve "activation" (drying)

Before using molecular sieves as a drying agent, they must be "activated" by removing all traces of water and other volatile compounds. Therefore, the appropriate amount of molecular sieve 4A was added to a dry flask and heated in a microwave for 2 minutes at 500 W (no stirring needed). The flask was immediately connected to a vacuum pump. When the flask had cooled down to room temperature (in approximately 15 minutes), the flask was isolated from the vacuum pump, and purged with dry dinitrogen (Alphagaz N<sub>2</sub> (1) purchased from Air Liquide) for 3 minutes. By repeating the process again three times, the molecular sieves are "activated" (dried) and ready to use.

### 2.2.- Solvent preparation

The electrolytic medium was prepared by mixing analytical grade of choline chloride (HOC<sub>2</sub>H<sub>4</sub>N(CH<sub>3</sub>)<sub>3</sub>Cl, Sigma-Aldrich >98%) and ethylene glycol (HOCH<sub>2</sub>CH<sub>2</sub>OH, Sigma-Aldrich 99.8%) in a 1:2 molar ratio (ChCl-EG (1:2)). This mixture was kept in an oven at 70°C until a colourless homogeneous liquid was formed. Due to the hygroscopicity of the solvent, activated molecular sieve was added to the mixture in a proportion of 15 g per 100 mL of ChCl-EG (1:2). Afterwards, the container was hermetically closed with a Septum and an atmosphere of N<sub>2</sub> was maintained by means of a balloon. The dried solvent can be used after 10 days (i.e. when the water content remains constant).

Karl-Fischer analysis was performed to determine the water content of the electrolyte, using an automatic titrator (Mettler Toledo C20 KF Coulometer). The water content of the dried DES was 145 ± 5 ppm.

The density and viscosity of the solvent, gathered in Table 1, were also determined at several temperatures by using a Stabinger Viscosimeter SVM 3000, Anton Paar. The experimentally measured density of ChCl-EG (1:2) is found to vary lineally with the absolute temperature and was fitted to the following equation:

$$\rho(\text{g cm}^{-3}) = (1.2835 \pm 0.0008) - (5.529 \pm 0.024) \times 10^{-4} \times T \quad (1)$$

Although the measured viscosity of ChCl-EG (1:2) may be described by the simplest Arrhenius model over the temperature range studied (293-373 K), the Vogel-Fulcher-Tamman (VFT) model appears to more satisfactorily describe the viscosity as follows:

$$\eta(\text{mPa.s}) = (0.07614) \exp \frac{1046.22}{[T-137]} \quad (2)$$

### 2.3. The cell

A portion of the electrolyte, stored in an airtight glass bottle, was transferred to the electrochemical conical cell with thermostat jacket, Metrohm 6.1418.150, made of glass to enable visual inspection of the electrodes and electrolyte. The cell was connected to a TAMPSON TC6B thermostat in order to

control the temperature to  $\pm 1$  K, and dry dinitrogen (Alphagaz N<sub>2</sub> (1)) was bubbled through the solution continuously to ensure the absence of oxygen and water.

Later, the required mass of anhydrous InCl<sub>3</sub> (Sigma Aldrich >99.999%), and InCl (Sigma Aldrich 99.999%), stored in a MBaun Labstar 50 glove box in Ar atmosphere), were added to the dried solvent.

#### 2.4.- Electrochemical measurements

The reference electrode, consisted of a silver wire (Sigma Aldrich 99.9 %  $\phi=1$  mm) dipped into an electrolyte vessel (Metrohm 6.1240.000) with PTFE capillary and ceramic diaphragm (3 mm), filled with a solution 0.10 mol kg<sup>-1</sup> AgCl in the mixture ChCl-EG (1:2). Unless otherwise stated, all potentials are referred to this reference Ag(I)/Ag.

For cyclic voltammetry, and pulse techniques, a tungsten, W, rod (Metrohm 6.1248.050  $\phi= 2$  mm ), a glassy carbon, GC, rod (Metrohm 6.1248.040  $\phi= 2$  mm), and a copper, Cu, wire (Sigma Aldrich  $\phi= 1$  mm) were used as working electrodes. As counter electrode a GC rod (Sofacel  $\phi= 3$  mm) was used.

Potentiostatic and intensiostatic electrolysis were conducted with both a 0.25 mm thick tungsten foil (Sigma Aldrich, 99.999%) and a 0.5 mm thick copper foil (Sigma Aldrich 99,98%), as cathodes and a glassy carbon rod (Sofacel) as counter electrode.

The electrochemical experiments were carried out under a N<sub>2</sub> atmosphere with: (i) a PAR EG&G Model 273A potentiostat/galvanostat controlled by a computer using the EG&G M270 software package and (ii) an Autolab PGSTAT 320N potentiostat/galvanostat controlled by the research software NOVA 1.10.

#### 2.5.- Deposit characterization

After electrolysis, samples were cleaned by immersion in ultrapure water Milli-Q, and finally in ethanol. X-ray diffraction (XRD) measurements were performed using a Bruker D8 Discover A25 X-Ray diffractometer with CuK $\alpha$  radiation (40kV, 30 mA). The surface morphology was analyzed with a scanning electron microscope (SEM, FEI Model Quanta 200F) equipped with energy dispersive spectroscopy (EDAX, SDD Apolo) for characterization of the elemental composition.

### RESULTS AND DISCUSSION.

#### 3.1.- Electrochemical window of the ChCl-EG (1:2) on GC, W and Cu electrodes.

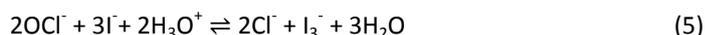
Figure 1 depicts examples of the electrochemical window achieved in the eutectic ChCl-EG (1:2) mixture at 343 K when the aforementioned working electrodes were used.

On GC and W substrates, the anodic limit of the electrochemical window is due to the oxidation of the chloride ions of the solvent into chlorine by means of the reaction:

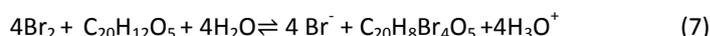


On the contrary to the results reported by Haerens et al [10], the chlorine emission has been identified, to our knowledge for the first time, in macro-electrolysis experiments using as anode and cathode W

plates and GC rods in their 4 possible combinations, being N<sub>2</sub> continuously bubbled in the proximity of the anode. With the aim to collect the released Cl<sub>2</sub>(g) and generate hypochlorite ions (reaction 4), the gasses were passed over a NaOH solution 0.25 mol L<sup>-1</sup>, and the obtained solution was treated with KI and H<sub>2</sub>SO<sub>4</sub> to generate I<sub>3</sub><sup>-</sup> (reaction 5), that was extracted with Cl<sub>4</sub>C giving a pink colour to the organic phase (Figure 2.a)



The chlorine emission was also detected placing in the proximity of the anode a filter paper strip impregnated with a solution of KBr and fluorescein (C<sub>20</sub>H<sub>12</sub>O<sub>5</sub>). In the presence of Cl<sub>2</sub>, pink eosin (C<sub>20</sub>H<sub>8</sub>Br<sub>4</sub>O<sub>5</sub>) is generated (Figure 2.b) according to the following reactions [11]:



On the other hand, if the solubility of chlorine in the solvent is high enough, some of the Cl<sub>2</sub>(g) formed at the anode could react with the Cl<sup>-</sup> ions of the solvent giving Cl<sub>3</sub><sup>-</sup>.



The presence of Cl<sub>3</sub><sup>-</sup> in the solution used in the macro-electrolysis experiments was also tested by UV-Vis using a *Hewlett Packard 8453 (G1103A) Diode-Array Spectrophotometer*. As can be seen in figure 3, the spectrum shows a maximum absorbance at approximately 220 nm, which corresponds relatively well with the value reported by Haerens et al [10] for Cl<sub>3</sub><sup>-</sup> in the same solvent.

Conversely, at a Cu electrode the anodic region is limited by the dissolution of the electrode material, according to the following reaction:



On the three working electrodes, the cathodic limit of the electrochemical window occurs simultaneously with the formation of small bubbles on the electrode surface, and can be assigned to the reduction of the hydroxyl groups of ethylene glycol (EG), choline ions (Ch<sup>+</sup>) or traces of water with formation of H<sub>2</sub> (g) [7, 12,13]. As can be seen in Figure 1, hydrogen evolution depends on the electrode material, a phenomenon previously reported by Vieira et al [13].

### 3.2.- Stable oxidation states of indium in the eutectic ChCl-EG (1:2)

#### a) Results obtained with addition of InCl<sub>3</sub>

InCl<sub>3</sub> dissolved in the rich chloride solvent producing a colourless solution with the formation of InCl<sub>p</sub><sup>3-p</sup> complex [1, 14] hereafter In(III). An example of the cyclic voltammograms obtained with a solution of In(III) 7.29 x 10<sup>-5</sup> mol cm<sup>-3</sup> on a tungsten electrode at 343 K is displayed in Figure 4. The electroreduction of In(III) proceeds via a one step process, being developed a peak marked as "I<sub>c</sub>" with the wonted shape for the formation of a new phase, steep rise of the cathodic current and slow decay. In the reverse scan,

a peak “I<sub>a</sub>” is **built up**, which corresponds to the reoxidation of the indium metal deposited during the cathodic scan. On top of that, an important nucleation loop can be observed in the voltammograms, indicating that the onset of massive deposition of In requires the application of an important overpotential [15].

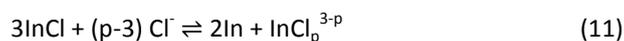
In order to prove the formation of metallic indium, intensiostatic pulse electrolysis were conducted on W foils from the electrolyte containing In(III). Each pulse consists of an ON-Time (t<sub>ON</sub>) during which a current is applied, and an OFF-Time (t<sub>OFF</sub>) during which no current is applied. The solution was stirred by bubbling dried N<sub>2</sub> during the experiments. After the electrolysis, the deposits were washed with ultrapure water and ethanol and analysed by XRD (Figure 5) and SEM-EDAX (Figures 6 (a-b)). In all the cases the deposits consist of pure metallic indium. Moreover, the deposits present a homogeneous morphology (Fig. 6a) with small clusters of particles with the tetragonal crystal structure (Fig. 6b).

Taken together, the foregoing results lead to the conclusion that the electrochemical signal I<sub>c</sub> displayed in Figure 4 was due to the following reaction:



**b) Results obtained with addition of InCl(s).**

The addition of anhydrous InCl(s) to the solvent gives place to a colourless solution and a solid with metallic appearance at the bottom of the cell. At first glance, the voltammograms obtained with this solution and illustrated in Figure 7, appeared to be identical to those shown in Figure 4, indicating the presence of InCl<sub>p</sub><sup>3-p</sup> in solution, and suggesting that InCl has undergone the following disproportionation reaction when dissolved in the DES:



In order to endorse the disproportionation of InCl, the solid **formed at the bottom of the cell** was analysed by XRD (Figure 8) and SEM-EDAX (Figure 9) being confirmed the presence of metallic indium.

**3.3.- Electrochemical nucleation of indium on a tungsten electrode in the eutectic ChCl-EG (1:2)**

The nucleation/growth process of indium **on** a tungsten electrode was studied with a solution of In(III), analyzing the chronoamperometric responses to single potential steps. With the aim to obtain accurate results the electrode and the diffusion layer must be renewed before each measurement. Therefore, the following renewal procedure of the electrode/electrolyte interface was applied:

- 1) after every potential-step measurement, the solution was stirred and the electrode polarized for 120 s at a potential value sufficiently anodic to ensure that the deposited indium metal was totally removed from the surface
- 2) afterwards, the solution stirring was stopped and 15 s were waited without applying any voltage before running the new measurement.

Figure 10 shows examples of the responses resulting from such experiments. In the very beginning, each transient displays a current spike due to the charging of the electrode double layer, which is followed almost immediately by a rising current due to the formation and growth of indium nuclei. The rising part of the current culminates in a current maximum,  $i_m$ , at a time  $t_m$ . The values of  $i_m$  and  $t_m$  depend on the magnitude of the potential step (i.e.  $i_m$  achieves greater values and  $t_m$  decreases when the applied potential is more cathodic). Finally the current decays converging at long times to the limiting behaviour described by the Cottrell equation.

With the aim to identify the indium nucleation mode, the dimensionless experimental current-time transient obtained at several cathodic potentials and temperatures were compared to the theoretical model derived by Scharifker and Hills [16]. The model distinguishes between the two limiting nucleation mechanisms: i) instantaneous nucleation that corresponds to a rapid nucleation on a fixed number of active sites and ii) progressive nucleation at a more slowly rate on an infinite number of active sites [17]. Scharifker and Hills model includes algebraic expressions for instantaneous and progressive nucleation as shown in Eqs. 12 and 13 respectively [16].

$$\left(\frac{i}{i_m}\right)^2 = 1.9542 \frac{[1 - \exp(-1.2564(t/t_m))]^2}{(t/t_m)} \quad (12)$$

$$\left(\frac{i}{i_m}\right)^2 = 1.2254 \frac{[1 - \exp(-2.3367(t/t_m)^2)]^2}{(t/t_m)} \quad (13)$$

In order to make a better comparison between the nucleation model and experimental results, the induction time,  $t_0$ , between the application of the potential step and the onset of nucleation and growth has to be taken into account [18-21]. Estimates of  $t_0$  can be obtained from the intercept of the plots of  $(i/i_m)^2$  vs  $t$  and  $(i/i_m)^{2/3}$  vs  $t$  for instantaneous and progressive nucleation respectively [20, 21].

Plots of  $(i/i_m)^2$  vs  $(t'/t'_m)$  (being  $t' = t - t_0$ ,  $t'_m = t_m - t_0$ ) calculated from Eqs. 12 and 13 are shown in Figure 11 together with the dimensionless experimental data, taken from the chronoamperometric curves as those gathered in Figure 10. According to Figures 11 the initial stages of electrochemical deposition of indium onto a tungsten electrode in the deep eutectic solvent ChCl-EG (1:2) can be explained in terms of a model involving instantaneous nucleation with three-dimensional growth of the nuclei whatever the applied overpotential. On the other hand, the nucleation mode of indium is not influenced by temperature in the 323-363 K range.

### 3.4.- Determination of the $\text{InCl}_p^{3-p}$ diffusion coefficient. Verification of the Arrhenius's law.

Chronoamperometry (CA), chronopotentiometry (CP) and convolutive potential sweep voltammetry (CPSV) seem to be relevant techniques for the determination of the diffusion coefficient of  $\text{InCl}_p^{3-p}$ ,  $D_{\text{In(III)}}$ , in the deep eutectic solvent ChCl-EG (1:2), on condition that the adequate equations in the appropriate experimental conditions are used. The aim of the work is to identify if the three methods yield identical results or one among them is more appropriate than the others considering: i) the accuracy of the measurements, and ii) the simplicity of data acquisition [22]

### **Results obtained by chronoamperometry (CA)**

The diffusion coefficient of In(III) was calculated from the chronoamperometric responses obtained with a solution of In(III) at potential values in the mass-transport controlled region (i.e. where the surface concentration of In(III) is effectively zero). Figure 10 (b) shows the variation of the current versus  $1/t^{1/2}$ , confirming that the experimental data obey the Cottrell law [15, 23, 24].

$$I_d(t) = \frac{nFSD^{1/2}C_0}{\pi^{1/2}t^{1/2}} \quad (14)$$

where  $I_d(t)$  is the sampled current at time  $t$ ,  $C_0$ ,  $D$  and  $S$  are the concentration ( $\text{mol cm}^{-3}$ ), the diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ ), and the electroactive area ( $\text{cm}^2$ ), respectively. The diffusion coefficient,  $D_{\text{In(III)}}$ , was calculated from the slope of the straight lines and the results are gathered in table 1.

### **Results obtained by chronopotentiometry (CP).**

The diffusion coefficient of In(III) was also determined from the chronopotentiograms as those displayed in Figure 12, by means of Sand's equation [15, 23, 24].

$$I\tau^{1/2} = \frac{nFSD^{1/2}C_0\pi^{1/2}}{2} \quad (15)$$

where  $I$  is the applied current and  $\tau$  is the transition time measured in the chronopotentiograms.

In order to assure the renewal of the electrode and the same electrode/electrolyte interface conditions at the beginning of each chronopotentiogram, the same protocol described in the chronoamperometric experiments was applied.

As it is shown in Figure 12, the plateau corresponding to the reduction of In(III) can be clearly defined, and as predicted by Sand's equation the transition time becomes shorter increasing the applied current. Likewise, the square root of the transition time changed linearly with the applied current density (Figure 12 b), indicating that the fluxes of In(III) species were diffusion controlled and that all the requirements for using Sand's equation are fulfilled. The diffusion coefficient was calculated from the slope on Figure 12b by Eq. (18) being the mean values obtained at different temperatures gathered in Table 1.

### **Results obtained by convolutive potential sweep voltammetry (CPSV).**

The convolution of the cyclic voltammograms recorded at several scan rates on a W electrode was also carried out by means of the following expression [15, 23]:

$$m(t) = \frac{1}{\pi^{1/2}} \int_0^t \frac{i(u)}{(t-u)^{1/2}} du \quad (16)$$

where  $m(t)$  is the convoluted current, and  $i(u)$  the current from the voltammogram.

Fig. 13 depicts examples of the voltammograms recorded with a solution of In(III) and its corresponding semiintegrated curves. In the convoluted curves (pink lines), the peaks have disappeared and instead, a plateau of height  $m^*$ , is developed at potential values sufficiently cathodic to ensure zero surface concentration of the reactant. The convoluted curves exhibited well defined limiting currents, indicating

that there is no change in the electrode surface area during the scan, to the point that it affects the limiting current for the In(III) reduction wave. Hence the In(III) diffusion coefficient could be computed from the boundary semi-integral values by means of the relationship [15,23,24]:

$$m^* = nFSC_0D^{1/2} \quad (17)$$

A summary of the values of the diffusion coefficient obtained by using the aforementioned techniques are displayed in Table 1.

A two-way (temperature - technique) analysis of variance (ANOVA) [25] was carried out in order to know if there are significant differences between the calculated data using: i) different techniques, and ii) different working temperatures, being the null hypothesis the non-existence of significant differences between the calculated units. Concerning the effect of the techniques, the calculated F statistics was lower than the critical F value ( $F_{cal} = 6.02 < F_{crit.} = 6.94$ ), then the null hypothesis must be maintained. On the contrary, for the temperature effect the calculated F statistics was higher than the critical F value, ( $F_{cal} = 103.42 > F_{crit.} = 6.94$ ) and consequently the null hypothesis must be rejected. As a result, it can be concluded that with a 95% confidence level: i) all the methods used to calculate the diffusion coefficients lead to the same values, and ii) **as expected** the diffusion coefficients change with temperature. Hence, in order to calculate the activation energy for diffusion, the diffusion coefficient was determined at three more temperatures (313, 333 and 353 K) by using only the convoluted technique due to the simplicity of data acquisition. The obtained diffusion coefficient values showed a good linearity in the Arrhenius plot (Fig. 14), and with a number of observations  $n=103$ , it was possible to formulate the following empirical expression for the temperature dependence of the diffusion coefficient of In(III) in ChCl-EG (1:2) as follows:

$$\ln D = -(3.57 \pm 0.21) - (3664 \pm 72)T^{-1} \quad (D_{in}: \text{cm}^2 \text{ s}^{-1} \text{ and } T: \text{K}) \quad (18)$$

From this relationship, the value of the activation energy,  $E_a$ , for the diffusion of In(III), was found to be  $30.5 \pm 0.6 \text{ kJ mol}^{-1}$ .

Additionally, in order to characterize the solute global mass transport through its environment, the effect of the viscosity on the diffusion coefficient has been taken into account through the dimensionless Schmidt number ( $Sc = \nu/D$ ) also reported in Table 1. Experimental kinematic and dynamic viscosities as well as density are also summarized in Table 1.

### 3.5. Results obtained on solid Copper cathodes.

To investigate the formation of In-Cu precursors by an electrochemical route, the electrochemical behaviour of In(III) solutions at a copper substrate was also studied by cyclic voltammetry and potentiostatic and intensiostatic electrolysis.

#### **Qualitative information.**

In Figure 15 the cyclic voltammograms obtained with an In(III) solution in the eutectic mixture at W and Cu electrodes are compared. As we showed above, when the electrode substrate is an inert electrode

an important overpotential must be applied in the cathodic scan, in order to initiate the nucleation and subsequent growth of In. The reaction scheme proceeds according to the following deposition mechanism:



When the scan is reversed, the reduction current continues to flow and the deposition of indium now takes place on a less “hostile” surface of previously deposited In rather than on a bare W electrode, being this fact the cause of the current loop observed in the voltammogram. When the applied potential achieved values higher than the equilibrium potential adopted by the W electrode coated by In, the oxidation peak I<sub>a</sub> corresponding to the following dissolution mechanism can be observed:



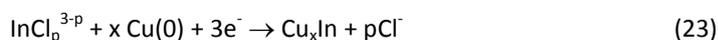
Conversely, when a Cu electrode was used a peak II<sub>c</sub> appears at less cathodic potential values than those for pure In deposition on a W electrode (peak I<sub>c</sub>), evidencing that it is not yet necessary to apply the nucleation overpotential required on the W substrate. Due to the possibility of In-Cu alloy formation, the electroreduction of In(III) in peak II<sub>c</sub> proceeds according to the following mechanism:



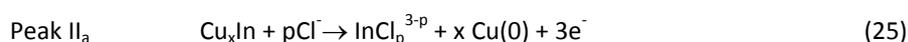
followed by the In reaction with the subjacent substrate Cu



being the overall process:



When the scan is reversed, in the anodic region two oxidation peaks are displayed, the peak I<sub>a</sub> due to the oxidation of In(0) and the peak II<sub>a</sub> due to the oxidation of Cu<sub>x</sub>In.



### **Potentiostatic and intensiostatic electrolysis. Characterization of the In-Cu alloys**

Based on the previous results, alloys samples were prepared by both potentiostatic and intensiostatic electrolysis. All the experiments were conducted using 0.5 mm copper plates as working electrodes. After electrolysis, the samples were washed by immersion in ultrapure water Milli-Q, and finally in ethanol. The dried samples were analysed by XRD, SEM and EDAX techniques. A summary of the XRD analysis is gathered in Table 2.

Samples (1-3) obtained under potentiostatic conditions provided similar results. Fig. 16 shows the XRD pattern of sample (3) obtained at -1.1 V vs (Ag(I)/Ag). The observed peaks were identified as CuIn, In and Cu substrate, being the intensities of the Cu and In peaks predominant over those of the CuIn phase, which shows that the thickness of the CuIn film on the Cu substrate was thin. The surface morphology of

the obtained deposit was also observed by scanning electron microscopy (SEM) (Fig. 17 (a-b)). The deposit is made up of clusters vertically aligned and parallel to each other, making the surface of the deposit porous.

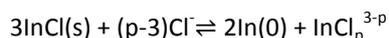
Intensiostatic pulse electrolysis was also conducted. Each pulse consists of an ON-Time ( $t_{ON}$ ) during which a current is applied, and an OFF-Time ( $t_{OFF}$ ) during which no current is applied, in order to allow In diffusion into the massive Cu plate. The XRD analysis of samples (4-6) also evidence the formation of the stoichiometric phase CuIn (Figure 18).

The surface morphology of sample (5) was also observed by SEM and analysed by EDAX. Figures 19 (a-b) show compact clusters of In over a network-like structure of the intermetallic CuIn. The effect of annealing on the crystal structure of thin film of sample (5) is shown in Figure 20, observing that the metastable phase CuIn obtained at 343 K can be transformed into  $Cu_{11}In_9$  at a higher temperature (e.g. 430 K). The surface morphology is also displayed in Figure 21.

## Conclusions

A procedure for drying the DES, ChCl-EG (1:2), based on the use of molecular sieves has been developed, being the water content of the electrolyte  $145 \pm 5$  ppm.

The stability of anhydrous InCl and InCl<sub>3</sub> dissolved in the dried DES has been investigated using cyclic voltammetry, x-Ray diffraction analysis and scanning electron microscopy. Experiments performed in a controlled N<sub>2</sub> atmosphere cell, show that anhydrous InCl<sub>3</sub> dissolved in the rich chloride media as  $InCl_p^{3-p}$  is reduced on an inert electrode (i.e W) to indium metal via only one electrochemical step. Conversely, InCl undergoes the following disproportionation reaction when dissolved in the eutectic ChCl-EG (1:2)



generating In(0) and  $InCl_p^{3-p}$  that provides identical voltammograms as those obtained after the addition of InCl<sub>3</sub> to the DES.

The electrochemical behaviour of  $InCl_p^{3-p}$  solutions has been studied using different substrates: i) W, an inert working electrode, and ii) Cu, a more noble metal than In with possibility of alloy formation.

Voltammetric and chronoamperometric experiments on a W electrode showed that nucleation and growth of the metallic indium plays an important role in the overall electrodeposition process. Chronoamperometric studies showed that the deposition process on the inert electrode involves, whatever the applied overpotential, instantaneous three dimensional nucleation on a finite number of active sites with diffusion controlled growth of the nuclei. Not being the nucleation mode of indium influenced by temperature in the 323-363 K range.

The applicability of several electrochemical techniques (CA, CP and CPSV) for accuracy measurements of the diffusion coefficient of  $InCl_p^{3-p}$  was also investigated, verifying the validity of the assumptions used in their theoretical analysis, and ensuring reproducible conditions at the electrode/electrolyte interface. A two-way analysis of variance, ANOVA has shown that with a 95% confidence level: i) the three

electrochemical techniques used to calculate the diffusion coefficients lead to the same values, and ii) the diffusion coefficient changes with temperature following the Arrhenius law, being the activation energy for diffusion  $30.5 \pm 0.6 \text{ kJ mol}^{-1}$ . The dimensionless Schmidt numbers, defined as the ratio between solvent viscosity and solute diffusivity ( $Sc=v/D$ ), have also been calculated to characterize the solute global mass transport through its environment.

To investigate the formation of In-Cu precursors by an electrochemical route, the electrochemical behaviour of In(III) solutions at a copper substrate was also studied by cyclic voltammetry and potentiostatic and intensiostatic electrolysis. The resulting cyclic voltammograms exhibited signals that could be attributed to the presence of In-Cu intermetallic compounds. Thin layers of the intermetallic compounds were obtained by electrosynthesis and characterized by X-ray diffraction and scanning electron microscopy (SEM) revealing in all cases the formation of stoichiometric CuIn. The metastable CuIn phase was transformed into  $\text{Cu}_{11}\text{In}_9$  by thermal annealing.

The deposits obtained under continuous potentiostatic electrolysis were made up of clusters vertically aligned and parallel to each other, making the surface of the deposits porous. Conversely, the films obtained by intensiostatic pulse electrolysis consisted on compact clusters of In over a network-like structure of the stoichiometric CuIn.

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Table 1.- Variation of the diffusion coefficient of In(III) with the temperature in the DES ChCl-EG (1:2) calculated by different electrochemical techniques, density ( $\rho$ ), dynamic viscosity ( $\eta$ ), kinematic viscosity ( $\nu$ ), and Schmidt number.

$D \text{InCl}_p^{3-p} / 10^{-7} \text{ cm}^2 \text{ s}^{-1}$						
T/K	313	323	333	343	353	363
CA		$3.99 \pm 0.15$		$7.64 \pm 0.26$		$12.88 \pm 0.33$
CP		$2.99 \pm 0.17$		$6.01 \pm 0.20$		$9.61 \pm 0.34$
CPSV	$2.47 \pm 0.06$	$3.22 \pm 0.83$	$4.79 \pm 0.11$	$6.70 \pm 0.09$	$9.52 \pm 0.22$	$12.17 \pm 0.39$
Mean value	$2.47 \pm 0.06$	$3.25 \pm 0.35$	$4.79 \pm 0.11$	$6.56 \pm 0.59$	$9.52 \pm 0.22$	$11.43 \pm 1.43$
$\rho / \text{kg m}^{-3}$	1110.4	1104.7	1099.2	1093.6	1088.1	1082.7
$\eta / \text{kg m}^{-1} \text{ s}^{-1}$	0.028940	0.020967	0.015848	0.012238	0.0096892	0.0077822
$\nu / \text{cm}^2 \text{ s}^{-1}$	0.26063	0.18980	0.14418	0.11191	0.089047	0.071878
$Sc / 10^4$	105.5	58.4	30.1	17.1	9.4	6.3

Table 2- Electrolysis experiments and identification of the different phases in the obtained samples.

Potentiostatic electrolysis				
Sample	[In(III)] / mol cm <sup>-3</sup>	E <sub>applied</sub> vs (Ag(I)/Ag)/V	Time/s	Identified phase
1	2.6×10 <sup>-5</sup>	-0.8	240	Cu, CuIn
2	6.8×10 <sup>-5</sup>	-0.9	7200	Cu, In, CuIn
3	6.8×10 <sup>-5</sup>	-1.1	3600	Cu, In, CuIn
Intensiostatic pulse electrolysis				
Sample	[In(III)] / mol cm <sup>-3</sup>	J <sub>applied</sub> / mA cm <sup>-2</sup>	Time/s	Identified phase
4	2.7×10 <sup>-5</sup>	-0.79 (t <sub>ON</sub> =2s; t <sub>off</sub> =4s)	6340	Cu, In, CuIn
5	6.3×10 <sup>-5</sup>	-2.22 (t <sub>ON</sub> =2s; t <sub>off</sub> =6s)	1040	Cu, In, CuIn
6	6.3×10 <sup>-5</sup>	-2.07 (t <sub>ON</sub> =2s; t <sub>off</sub> =6s)	3230	Cu, In, CuIn

### Legends of the figures.

Fig. 1.- Electrochemical window on GC (—), W (—) and Cu (—) electrodes in the deep eutectic solvent ChCl-EG (1:2) at 343 K.

Fig.2.- Chlorine detection: (a) photo of the aqueous and organic phase after extraction of  $I_3^-$  (b) filter paper strip impregnated with fluorescein ( $C_{20}H_{12}O_5$ ) and KBr, showing the formation of pink eosin ( $C_{20}H_8Br_4O_5$ ).

Fig.3.- UV-Vis spectrum of the eutectic ChCl-EG (1:2) after electrolysis using as reference pure ChCl-EG (1:2).

Fig.4.- Cyclic voltammogram obtained with a solution of  $InCl_p^{3-p}$  ( $C_0=7.29 \times 10^{-5} \text{ mol cm}^{-3}$ ) on a tungsten electrode at  $100 \text{ mV s}^{-1}$  and 343 K. Pink line corresponds to a cyclic voltammogram of the ChCl-EG (1:2) in absence of  $InCl_p^{3-p}$

Fig. 5.- XRD pattern of In films obtained on a W foil from the electrolyte containing  $InCl_p^{3-p}$  under galvanostatic intermittent electrolysis ( $J_{app} = -6.5 \text{ mA cm}^{-2}$ ,  $t_{off} = 2 \text{ s}$ ,  $t_{on} = 5 \text{ s}$ ,  $t_{total \text{ elec}} = 72 \text{ minutes}$ ). (●) In, (■) W.

Fig.6.- SEM micrographs of a W foil coated by an In film (a) surface appearance, (b) details.

Fig.7.- Cyclic voltammograms recorded at different inversion potentials on a tungsten electrode at  $100 \text{ mV s}^{-1}$  and 343 K after the addition of anhydrous InCl to ChCl-EG (1:2).

Fig. 8.- XRD pattern of the solid formed at the bottom of the cell after the addition of anhydrous InCl(s) to the DES (●) In.

Fig. 9.- (a) SEM micrograph of the solid formed at the bottom of the cell after the addition of anhydrous InCl(s) to the DES. (b) EDX analysis.

Fig.10.- (a) Evolution of the chronoamperograms of a  $InCl_p^{3-p}$  solution ( $C_0= 6.21 \times 10^{-5} \text{ mol cm}^{-3}$ ) at a tungsten electrode ( $S = 0.46 \text{ cm}^2$ ) at various applied potentials  $-0.870$  (---);  $-0.890$ (---);  $-0.920$  (---);  $-0.930$  (---);  $-0.940$  (---);  $-0.950$  (---);  $-0.970$  (---);  $-1.000$  (---);  $-1.020$  (---);  $-1.040$  (---);  $-1.060$  (---);  $1.080$  (---) and  $-1.100$  (---) V vs Ag(I)/Ag, at 323 K. (b) Relation between square root of time and current at potential values (e.g.  $E = -1.100 \text{ V}$ ) where the reaction is diffusion controlled.

Fig.11.- Comparison of the dimensionless experimental data obtained from the current-time transients, represented in Figure 10, with the theoretical model for (---) instantaneous and (---) progressive nucleation at various applied potentials. (▲)  $-0.930$ , (■)  $-0.970$ , (●)  $-1.000$ , (◇)  $-1.040$ , (■)  $-1.060$ , (○)  $-1.020$ , (▲)  $-1.080 \text{ V}$  vs (Ag(I)/Ag.

Fig.12.- (a) Evolution of the chronopotentiograms of a  $InCl_p^{3-p}$  solution ( $C_0= 6.21 \times 10^{-5} \text{ mol cm}^{-3}$ ) at a tungsten electrode ( $S = 0.46 \text{ cm}^2$ ) at various applied currents  $-3.0$ ;  $-3.1$ ;  $-3.2$ ;  $-3.4$ ;  $-3.5$ ;  $-3.6$ ;  $-3.8$ ;  $-3.9$ ;  $-4.2$ ;  $-4.3$ ;  $-4.4$  and  $-4.5 \text{ mA}$ , at 323 K. (b) Relation between square root of transition time and the applied current.

Fig.13.- Evolution of the voltammograms (blue) and convoluted (pink) curves obtained with a  $\text{InCl}_p^{3-p}$  solution ( $C_0 = 6.15 \times 10^{-5} \text{ mol cm}^{-3}$ ) at a tungsten electrode and 343 K, sweep rate: (---) 50, (—) 100 and (— · —)  $200 \text{ mV s}^{-1}$ .

Fig 14.- Variation of diffusion coefficient of In(III) with temperature in ChCl-EG (1:2). Verification of the Arrhenius law.

Fig. 15.- Cyclic voltammograms obtained at different potential limits (-0.76; -0.78; -0.79; -0.80; -0.85; and -0.90 V vs Ag(I)/Ag) with a In(III) solution ( $C_0 = 7.29 \times 10^{-5} \text{ mol cm}^{-3}$ ) at a W electrode (grey line) and a Cu electrode (dotted lines) at 343 K. Scan rate:  $10 \text{ mV s}^{-1}$ .

Fig. 16.- XRD pattern of sample (3) obtained on a Cu plate from the electrolyte containing  $\text{InCl}_p^{3-p}$  under potentiostatic electrolysis ( $E_d = -1.1 \text{ V vs Ag(I)/Ag}$ ,  $t_d = 3600 \text{ s}$ ). (●) In, (▲) CuIn, (◆) Cu

Figure 17.- SEM micrographs of sample (3); (a) surface appearance, (b) details.

Fig. 18. XRD pattern of sample (6). (●) In, (▲) CuIn, (◆) Cu

Fig. 19.- SEM micrographs of sample (5); (a) surface appearance, (b) details and EDXs

Fig.20.- XRD pattern of sample (5) after annealing at 430 K for 2 hours. (▲)  $\text{Cu}_{11}\text{In}_9$ , (◆) Cu

Fig. 21.- SEM micrograph of sample (5) after annealing.

**Electrodeposition of Indium on W and Cu electrodes in the Deep Eutectic Solvent choline chloride-ethylene glycol (1:2)**

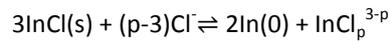
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## ABSTRACT

A procedure for drying the deep eutectic solvent (DES) choline chloride - ethylene glycol, ChCl-EG (1:2), based on the use of molecular sieves has been developed, being the final water content of the electrolyte  $145 \pm 5$  ppm. In this dried DES, the stability of InCl and InCl<sub>3</sub> as well as the electrochemical behaviour of their solutions have been investigated using electrochemical techniques, X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM). Experiments performed under a N<sub>2</sub> atmosphere show that InCl<sub>3</sub>, dissolved in the rich chloride media as InCl<sub>p</sub><sup>3-p</sup>, is reduced on a tungsten electrode to indium metal via only one electrochemical step. Conversely, InCl undergoes the following disproportionation reaction when dissolved in the eutectic ChCl-EG (1:2)



generating In(0) and giving place to identical electrochemical signals as those obtained after the addition of InCl<sub>3</sub> to the DES.

On a tungsten electrode, nucleation and crystal growth of In plays an important role in the electrodeposition process. Chronoamperometric results were consistent with instantaneous three dimensional nucleation on a finite number of active sites with diffusion controlled growth of the nuclei, whatever the applied overpotential and temperature. Mass transport towards the electrode is a diffusion process, and the following empirical expression for the temperature dependence of the diffusion coefficient was calculated

$$\ln D = -(3.58 \pm 0.22) - (3665 \pm 76) T^{-1}$$

The electro-reduction of In(III) solutions was also investigated at a copper substrate. The resulting cyclic voltammograms evidenced the formation of In-Cu intermetallic compounds. Hence, In-Cu alloy films were obtained by continuous potentiostatic electrolysis and intensiostatic pulse electrolysis. The obtained samples, characterized by XRD and SEM, revealed the formation of the metastable CuIn phase that could be transformed into Cu<sub>11</sub>In<sub>9</sub> by thermal annealing.

*Keywords: Deep eutectic solvents, indium, disproportionation, diffusion coefficient, Cu-In intermetallic compounds.*

## 1.- INTRODUCTION

Indium and its alloys are suitable materials for producing semiconductor compounds such as the binaries (InP, InSb, InAs), ternaries (InGaP, GaInAs, CuInSe<sub>2</sub>) and quaternaries (CuInSSe and Cu(In,Ga)Se<sub>2</sub>) which are widely used in electronic and optoelectronic technology [1-3]. In this context, polycrystalline thin films of the chalcopyrite materials CuInSe<sub>2</sub> and Cu(In,Ga)Se<sub>2</sub> are proposed as absorbent materials for photovoltaic solar cells, due to their high optical absorption coefficient of approximately  $10^{-5}$ , and p-i-n-type electrical conductivity with band gaps of 1.0 eV for CuInSe<sub>2</sub> and 1.09 eV for Cu(In,Ga)Se<sub>2</sub> respectively, [2,3].

Electrosynthesis is an attractive option to prepare advanced materials under the form of coatings or thin layers, due to its many advantages: i) economics (e.g. low investment is required for an easy composition control, with large coverage areas and high deposition rates), and ii) ecologic (no product loss, and efficient use of raw materials) [3, 4]. The processes to prepare chalcopyrite absorber layers involve electrodeposition of precursor films of Cu-In alloy, CuInSe<sub>2</sub>, Cu(In,Ga)Se<sub>2</sub> followed by recrystallization by thermal annealing at high temperature in selenium atmosphere [2]. The most usual approach to electrodeposit metal and alloys takes place in aqueous solutions. Nevertheless, aqueous electrolysis presents an important shortcoming; the hydrogen discharge that hinders the electrodeposition of very electronegative elements such as Ga and In, reduces the plating efficiency, and has destructive impacts on the thin film quality causing the appearance of pinholes and dendritic morphologies [5].

An alternative to aqueous electroplating solutions is to use as electrolytes low cost room temperature ionic liquids, as the deep eutectic solvents (DES) based on combinations of choline chloride with urea or ethylene glycol. DES exhibit important properties, including high conductivity, relatively wide potential range of electrochemical stability, low vapor pressure, and ability to solvate many metal salts [6]. All these properties make DES good candidates to be used as electrolytes for the electrodeposition of metals [7, 8], alloys [9] and semiconductors [2, 5].

Electrodeposition of precursor films of Cu-In alloy, CuInSe<sub>2</sub>, Cu(In,Ga)Se<sub>2</sub> deals with the electrochemical behaviour of several elements, each of them with specific electrochemical properties, making the overall system very complex. Therefore, the electrochemical production of precursor films can only be rationally conceived via a deep understanding of the chemistry and electrochemistry of the elements in the selected electrolytic bath. In this context, the present work examined the feasibility of using the mixture choline chloride (ChCl)-ethylene glycol (EG) in the eutectic composition, ChCl-EG (1:2), for the electrodeposition of In on different substrates: i) W, as an inert material, and ii) Cu, a metal with possibility of alloy formation. The electrochemical behaviour of InCl<sub>3</sub> and InCl solutions on the W substrate have been studied, to our knowledge for the first time, by using electrochemical techniques, including cyclic voltammetry, chronoamperometry and chronopotentiometry. The electrodeposition of Cu-In alloys is also reported, being the obtained electrodeposits analysed by X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX).

## 2. EXPERIMENTAL.

### 2.1.- Molecular sieve "activation" (drying)

Before using molecular sieves as a drying agent, they must be "activated" by removing all traces of water and other volatile compounds. Therefore, the appropriate amount of molecular sieve 4A was added to a dry flask and heated in a microwave for 2 minutes at 500 W (no stirring needed). The flask was immediately connected to a vacuum pump. When the flask had cooled down to room temperature (in approximately 15 minutes), the flask was isolated from the vacuum pump, and purged with dry dinitrogen (Alphagaz N<sub>2</sub> (1) purchased from Air Liquide) for 3 minutes. By repeating the process again three times, the molecular sieves are "activated" (dried) and ready to use.

### 2.2.- Solvent preparation

The electrolytic medium was prepared by mixing analytical grade of choline chloride (HOC<sub>2</sub>H<sub>4</sub>N(CH<sub>3</sub>)<sub>3</sub>Cl, Sigma-Aldrich >98%) and ethylene glycol (HOCH<sub>2</sub>CH<sub>2</sub>OH, Sigma-Aldrich 99.8%) in a 1:2 molar ratio (ChCl-EG (1:2)). This mixture was kept in an oven at 70<sup>o</sup>C until a colourless homogeneous liquid was formed. Due to the hygroscopicity of the solvent, activated molecular sieve was added to the mixture in a proportion of 15 g per 100 mL of ChCl-EG (1:2). Afterwards, the container was hermetically closed with a Septum and an atmosphere of N<sub>2</sub> was maintained by means of a balloon. The dried solvent can be used after 10 days (i.e. when the water content remains constant).

Karl-Fischer analysis was performed to determine the water content of the electrolyte, using an automatic titrator (Mettler Toledo C20 KF Coulometer). The water content of the dried DES was 145 ± 5 ppm.

The density and viscosity of the solvent, gathered in Table 1, were also determined at several temperatures by using a Stabinger Viscosimeter SVM 3000, Anton Paar. The experimentally measured density of ChCl-EG (1:2) is found to vary lineally with the absolute temperature and was fitted to the following equation:

$$\rho(\text{g cm}^{-3}) = (1.2835 \pm 0.0008) - (5.529 \pm 0.024) \times 10^{-4} \times T \quad (1)$$

Although the measured viscosity of ChCl-EG (1:2) may be described by the simplest Arrhenius model over the temperature range studied (293-373 K), the Vogel–Fulcher–Tamman (VFT) model appears to more satisfactorily describe the viscosity as follows:

$$\eta(\text{mPa} \cdot \text{s}) = (0.07614) \exp \frac{1046.22}{[T-137]} \quad (2)$$

### 2.3. The cell

A portion of the electrolyte, stored in an airtight glass bottle, was transferred to the electrochemical conical cell with thermostat jacket, Metrohm 6.1418.150, made of glass to enable visual inspection of the electrodes and electrolyte. The cell was connected to a TAMPSON TC6B thermostat in order to

control the temperature to  $\pm 1$ K, and dry dinitrogen (Alphagaz N<sub>2</sub> (1)) was bubbled through the solution continuously to ensure the absence of oxygen and water.

Later, the required mass of anhydrous InCl<sub>3</sub> (Sigma Aldrich >99.999%), and InCl (Sigma Aldrich 99.999%), stored in a MBaun Labstar 50 glove box in Ar atmosphere), were added to the dried solvent.

#### 2.4.- Electrochemical measurements

The reference electrode, consisted of a silver wire (Sigma Aldrich 99.9 %  $\phi=1$  mm) dipped into an electrolyte vessel (Metrohm 6.1240.000) with PTFE capillary and ceramic diaphragm (3 mm), filled with a solution 0.10 mol kg<sup>-1</sup> AgCl in the mixture ChCl-EG (1:2). Unless otherwise stated, all potentials are referred to this reference Ag(I)/Ag.

For cyclic voltammetry, and pulse techniques, a tungsten, W, rod (Metrohm 6.1248.050  $\phi= 2$  mm ), a glassy carbon, GC, rod (Metrohm 6.1248.040  $\phi= 2$  mm), and a copper, Cu, wire (Sigma Aldrich  $\phi= 1$  mm) were used as working electrodes. As counter electrode a GC rod (Sofacel  $\phi= 3$  mm) was used.

Potentiostatic and intensiostatic electrolysis were conducted with both a 0.25 mm thick tungsten foil (Sigma Aldrich, 99.999%) and a 0.5 mm thick copper foil (Sigma Aldrich 99,98%), as cathodes and a glassy carbon rod (Sofacel) as counter electrode.

The electrochemical experiments were carried out under a N<sub>2</sub> atmosphere with: (i) a PAR EG&G Model 273A potentiostat/galvanostat controlled by a computer using the EG&G M270 software package and (ii) an Autolab PGSTAT 320N potentiostat/galvanostat controlled by the research software NOVA 1.10.

#### 2.5.- Deposit characterization

After electrolysis, samples were cleaned by immersion in ultrapure water Milli-Q, and finally in ethanol. X-ray diffraction (XRD) measurements were performed using a Bruker D8 Discover A25 X-Ray diffractometer with CuK $\alpha$  radiation (40kV, 30 mA). The surface morphology was analyzed with a scanning electron microscope (SEM, FEI Model Quanta 200F) equipped with energy dispersive spectroscopy (EDAX, SDD Apollo) for characterization of the elemental composition.

### RESULTS AND DISCUSSION.

#### 3.1.- Electrochemical window of the ChCl-EG (1:2) on GC, W and Cu electrodes.

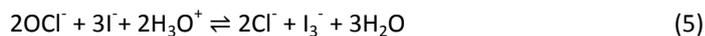
Figure 1 depicts examples of the electrochemical window achieved in the eutectic ChCl-EG (1:2) mixture at 343 K when the aforementioned working electrodes were used.

On GC and W substrates, the anodic limit of the electrochemical window is due to the oxidation of the chloride ions of the solvent into chlorine by means of the reaction:

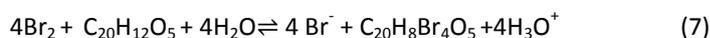


On the contrary to the results reported by Haerens et al [10], the chlorine emission has been identified, to our knowledge for the first time, in macro-electrolysis experiments using as anode and cathode W

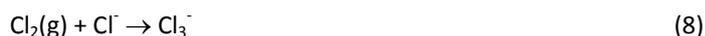
plates and GC rods in their 4 possible combinations, being N<sub>2</sub> continuously bubbled in the proximity of the anode. With the aim to collect the released Cl<sub>2</sub>(g) and generate hypochlorite ions (reaction 4), the gasses were passed over a NaOH solution 0.25 mol L<sup>-1</sup>, and the obtained solution was treated with KI and H<sub>2</sub>SO<sub>4</sub> to generate I<sub>3</sub><sup>-</sup> (reaction 5), that was extracted with Cl<sub>4</sub>C giving a pink colour to the organic phase (Figure 2.a)



The chlorine emission was also detected placing in the proximity of the anode a filter paper strip impregnated with a solution of KBr and fluorescein (C<sub>20</sub>H<sub>12</sub>O<sub>5</sub>). In the presence of Cl<sub>2</sub>, pink eosin (C<sub>20</sub>H<sub>8</sub>Br<sub>4</sub>O<sub>5</sub>) is generated (Figure 2.b) according to the following reactions [11]:



On the other hand, if the solubility of chlorine in the solvent is high enough, some of the Cl<sub>2</sub>(g) formed at the anode could react with the Cl<sup>-</sup> ions of the solvent giving Cl<sub>3</sub><sup>-</sup>.



The presence of Cl<sub>3</sub><sup>-</sup> in the solution used in the macro-electrolysis experiments was also tested by UV-Vis using a *Hewlett Packard 8453 (G1103A) Diode-Array Spectrophotometer*". As can be seen in figure 3, the spectrum shows a maximum absorbance at approximately 220 nm, which corresponds relatively well with the value reported by Haerens et al [10] for Cl<sub>3</sub><sup>-</sup> in the same solvent.

Conversely, at a Cu electrode the anodic region is limited by the dissolution of the electrode material, according to the following reaction:



On the three working electrodes, the cathodic limit of the electrochemical window occurs simultaneously with the formation of small bubbles on the electrode surface, and can be assigned to the reduction of the hydroxyl groups of ethylene glycol (EG), choline ions (Ch<sup>+</sup>) or traces of water with formation of H<sub>2</sub> (g) [7, 12,13]. As can be seen in Figure 1, hydrogen evolution depends on the electrode material, a phenomenon previously reported by Vieira et al [13].

### **3.2.- Stable oxidation states of indium in the eutectic ChCl-EG (1:2)**

#### **a) Results obtained with addition of InCl<sub>3</sub>**

InCl<sub>3</sub> dissolved in the rich chloride solvent producing a colourless solution with the formation of InCl<sub>p</sub><sup>3-p</sup> complex [1, 14] hereafter In(III). An example of the cyclic voltammograms obtained with a solution of In(III) 7.29 x 10<sup>-5</sup> mol cm<sup>-3</sup> on a tungsten electrode at 343 K is displayed in Figure 4. The electroreduction of In(III) proceeds via a one step process, being developed a peak marked as "I<sub>c</sub>" with the wonted shape for the formation of a new phase, steep rise of the cathodic current and slow decay. In the reverse scan,

a peak “I<sub>a</sub>” is built up, which corresponds to the reoxidation of the indium metal deposited during the cathodic scan. On top of that, an important nucleation loop can be observed in the voltammograms, indicating that the onset of massive deposition of In requires the application of an important overpotential [15].

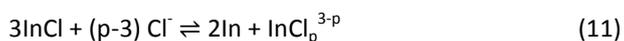
In order to prove the formation of metallic indium, intensiostatic pulse electrolysis were conducted on W foils from the electrolyte containing In(III). Each pulse consists of an ON-Time (t<sub>ON</sub>) during which a current is applied, and an OFF-Time (t<sub>OFF</sub>) during which no current is applied. The solution was stirred by bubbling dried N<sub>2</sub> during the experiments. After the electrolysis, the deposits were washed with ultrapure water and ethanol and analysed by XRD (Figure 5) and SEM-EDAX (Figures 6 (a-b)). In all the cases the deposits consist of pure metallic indium. Moreover, the deposits present a homogeneous morphology (Fig. 6a) with small clusters of particles with the tetragonal crystal structure (Fig. 6b).

Taken together, the foregoing results lead to the conclusion that the electrochemical signal I<sub>c</sub> displayed in Figure 4 was due to the following reaction:



**b) Results obtained with addition of InCl(s).**

The addition of anhydrous InCl(s) to the solvent gives place to a colourless solution and a solid with metallic appearance at the bottom of the cell. At first glance, the voltammograms obtained with this solution and illustrated in Figure 7, appeared to be identical to those shown in Figure 4, indicating the presence of InCl<sub>p</sub><sup>3-p</sup> in solution, and suggesting that InCl has undergone the following disproportionation reaction when dissolved in the DES:



In order to endorse the disproportionation of InCl, the solid formed at the bottom of the cell was analysed by XRD (Figure 8) and SEM-EDAX (Figure 9) being confirmed the presence of metallic indium.

**3.3.- Electrochemical nucleation of indium on a tungsten electrode in the eutectic ChCl-EG (1:2)**

The nucleation/growth process of indium on a tungsten electrode was studied with a solution of In(III), analyzing the chronoamperometric responses to single potential steps. With the aim to obtain accurate results the electrode and the diffusion layer must be renewed before each measurement. Therefore, the following renewal procedure of the electrode/electrolyte interface was applied:

- 1) after every potential-step measurement, the solution was stirred and the electrode polarized for 120 s at a potential value sufficiently anodic to ensure that the deposited indium metal was totally removed from the surface
- 2) afterwards, the solution stirring was stopped and 15 s were waited without applying any voltage before running the new measurement.

Figure 10 shows examples of the responses resulting from such experiments. In the very beginning, each transient displays a current spike due to the charging of the electrode double layer, which is followed almost immediately by a rising current due to the formation and growth of indium nuclei. The rising part of the current culminates in a current maximum,  $i_m$ , at a time  $t_m$ . The values of  $i_m$  and  $t_m$  depend on the magnitude of the potential step (i.e.  $i_m$  achieves greater values and  $t_m$  decreases when the applied potential is more cathodic). Finally the current decays converging at long times to the limiting behaviour described by the Cottrell equation.

With the aim to identify the indium nucleation mode, the dimensionless experimental current-time transient obtained at several cathodic potentials and temperatures were compared to the theoretical model derived by Scharifker and Hills [16]. The model distinguishes between the two limiting nucleation mechanisms: i) instantaneous nucleation that corresponds to a rapid nucleation on a fixed number of active sites and ii) progressive nucleation at a more slowly rate on an infinite number of active sites [17]. Scharifker and Hills model includes algebraic expressions for instantaneous and progressive nucleation as shown in Eqs. 12 and 13 respectively [16].

$$\left(\frac{i}{i_m}\right)^2 = 1.9542 \frac{[1 - \exp(-1.2564(t/t_m))]^2}{(t/t_m)} \quad (12)$$

$$\left(\frac{i}{i_m}\right)^2 = 1.2254 \frac{[1 - \exp(-2.3367(t/t_m)^2)]^2}{(t/t_m)} \quad (13)$$

In order to make a better comparison between the nucleation model and experimental results, the induction time,  $t_0$ , between the application of the potential step and the onset of nucleation and growth has to be taken into account [18-21]. Estimates of  $t_0$  can be obtained from the intercept of the plots of  $(i/i_m)^2$  vs  $t$  and  $(i/i_m)^{2/3}$  vs  $t$  for instantaneous and progressive nucleation respectively [20, 21].

Plots of  $(i/i_m)^2$  vs  $(t'/t'_m)$  (being  $t' = t - t_0$ ,  $t'_m = t_m - t_0$ ) calculated from Eqs. 12 and 13 are shown in Figure 11 together with the dimensionless experimental data, taken from the chronoamperometric curves as those gathered in Figure 10. According to Figures 11 the initial stages of electrochemical deposition of indium onto a tungsten electrode in the deep eutectic solvent ChCl-EG (1:2) can be explained in terms of a model involving instantaneous nucleation with three-dimensional growth of the nuclei whatever the applied overpotential. On the other hand, the nucleation mode of indium is not influenced by temperature in the 323-363 K range.

### **3.4.- Determination of the $\text{InCl}_p^{3-p}$ diffusion coefficient. Verification of the Arrhenius's law.**

Chronoamperometry (CA), chronopotentiometry (CP) and convolutive potential sweep voltammetry (CPSV) seem to be relevant techniques for the determination of the diffusion coefficient of  $\text{InCl}_p^{3-p}$ ,  $D_{\text{In(III)}}$ , in the deep eutectic solvent ChCl-EG (1:2), on condition that the adequate equations in the appropriate experimental conditions are used. The aim of the work is to identify if the three methods yield identical results or one among them is more appropriate than the others considering: i) the accuracy of the measurements, and ii) the simplicity of data acquisition [22]

### **Results obtained by chronoamperometry (CA)**

The diffusion coefficient of In(III) was calculated from the chronoamperometric responses obtained with a solution of In(III) at potential values in the mass-transport controlled region (i.e. where the surface concentration of In(III) is effectively zero). Figure 10 (b) shows the variation of the current versus  $1/t^{1/2}$ , confirming that the experimental data obey the Cottrell law [15, 23, 24].

$$I_d(t) = \frac{nFSD^{1/2}C_0}{\pi^{1/2}t^{1/2}} \quad (14)$$

where  $I_d(t)$  is the sampled current at time  $t$ ,  $C_0$ ,  $D$  and  $S$  are the concentration ( $\text{mol cm}^{-3}$ ), the diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ ), and the electroactive area ( $\text{cm}^2$ ), respectively. The diffusion coefficient,  $D_{\text{In(III)}}$ , was calculated from the slope of the straight lines and the results are gathered in table 1.

### **Results obtained by chronopotentiometry (CP).**

The diffusion coefficient of In(III) was also determined from the chronopotentiograms as those displayed in Figure 12, by means of Sand's equation [15, 23, 24].

$$I\tau^{1/2} = \frac{nFSD^{1/2}C_0\pi^{1/2}}{2} \quad (15)$$

where  $I$  is the applied current and  $\tau$  is the transition time measured in the chronopotentiograms.

In order to assure the renewal of the electrode and the same electrode/electrolyte interface conditions at the beginning of each chronopotentiogram, the same protocol described in the chronoamperometric experiments was applied.

As it is shown in Figure 12, the plateau corresponding to the reduction of In(III) can be clearly defined, and as predicted by Sand's equation the transition time becomes shorter increasing the applied current. Likewise, the square root of the transition time changed linearly with the applied current density (Figure 12 b), indicating that the fluxes of In(III) species were diffusion controlled and that all the requirements for using Sand's equation are fulfilled. The diffusion coefficient was calculated from the slope on Figure 12b by Eq. (18) being the mean values obtained at different temperatures gathered in Table 1.

### **Results obtained by convolutive potential sweep voltammetry (CPSV).**

The convolution of the cyclic voltammograms recorded at several scan rates on a W electrode was also carried out by means of the following expression [15, 23]:

$$m(t) = \frac{1}{\pi^{1/2}} \int_0^t \frac{i(u)}{(t-u)^{1/2}} du \quad (16)$$

where  $m(t)$  is the convoluted current, and  $i(u)$  the current from the voltammogram.

Fig. 13 depicts examples of the voltammograms recorded with a solution of In(III) and its corresponding semiintegrated curves. In the convoluted curves (pink lines), the peaks have disappeared and instead, a plateau of height  $m^*$ , is developed at potential values sufficiently cathodic to ensure zero surface concentration of the reactant. The convoluted curves exhibited well defined limiting currents, indicating

that there is no change in the electrode surface area during the scan, to the point that it affects the limiting current for the In(III) reduction wave. Hence the In(III) diffusion coefficient could be computed from the boundary semi-integral values by means of the relationship [15,23,24]:

$$m^* = nFSC_0D^{1/2} \quad (17)$$

A summary of the values of the diffusion coefficient obtained by using the aforementioned techniques are displayed in Table 1.

A two-way (temperature - technique) analysis of variance (ANOVA) [25] was carried out in order to know if there are significant differences between the calculated data using: i) different techniques, and ii) different working temperatures, being the null hypothesis the non-existence of significant differences between the calculated units. Concerning the effect of the techniques, the calculated F statistics was lower than the critical F value ( $F_{cal} = 6.02 < F_{crit.} = 6.94$ ), then the null hypothesis must be maintained. On the contrary, for the temperature effect the calculated F statistics was higher than the critical F value, ( $F_{cal} = 103.42 > F_{crit.} = 6.94$ ) and consequently the null hypothesis must be rejected. As a result, it can be concluded that with a 95% confidence level: i) all the methods used to calculate the diffusion coefficients lead to the same values, and ii) as expected the diffusion coefficients change with temperature. Hence, in order to calculate the activation energy for diffusion, the diffusion coefficient was determined at three more temperatures (313, 333 and 353 K) by using only the convoluted technique due to the simplicity of data acquisition. The obtained diffusion coefficient values showed a good linearity in the Arrhenius plot (Fig. 14), and with a number of observations  $n=103$ , it was possible to formulate the following empirical expression for the temperature dependence of the diffusion coefficient of In(III) in ChCl-EG (1:2) as follows:

$$\ln D = -(3.57 \pm 0.21) - (3664 \pm 72)T^{-1} \quad (D_{in}: \text{cm}^2 \text{s}^{-1} \text{ and } T: \text{K}) \quad (18)$$

From this relationship, the value of the activation energy,  $E_a$ , for the diffusion of In(III), was found to be  $30.5 \pm 0.6 \text{ kJ mol}^{-1}$ .

Additionally, in order to characterize the solute global mass transport through its environment, the effect of the viscosity on the diffusion coefficient has been taken into account through the dimensionless Schmidt number ( $Sc = \nu/D$ ) also reported in Table 1. Experimental kinematic and dynamic viscosities as well as density are also summarized in Table 1.

### 3.5. Results obtained on solid Copper cathodes.

To investigate the formation of In-Cu precursors by an electrochemical route, the electrochemical behaviour of In(III) solutions at a copper substrate was also studied by cyclic voltammetry and potentiostatic and intensiostatic electrolysis.

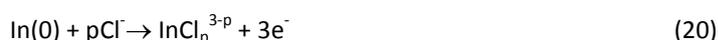
#### *Qualitative information.*

In Figure 15 the cyclic voltammograms obtained with an In(III) solution in the eutectic mixture at W and Cu electrodes are compared. As we showed above, when the electrode substrate is an inert electrode

an important overpotential must be applied in the cathodic scan, in order to initiate the nucleation and subsequent growth of In. The reaction scheme proceeds according to the following deposition mechanism:



When the scan is reversed, the reduction current continues to flow and the deposition of indium now takes place on a less “hostile” surface of previously deposited In rather than on a bare W electrode, being this fact the cause of the current loop observed in the voltammogram. When the applied potential achieved values higher than the equilibrium potential adopted by the W electrode coated by In, the oxidation peak  $I_a$  corresponding to the following dissolution mechanism can be observed:



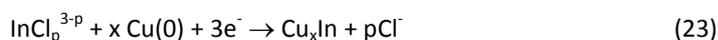
Conversely, when a Cu electrode was used a peak  $II_c$  appears at less cathodic potential values than those for pure In deposition on a W electrode (peak  $I_c$ ), evidencing that it is not yet necessary to apply the nucleation overpotential required on the W substrate. Due to the possibility of In-Cu alloy formation, the electroreduction of In(III) in peak  $II_c$  proceeds according to the following mechanism:



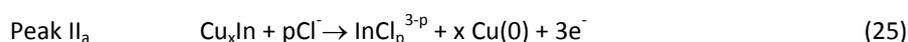
followed by the In reaction with the subjacent substrate Cu



being the overall process:



When the scan is reversed, in the anodic region two oxidation peaks are displayed, the peak  $I_a$  due to the oxidation of In(0) and the peak  $II_a$  due to the oxidation of  $\text{Cu}_x\text{In}$ .



### **Potentiostatic and intensiostatic electrolysis. Characterization of the In-Cu alloys**

Based on the previous results, alloys samples were prepared by both potentiostatic and intensiostatic electrolysis. All the experiments were conducted using 0.5 mm copper plates as working electrodes. After electrolysis, the samples were washed by immersion in ultrapure water Milli-Q, and finally in ethanol. The dried samples were analysed by XRD, SEM and EDAX techniques. A summary of the XRD analysis is gathered in Table 2.

Samples (1-3) obtained under potentiostatic conditions provided similar results. Fig. 16 shows the XRD pattern of sample (3) obtained at -1.1 V vs (Ag(I)/Ag). The observed peaks were identified as CuIn, In and Cu substrate, being the intensities of the Cu and In peaks predominant over those of the CuIn phase, which shows that the thickness of the CuIn film on the Cu substrate was thin. The surface morphology of

the obtained deposit was also observed by scanning electron microscopy (SEM) (Fig. 17 (a-b)). The deposit is made up of clusters vertically aligned and parallel to each other, making the surface of the deposit porous.

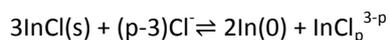
Intensiostatic pulse electrolysis was also conducted. Each pulse consists of an ON-Time ( $t_{ON}$ ) during which a current is applied, and an OFF-Time ( $t_{OFF}$ ) during which no current is applied, in order to allow In diffusion into the massive Cu plate. The XRD analysis of samples (4-6) also evidence the formation of the stoichiometric phase CuIn (Figure 18).

The surface morphology of sample (5) was also observed by SEM and analysed by EDAX. Figures 19 (a-b) show compact clusters of In over a network-like structure of the intermetallic CuIn. The effect of annealing on the crystal structure of thin film of sample (5) is shown in Figure 20, observing that the metastable phase CuIn obtained at 343 K can be transformed into  $Cu_{11}In_9$  at a higher temperature (e.g. 430 K). The surface morphology is also displayed in Figure 21.

## Conclusions

A procedure for drying the DES, ChCl-EG (1:2), based on the use of molecular sieves has been developed, being the water content of the electrolyte  $145 \pm 5$  ppm.

The stability of anhydrous InCl and InCl<sub>3</sub> dissolved in the dried DES has been investigated using cyclic voltammetry, x-Ray diffraction analysis and scanning electron microscopy. Experiments performed in a controlled N<sub>2</sub> atmosphere cell, show that anhydrous InCl<sub>3</sub> dissolved in the rich chloride media as  $InCl_p^{3-p}$  is reduced on an inert electrode (i.e W) to indium metal via only one electrochemical step. Conversely, InCl undergoes the following disproportionation reaction when dissolved in the eutectic ChCl-EG (1:2)



generating In(0) and  $InCl_p^{3-p}$  that provides identical voltammograms as those obtained after the addition of InCl<sub>3</sub> to the DES.

The electrochemical behaviour of  $InCl_p^{3-p}$  solutions has been studied using different substrates: i) W, an inert working electrode, and ii) Cu, a more noble metal than In with possibility of alloy formation.

Voltammetric and chronoamperometric experiments on a W electrode showed that nucleation and growth of the metallic indium plays an important role in the overall electrodeposition process. Chronoamperometric studies showed that the deposition process on the inert electrode involves, whatever the applied overpotential, instantaneous three dimensional nucleation on a finite number of active sites with diffusion controlled growth of the nuclei. Not being the nucleation mode of indium influenced by temperature in the 323-363 K range.

The applicability of several electrochemical techniques (CA, CP and CPSV) for accuracy measurements of the diffusion coefficient of  $InCl_p^{3-p}$  was also investigated, verifying the validity of the assumptions used in their theoretical analysis, and ensuring reproducible conditions at the electrode/electrolyte interface. A two-way analysis of variance, ANOVA has shown that with a 95% confidence level: i) the three

electrochemical techniques used to calculate the diffusion coefficients lead to the same values, and ii) the diffusion coefficient changes with temperature following the Arrhenius law, being the activation energy for diffusion  $30.5 \pm 0.6 \text{ kJ mol}^{-1}$ . The dimensionless Schmidt numbers, defined as the ratio between solvent viscosity and solute diffusivity ( $Sc=v/D$ ), have also been calculated to characterize the solute global mass transport through its environment.

To investigate the formation of In-Cu precursors by an electrochemical route, the electrochemical behaviour of In(III) solutions at a copper substrate was also studied by cyclic voltammetry and potentiostatic and intensiostatic electrolysis. The resulting cyclic voltammograms exhibited signals that could be attributed to the presence of In-Cu intermetallic compounds. Thin layers of the intermetallic compounds were obtained by electrosynthesis and characterized by X-ray diffraction and scanning electron microscopy (SEM) revealing in all cases the formation of stoichiometric CuIn. The metastable CuIn phase was transformed into  $\text{Cu}_{11}\text{In}_9$  by thermal annealing.

The deposits obtained under continuous potentiostatic electrolysis were made up of clusters vertically aligned and parallel to each other, making the surface of the deposits porous. Conversely, the films obtained by intensiostatic pulse electrolysis consisted on compact clusters of In over a network-like structure of the stoichiometric CuIn.

**Acknowledgements.**- Authors thank the Consejería de Educación of the Junta de Castilla y León Project VA171U14 for financial support. S. García, also thanks the youth employment operative programme (European Social Fund, ESF, and youth employment initiative, YEI).

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Table 1.- Variation of the diffusion coefficient of In(III) with the temperature in the DES ChCl-EG (1:2) calculated by different electrochemical techniques, density ( $\rho$ ), dynamic viscosity ( $\eta$ ), kinematic viscosity ( $\nu$ ), and Schmidt number.

$D \text{InCl}_p^{3-p} / 10^{-7} \text{ cm}^2 \text{ s}^{-1}$						
T/K	313	323	333	343	353	363
CA		$3.99 \pm 0.15$		$7.64 \pm 0.26$		$12.88 \pm 0.33$
CP		$2.99 \pm 0.17$		$6.01 \pm 0.20$		$9.61 \pm 0.34$
CPSV	$2.47 \pm 0.06$	$3.22 \pm 0.83$	$4.79 \pm 0.11$	$6.70 \pm 0.09$	$9.52 \pm 0.22$	$12.17 \pm 0.39$
Mean value	$2.47 \pm 0.06$	$3.25 \pm 0.35$	$4.79 \pm 0.11$	$6.56 \pm 0.59$	$9.52 \pm 0.22$	$11.43 \pm 1.43$
$\rho / \text{kg m}^{-3}$	1110.4	1104.7	1099.2	1093.6	1088.1	1082.7
$\eta / \text{kg m}^{-1} \text{ s}^{-1}$	0.028940	0.020967	0.015848	0.012238	0.0096892	0.0077822
$\nu / \text{cm}^2 \text{ s}^{-1}$	0.26063	0.18980	0.14418	0.11191	0.089047	0.071878
$Sc / 10^4$	105.5	58.4	30.1	17.1	9.4	6.3

Table 2- Electrolysis experiments and identification of the different phases in the obtained samples.

Potentiostatic electrolysis				
Sample	[In(III)] / mol cm <sup>-3</sup>	E <sub>applied</sub> vs (Ag(I)/Ag)/V	Time/s	Identified phase
1	2.6×10 <sup>-5</sup>	-0.8	240	Cu, CuIn
2	6.8×10 <sup>-5</sup>	-0.9	7200	Cu, In, CuIn
3	6.8×10 <sup>-5</sup>	-1.1	3600	Cu, In, CuIn
Intensiostatic pulse electrolysis				
Sample	[In(III)] / mol cm <sup>-3</sup>	J <sub>applied</sub> / mA cm <sup>-2</sup>	Time/s	Identified phase
4	2.7×10 <sup>-5</sup>	-0.79 (t <sub>ON</sub> =2s; t <sub>off</sub> =4s)	6340	Cu, In, CuIn
5	6.3×10 <sup>-5</sup>	-2.22 (t <sub>ON</sub> =2s; t <sub>off</sub> =6s)	1040	Cu, In, CuIn
6	6.3×10 <sup>-5</sup>	-2.07 (t <sub>ON</sub> =2s; t <sub>off</sub> =6s)	3230	Cu, In, CuIn

### Legends of the figures.

Fig. 1.- Electrochemical window on GC (—), W (—) and Cu (—) electrodes in the deep eutectic solvent ChCl-EG (1:2) at 343 K.

Fig.2.- Chlorine detection: (a) photo of the aqueous and organic phase after extraction of  $I_3^-$  (b) filter paper strip impregnated with fluorescein ( $C_{20}H_{12}O_5$ ) and KBr, showing the formation of pink eosin ( $C_{20}H_8Br_4O_5$ ).

Fig.3.- UV-Vis spectrum of the eutectic ChCl-EG (1:2) after electrolysis using as reference pure ChCl-EG (1:2).

Fig.4.- Cyclic voltammogram obtained with a solution of  $InCl_p^{3-p}$  ( $C_0=7.29 \times 10^{-5} \text{ mol cm}^{-3}$ ) on a tungsten electrode at  $100 \text{ mV s}^{-1}$  and 343 K. Pink line corresponds to a cyclic voltammogram of the ChCl-EG (1:2) in absence of  $InCl_p^{3-p}$

Fig. 5.- XRD pattern of In films obtained on a W foil from the electrolyte containing  $InCl_p^{3-p}$  under galvanostatic intermittent electrolysis ( $J_{app}=-6.5 \text{ mA cm}^{-2}$ ,  $t_{off}=2s$   $t_{on} = 5 s$ ,  $t_{total elec} = 72 \text{ minutes}$ ). (●) In, (■) W.

Fig.6.- SEM micrographs of a W foil coated by an In film (a) surface appearance, (b) details.

Fig.7.- Cyclic voltammograms recorded at different inversion potentials on a tungsten electrode at  $100 \text{ mV s}^{-1}$  and 343 K after the addition of anhydrous InCl to ChCl-EG (1:2).

Fig. 8.- XRD pattern of the solid formed at the bottom of the cell after the addition of anhydrous InCl(s) to the DES (●) In.

Fig. 9.- (a) SEM micrograph of the solid formed at the bottom of the cell after the addition of anhydrous InCl(s) to the DES. ( b ) EDX analysis.

Fig.10.- (a) Evolution of the chronoamperograms of a  $InCl_p^{3-p}$  solution ( $C_0= 6.21 \times 10^{-5} \text{ mol cm}^{-3}$ ) at a tungsten electrode ( $S = 0.46 \text{ cm}^2$ ) at various applied potentials -0.870 (—); -0.890(—); -0.920 (—); -0.930 (—); -0.940 (—); -0.950 (—); -0.970 (—); -1.000 (—);-1.020 (—);-1.040 (—) ; -1.060 (—) ; 1.080 (—) and -1.100 (—) V vs Ag(I)/Ag, at 323 K. (b) Relation between square root of time and current at potential values (e.g.  $E = -1.100 \text{ V}$ ) where the reaction is diffusion controlled.

Fig.11.- Comparison of the dimensionless experimental data obtained from the current-time transients, represented in Figure 10, with the theoretical model for (—) instantaneous and (—) progressive nucleation at various applied potentials. (▲) -0.930, (■) -0.970, (●)-1.000, (◇) -1.040, (■) -1.060, (○) -1.020, (▲) -1.080 V vs (Ag(I)/Ag.

Fig.12.- (a) Evolution of the chronopotentiograms of a  $InCl_p^{3-p}$  solution ( $C_0= 6.21 \times 10^{-5} \text{ mol cm}^{-3}$ ) at a tungsten electrode ( $S = 0.46 \text{ cm}^2$ ) at various applied currents -3.0; -3.1; -3.2; -3.4; -3.5; -3.6; -3.8; -3.9; -4.2; -4.3; -4.4 and -4.5 mA, at 323 K. (b) Relation between square root of transition time and the applied current.

Fig.13.- Evolution of the voltammograms (blue) and convoluted (pink) curves obtained with a  $\text{InCl}_p^{3-p}$  solution ( $C_0 = 6.15 \times 10^{-5} \text{ mol cm}^{-3}$ ) at a tungsten electrode and 343 K, sweep rate: (---) 50, (—) 100 and (---) 200  $\text{mV s}^{-1}$ .

Fig 14.- Variation of diffusion coefficient of In(III) with temperature in ChCl-EG (1:2). Verification of the Arrhenius law.

Fig. 15.- Cyclic voltammograms obtained at different potential limits (-0.76; -0.78; -0.79; -0.80; -0.85; and -0.90 V vs Ag(I)/Ag) with a In(III) solution ( $C_0 = 7.29 \times 10^{-5} \text{ mol cm}^{-3}$ ) at a W electrode (grey line) and a Cu electrode (dotted lines) at 343 K. Scan rate: 10  $\text{mV s}^{-1}$ .

Fig. 16.- XRD pattern of sample (3) obtained on a Cu plate from the electrolyte containing  $\text{InCl}_p^{3-p}$  under potentiostatic electrolysis ( $E_d = -1.1 \text{ V vs Ag(I)/Ag}$ ,  $t_d = 3600 \text{ s}$ ). (●) In, (▲) CuIn, (◆) Cu

Figure 17.- SEM micrographs of sample (3); (a) surface appearance, (b) details.

Fig. 18. XRD pattern of sample (6). (●) In, (▲) CuIn, (◆) Cu

Fig. 19.- SEM micrographs of sample (5); (a) surface appearance, (b) details and EDXs

Fig.20.- XRD pattern of sample (5) after annealing at 430 K for 2 hours. (▲)  $\text{Cu}_{11}\text{In}_9$ , (◆) Cu

Fig. 21.- SEM micrograph of sample (5) after annealing.

Figure 1  
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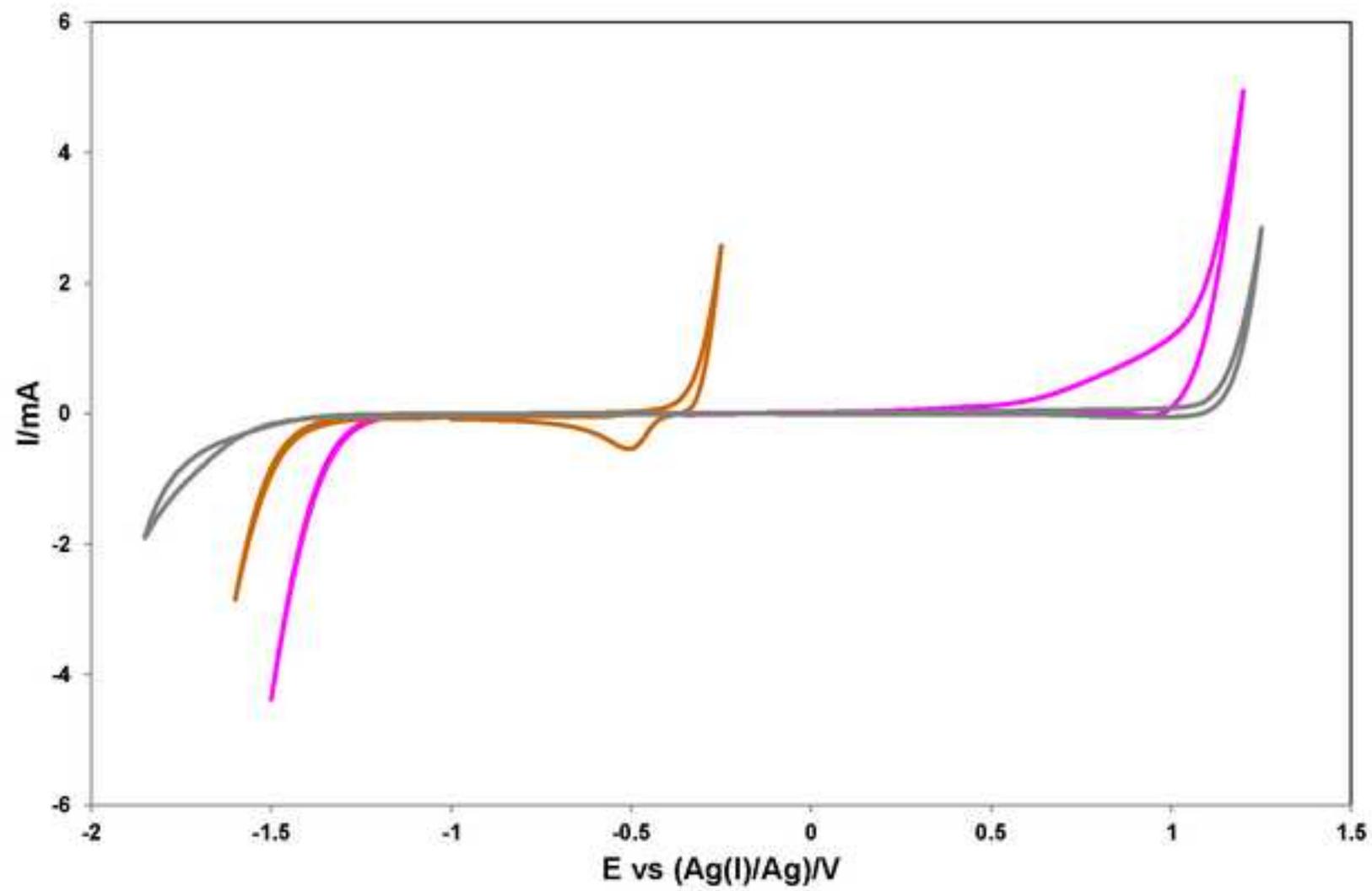


Figure 2  
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(a)



(b)

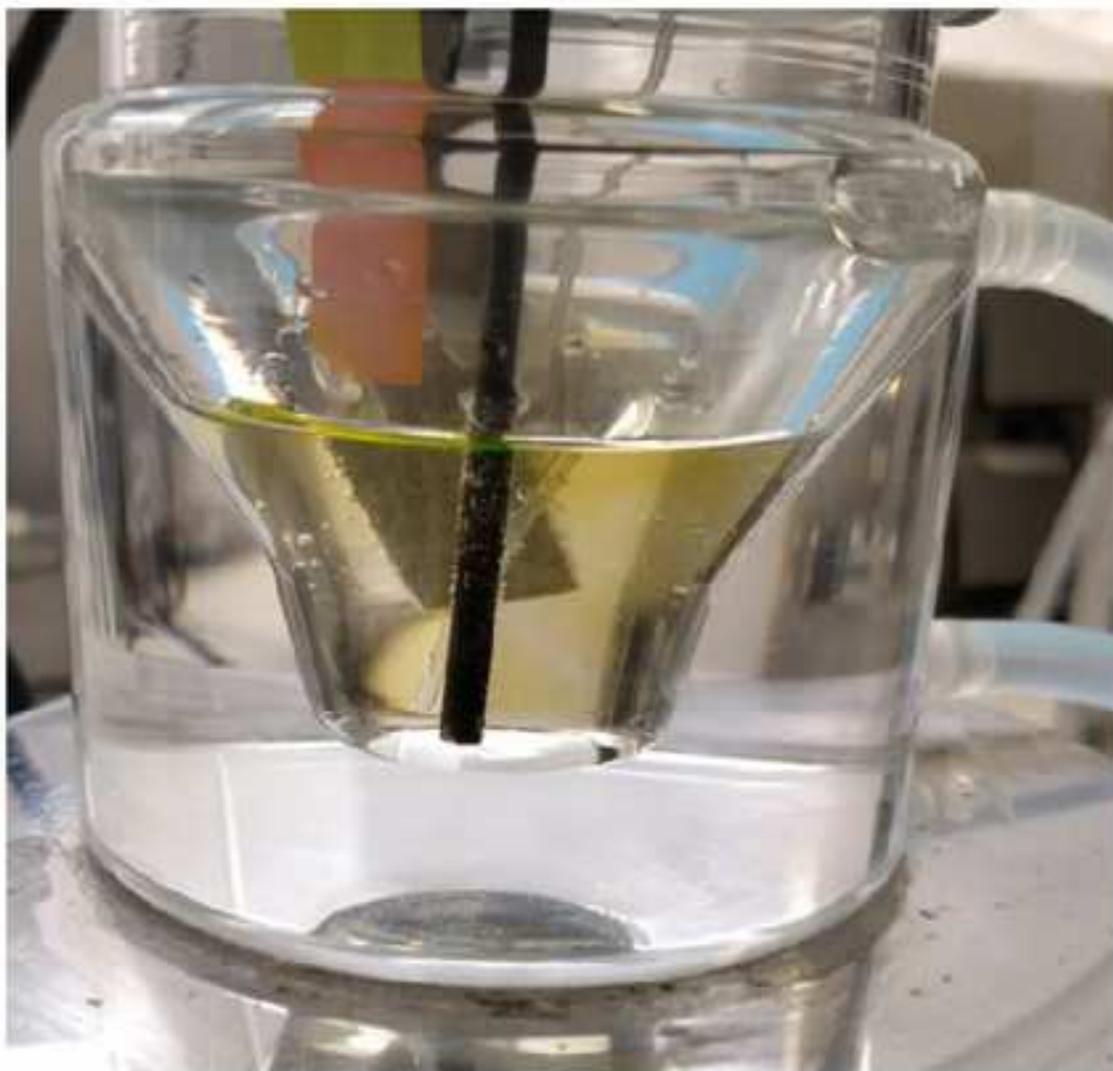


Figure 3  
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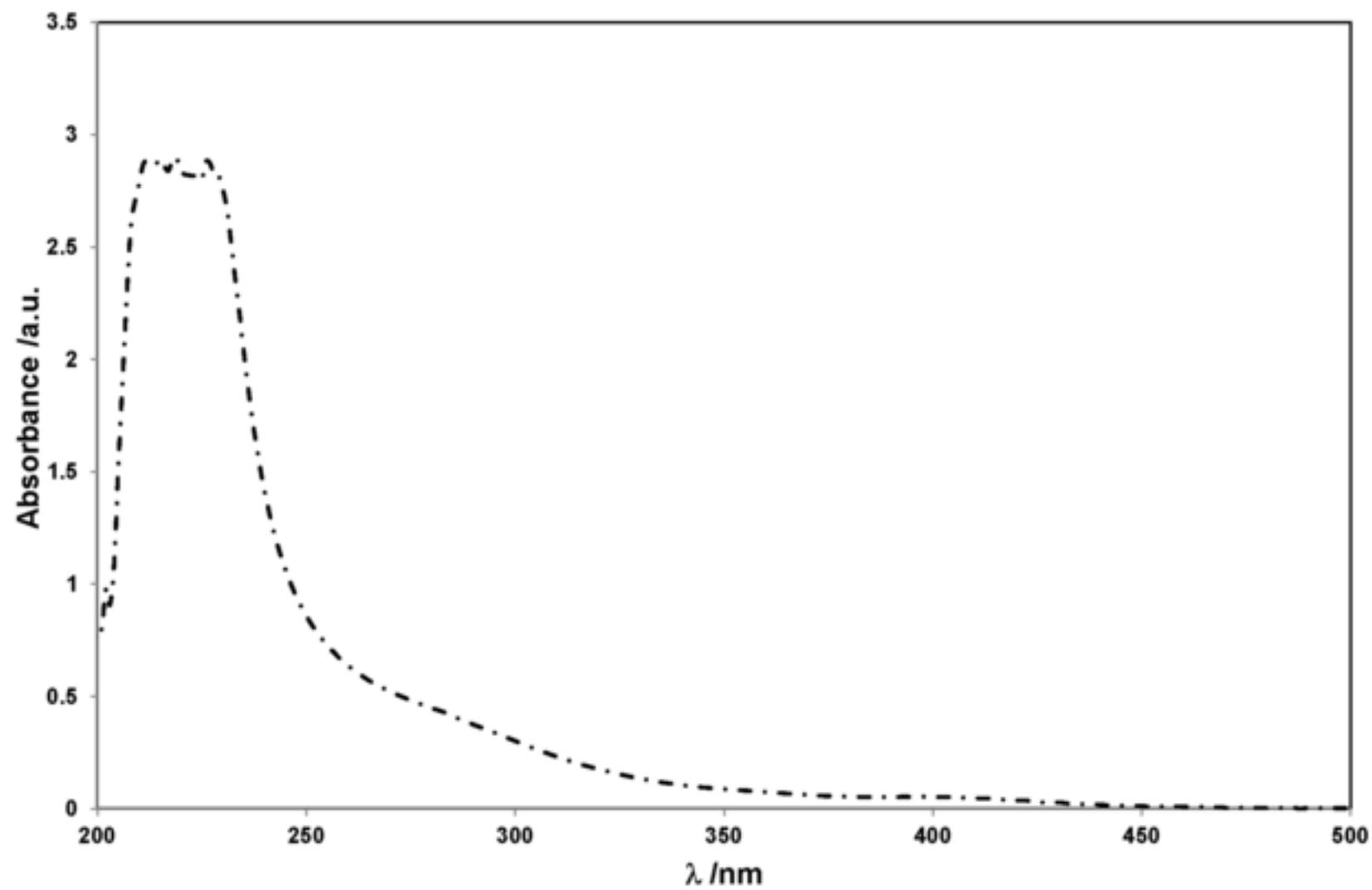


Figure 4  
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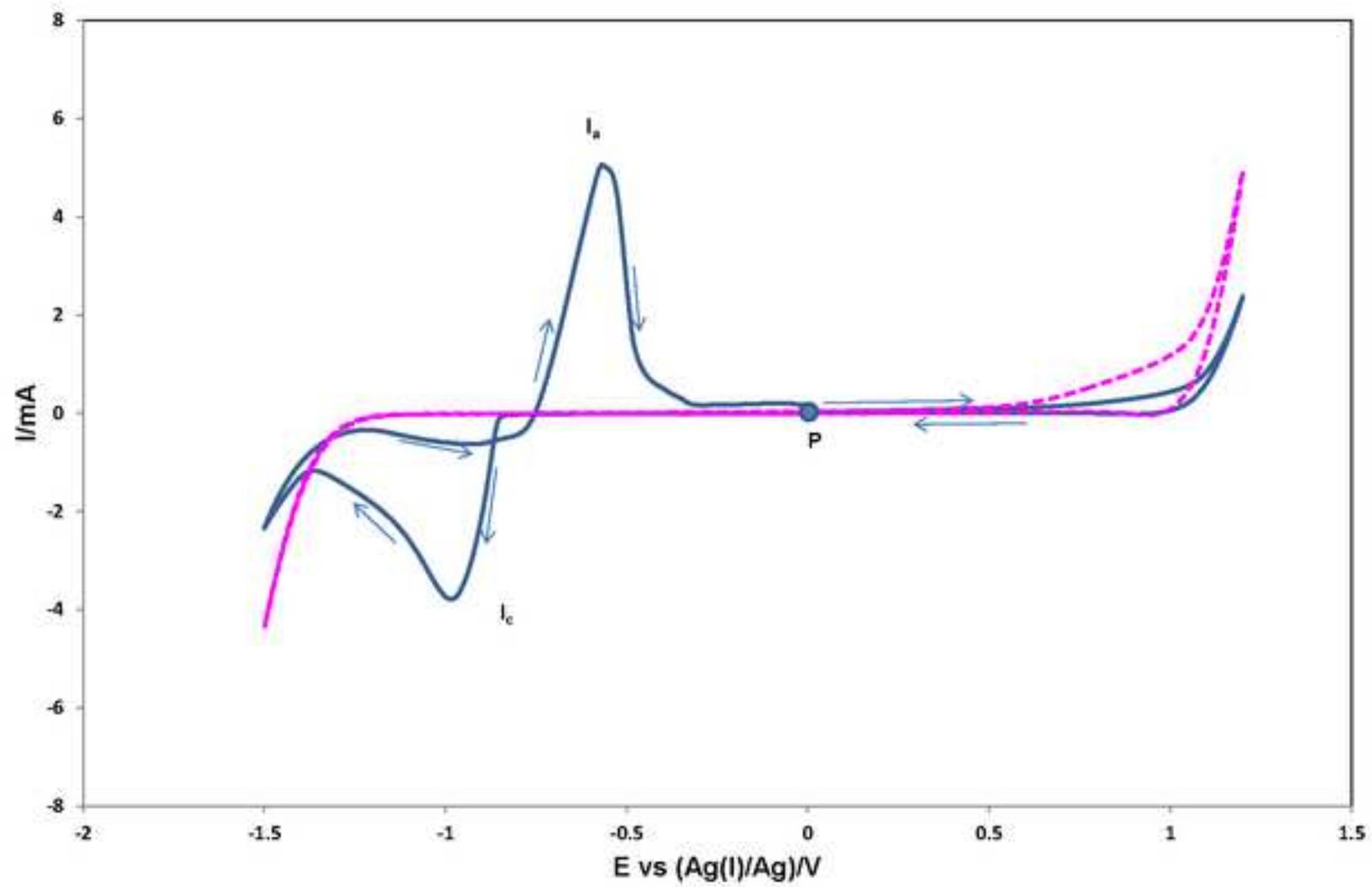


Figure 5  
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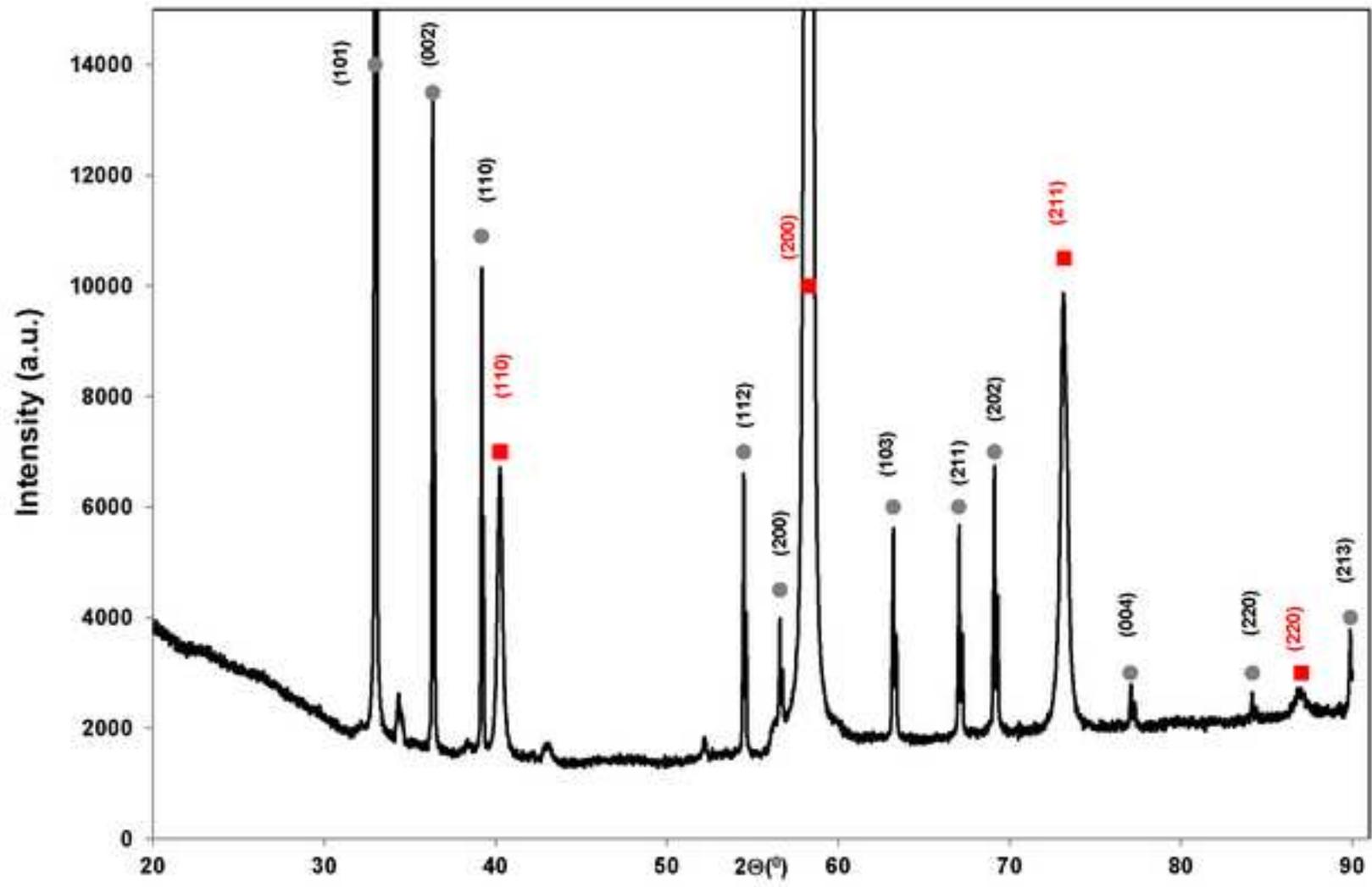


Figure 6 a

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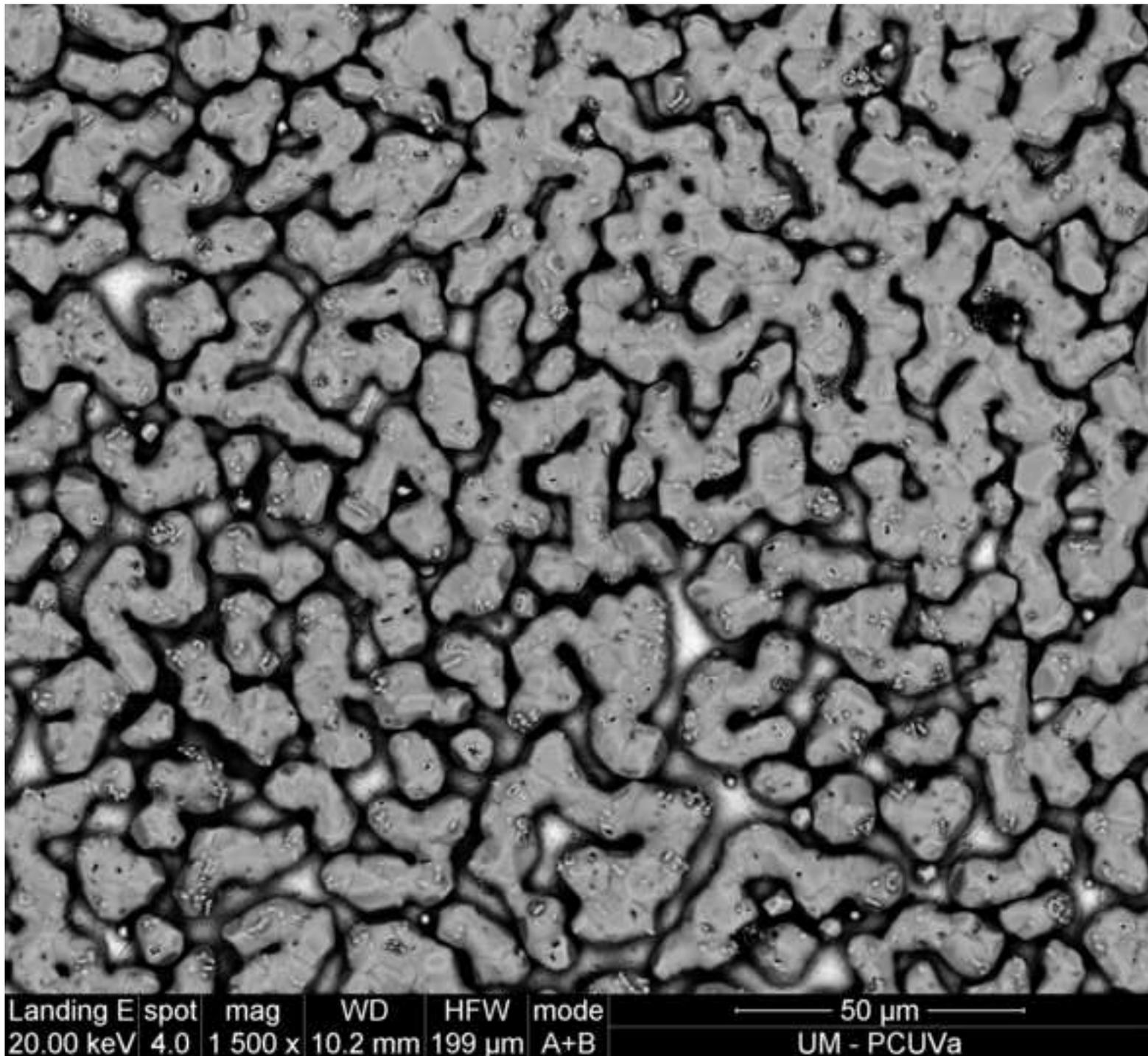


Figure 6 b

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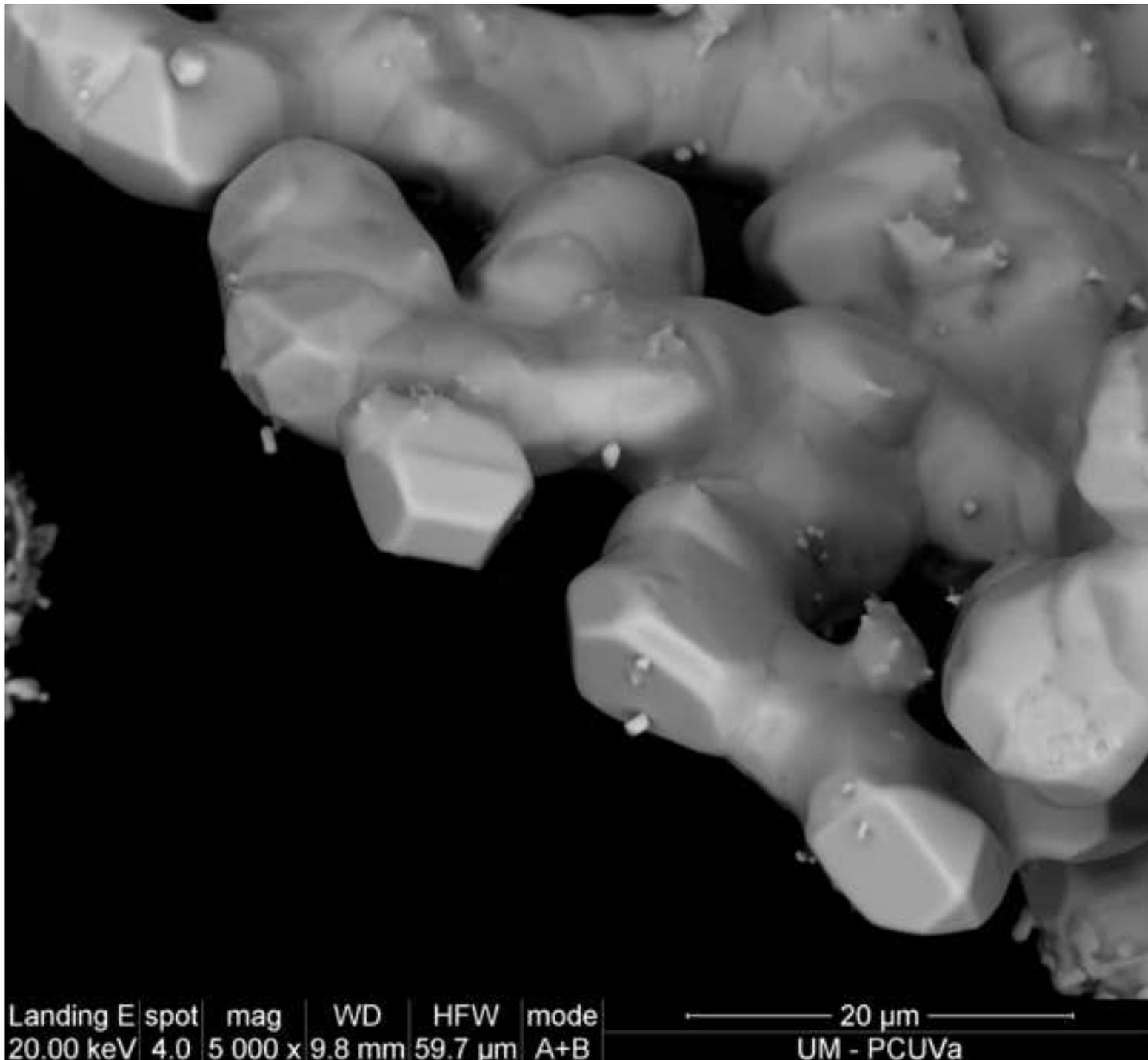


Figure 7  
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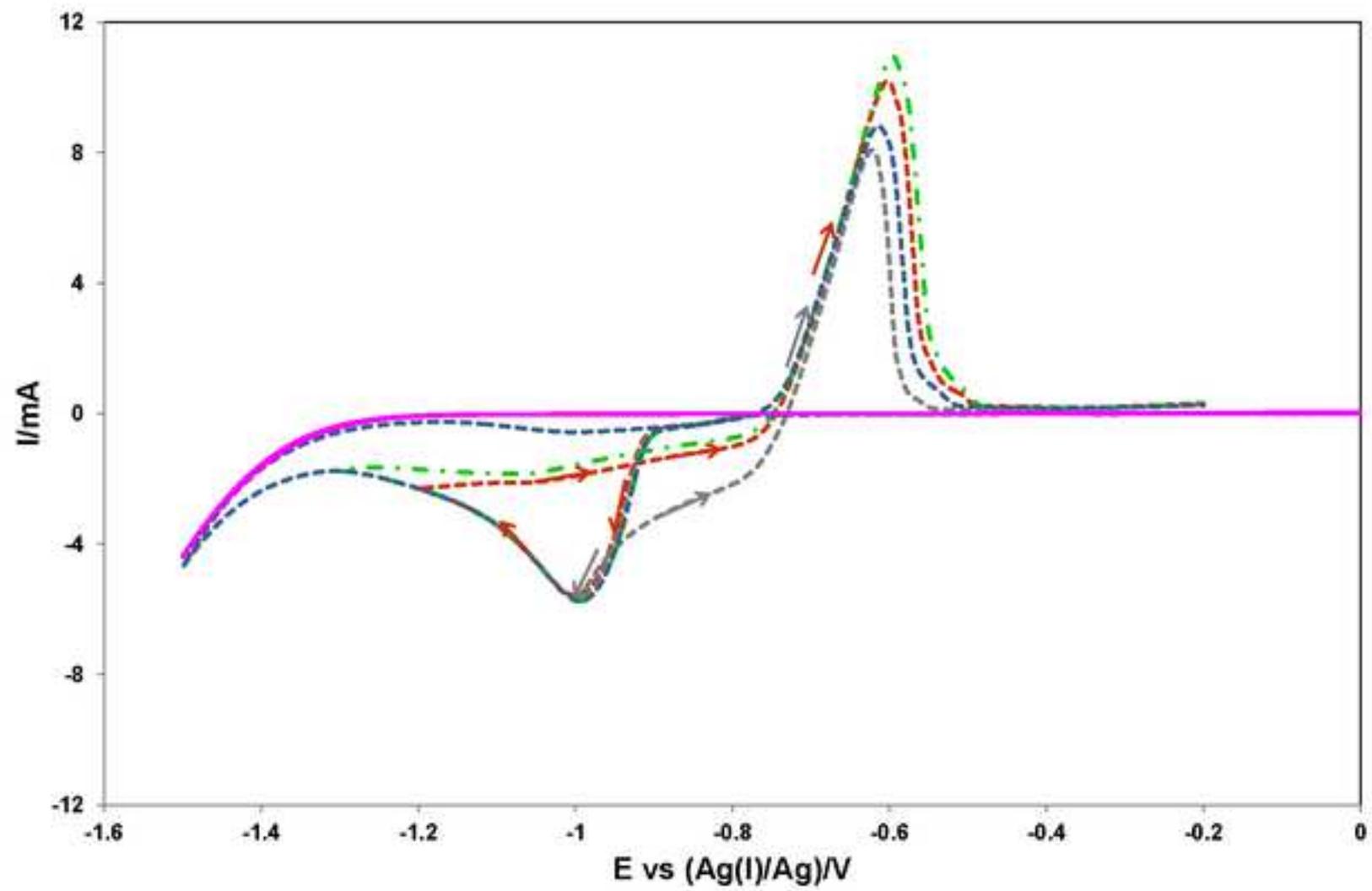


Figure 8  
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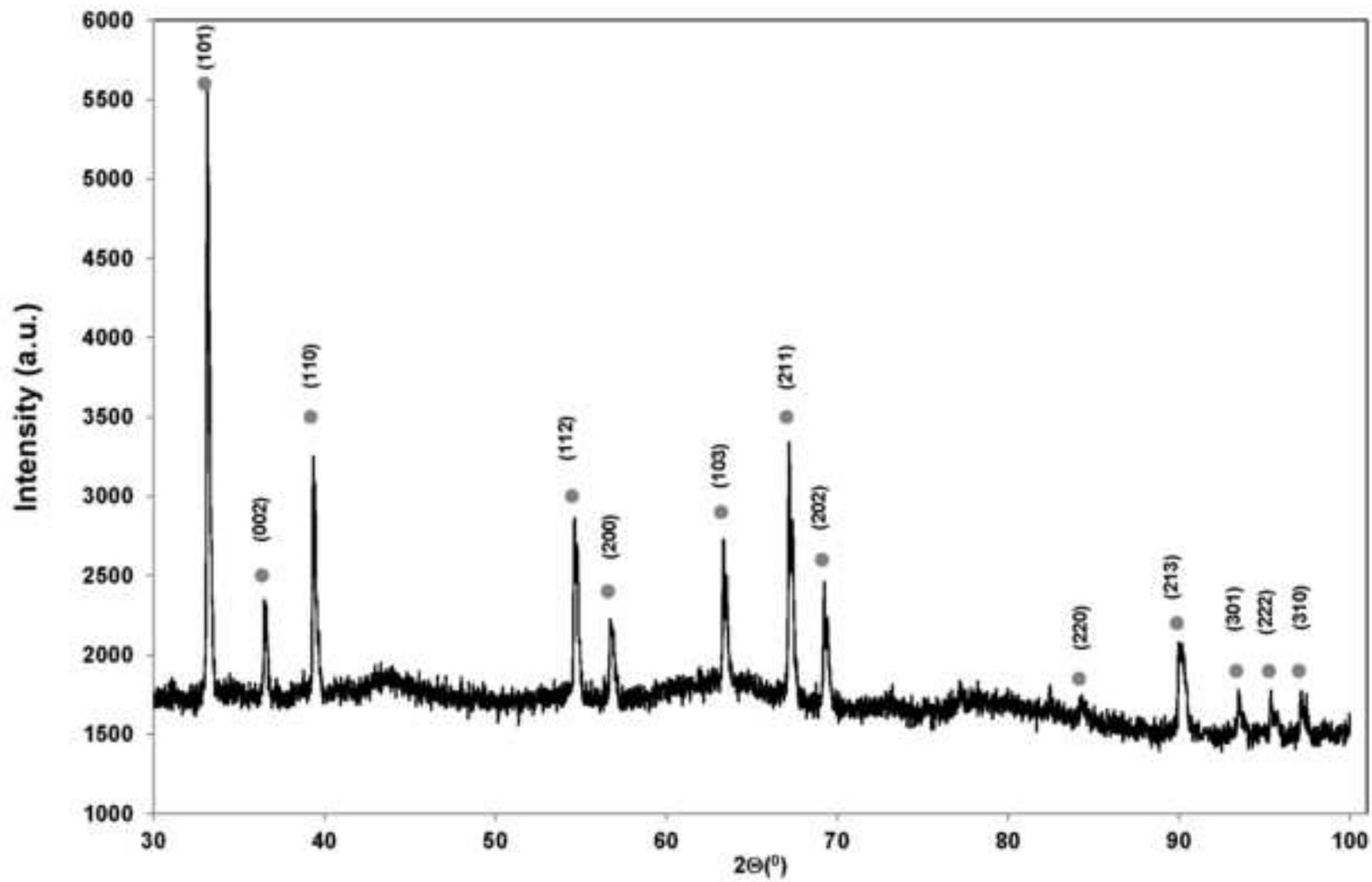
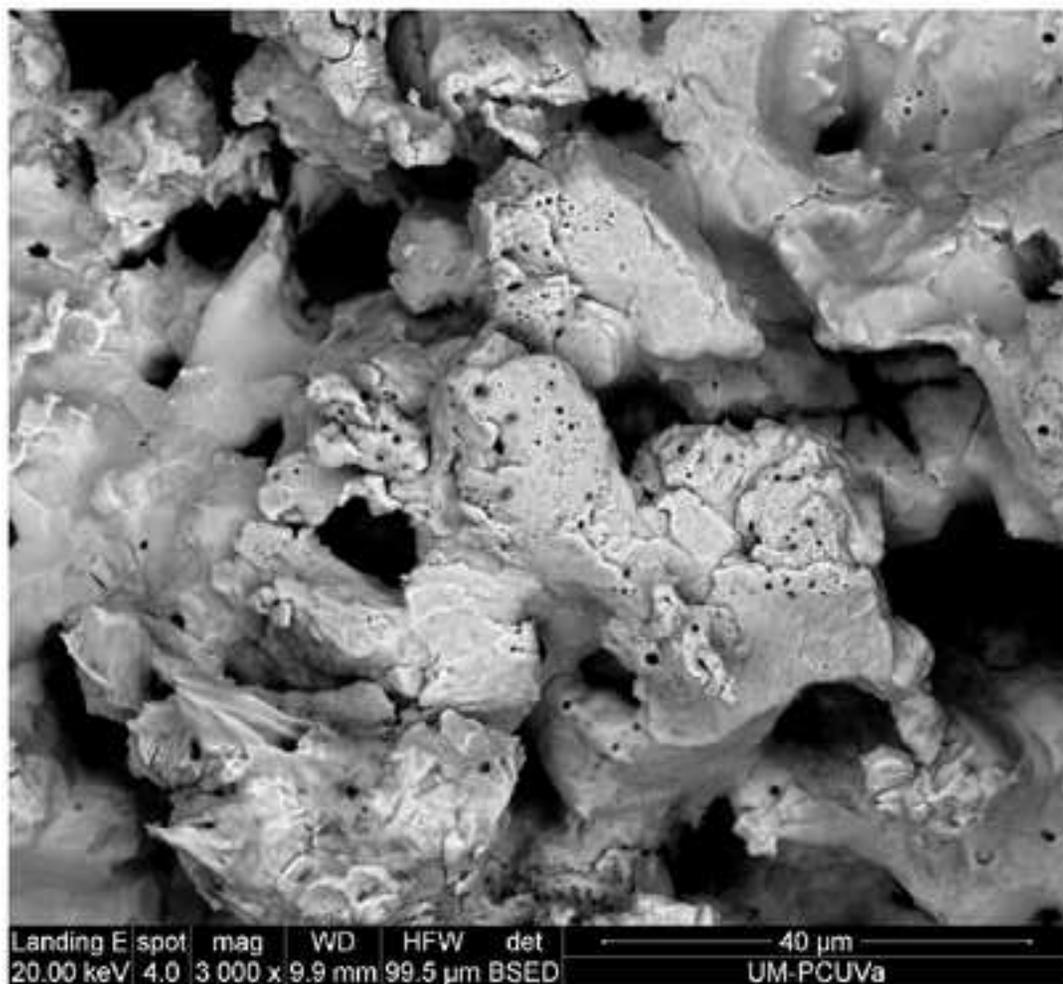


Figure 9  
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(a)



(b)

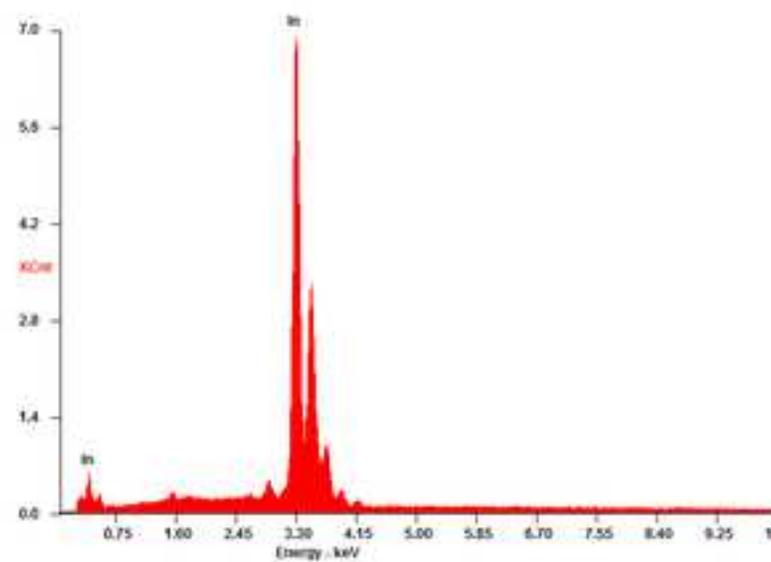


Figure 10  
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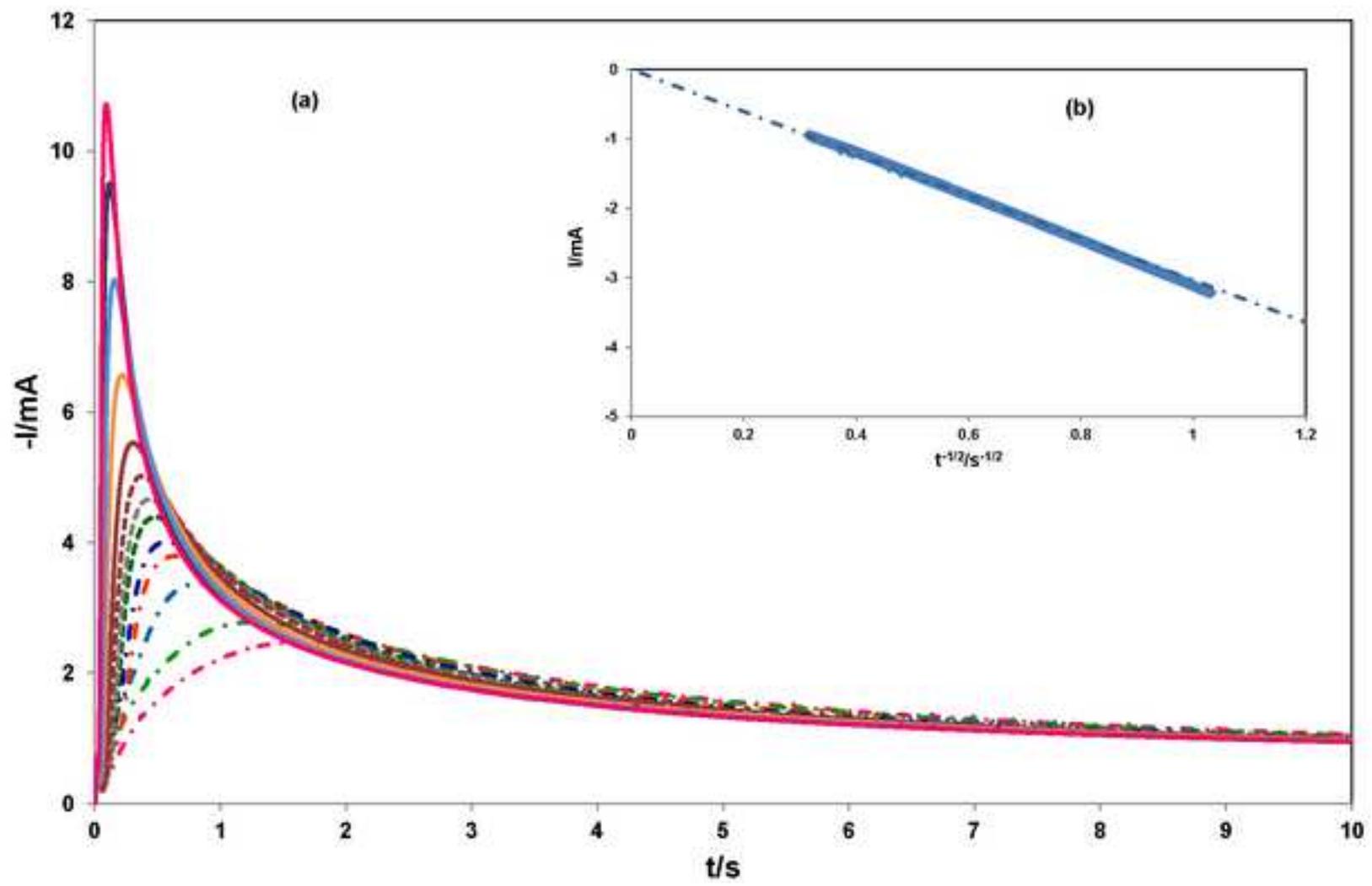


Figure 11  
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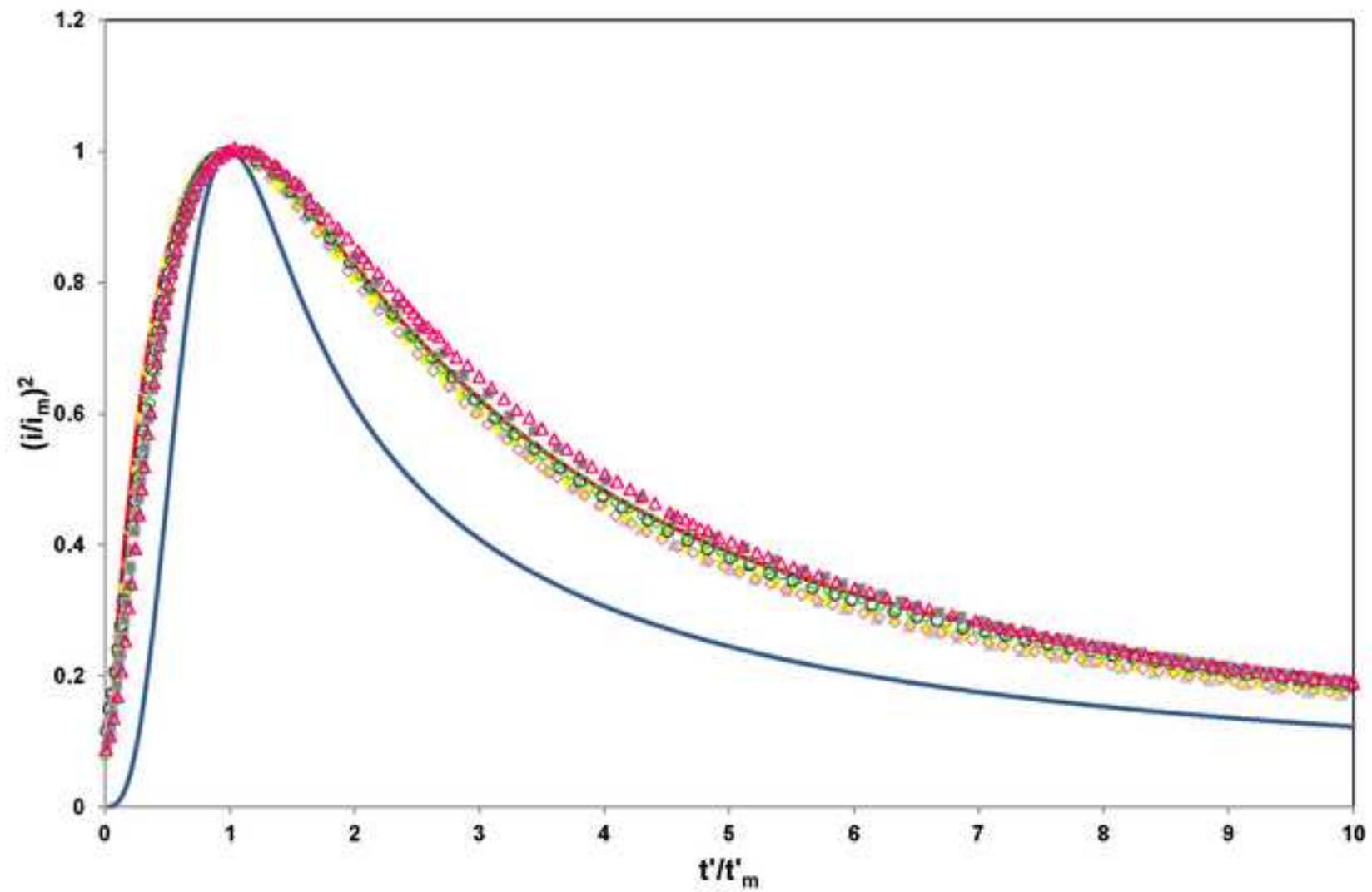


Figure 12  
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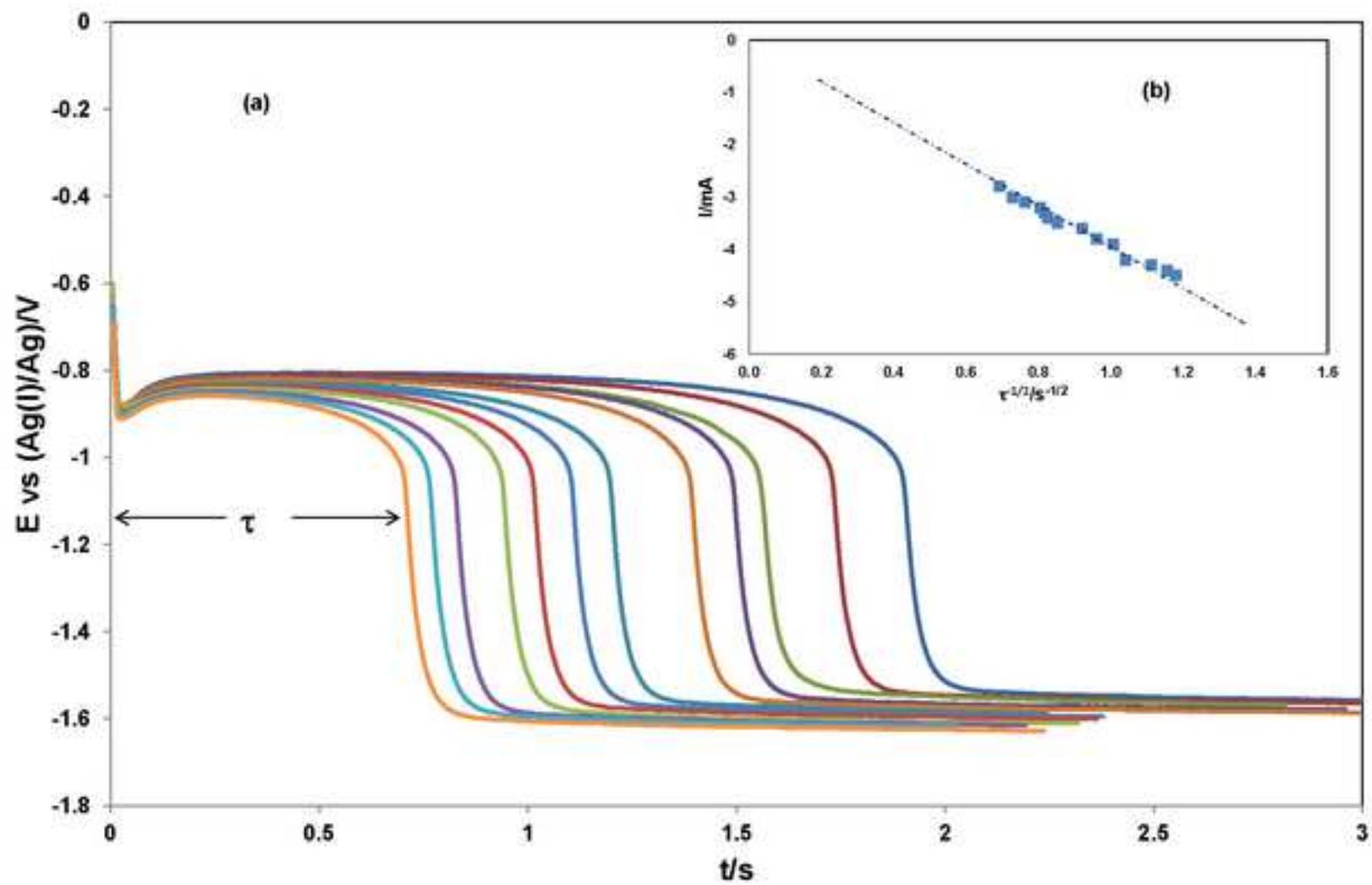


Figure 13  
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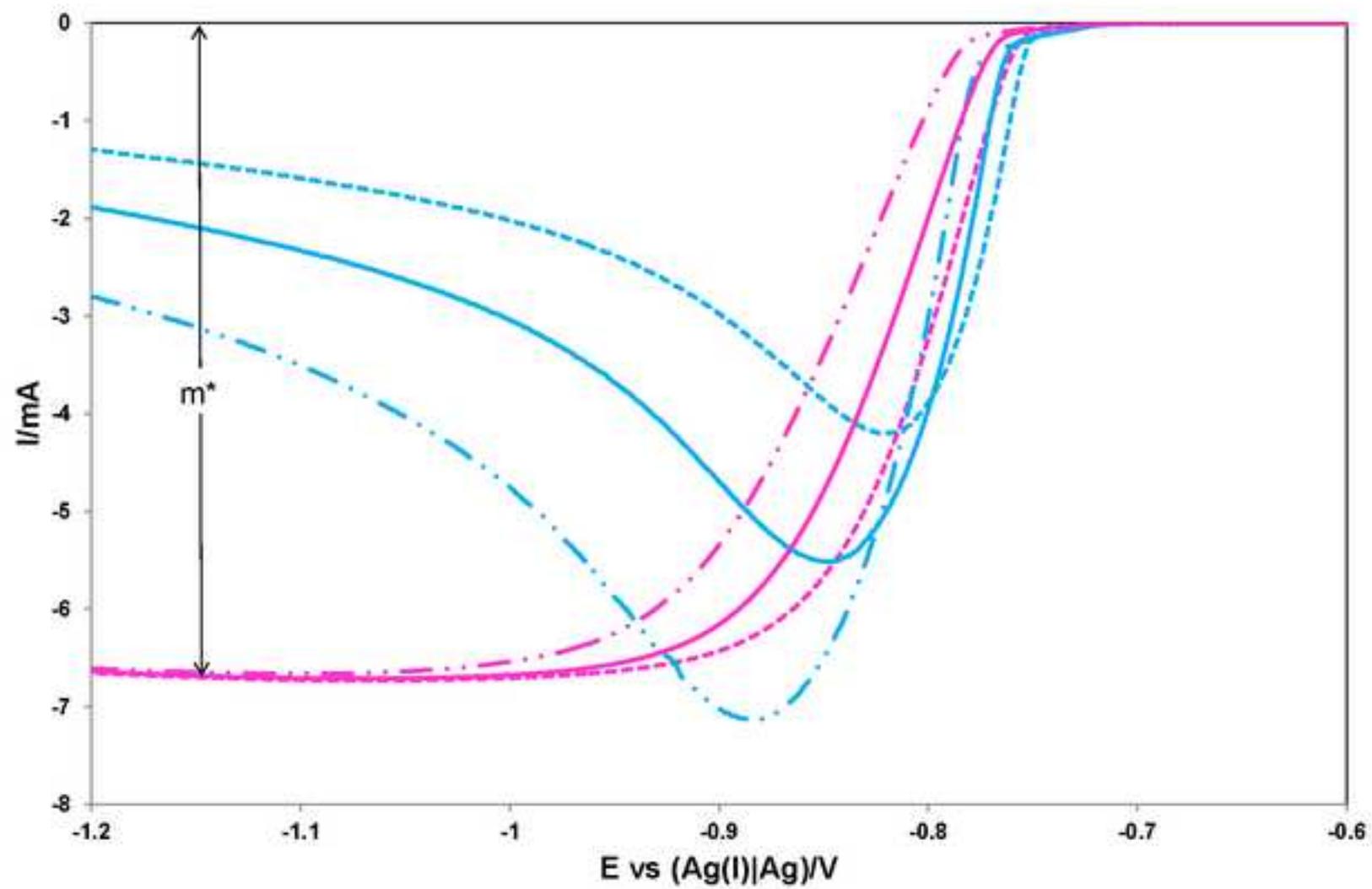


Figure 14  
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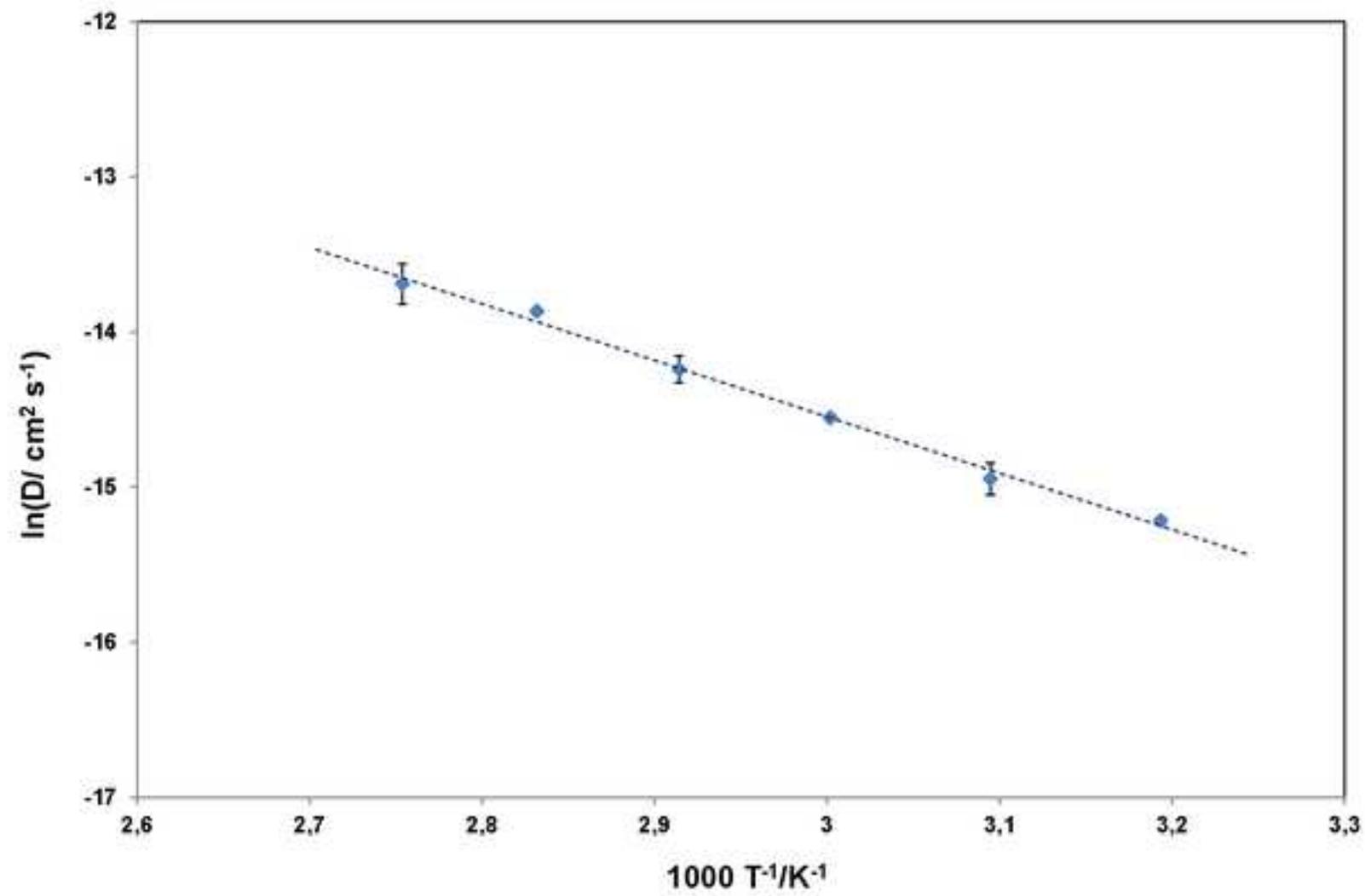


Figure 15  
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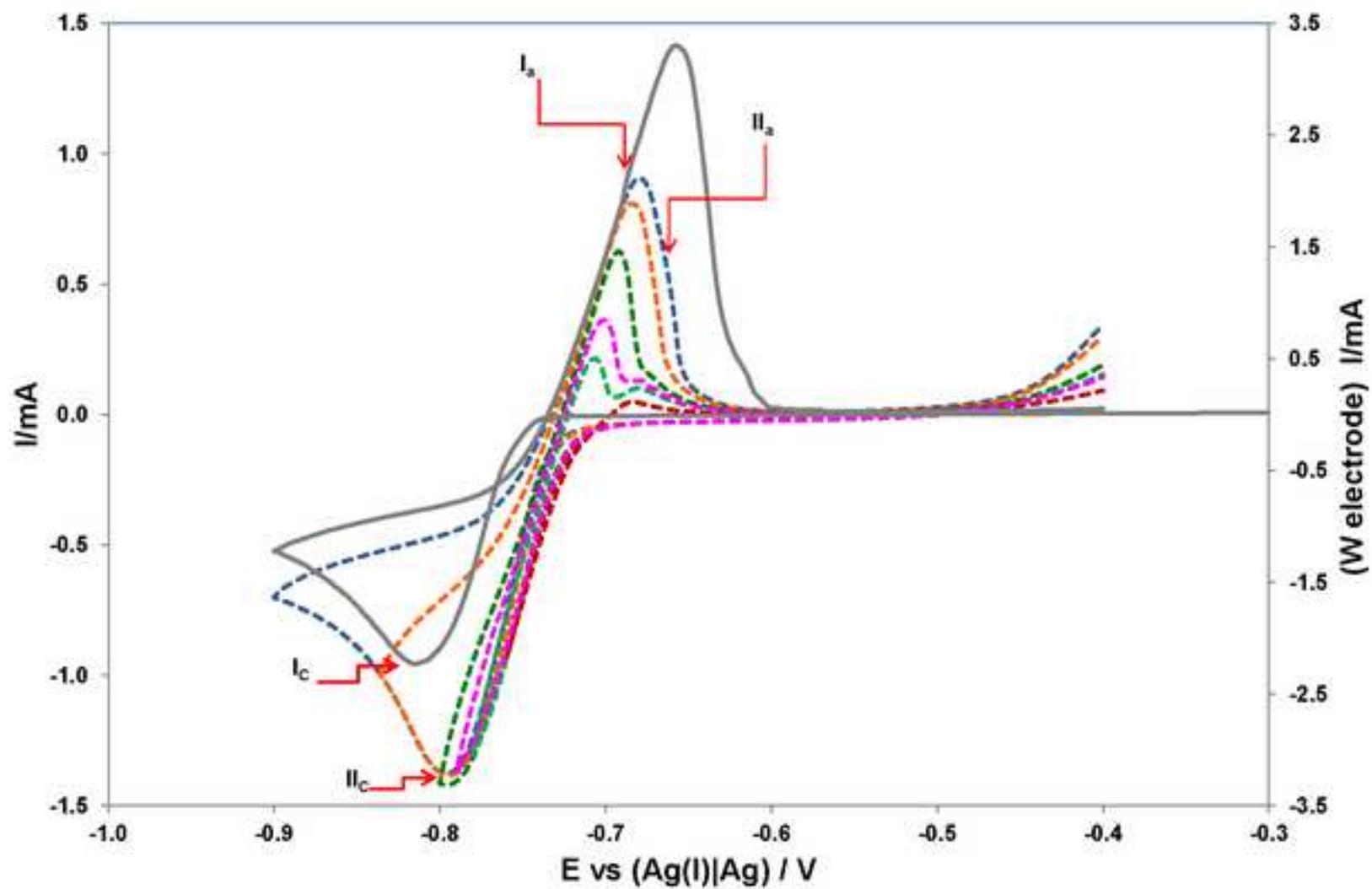


Figure 16  
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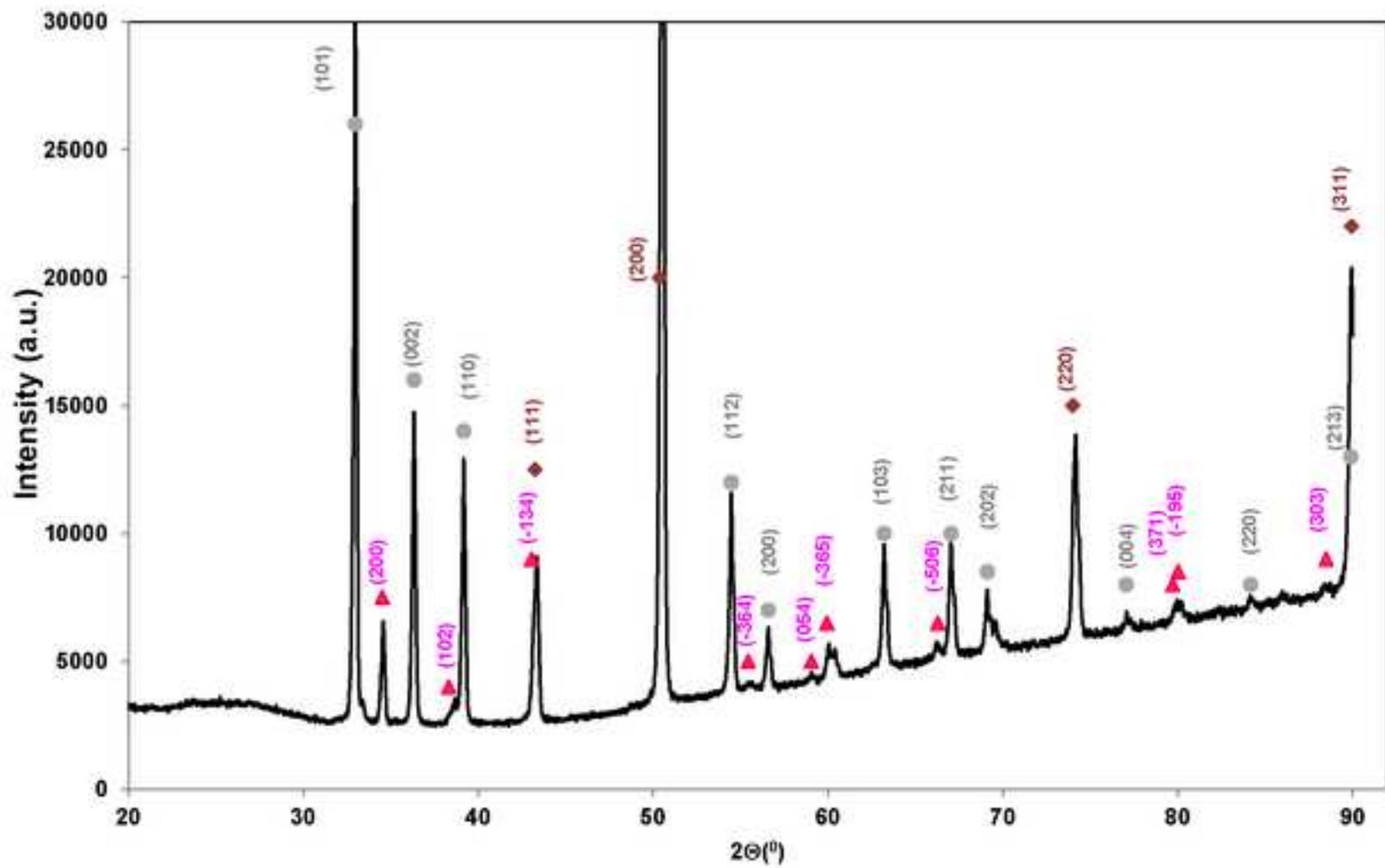


Figure 17 a

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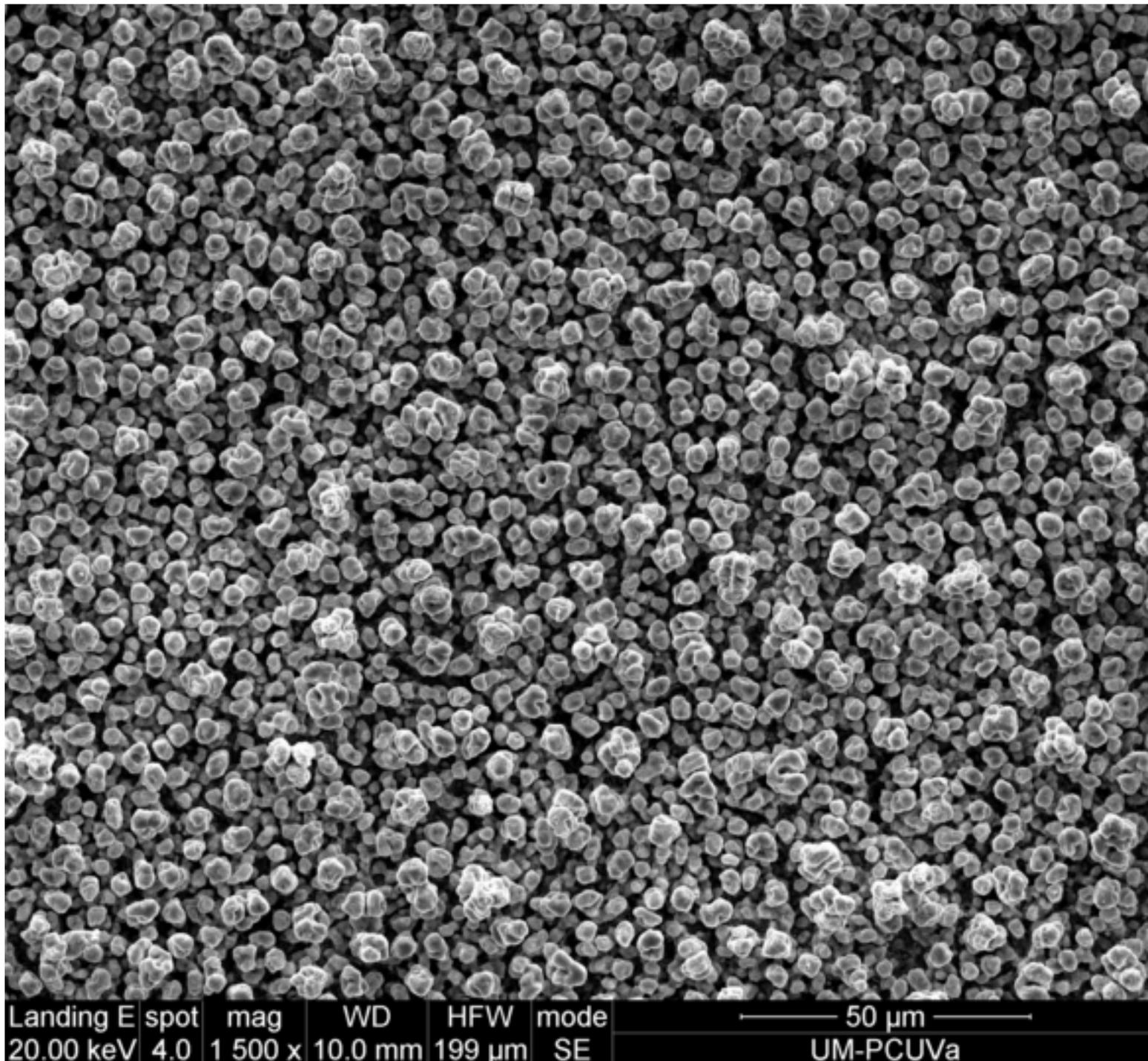


Figure 17 b

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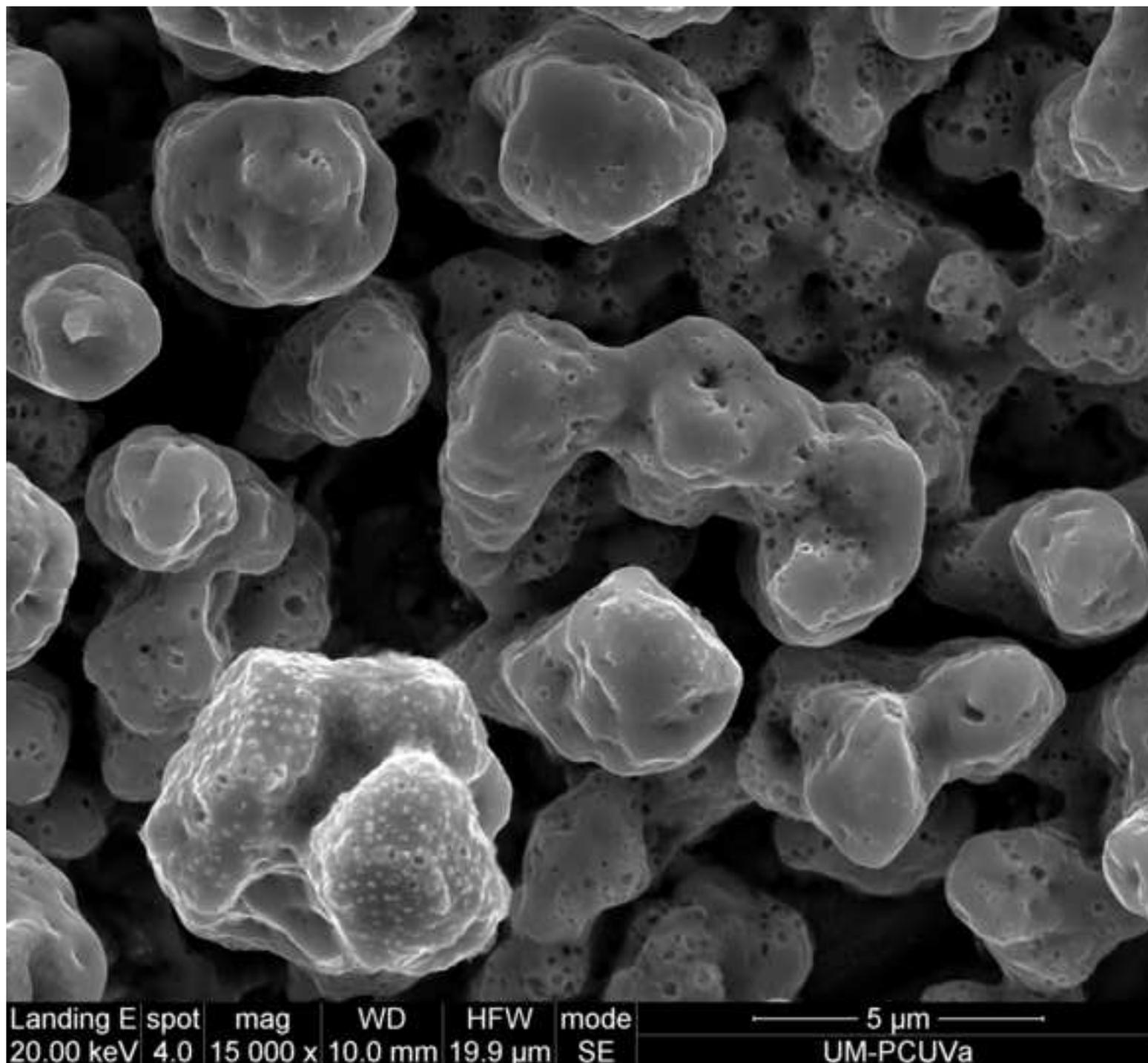


Figure 18

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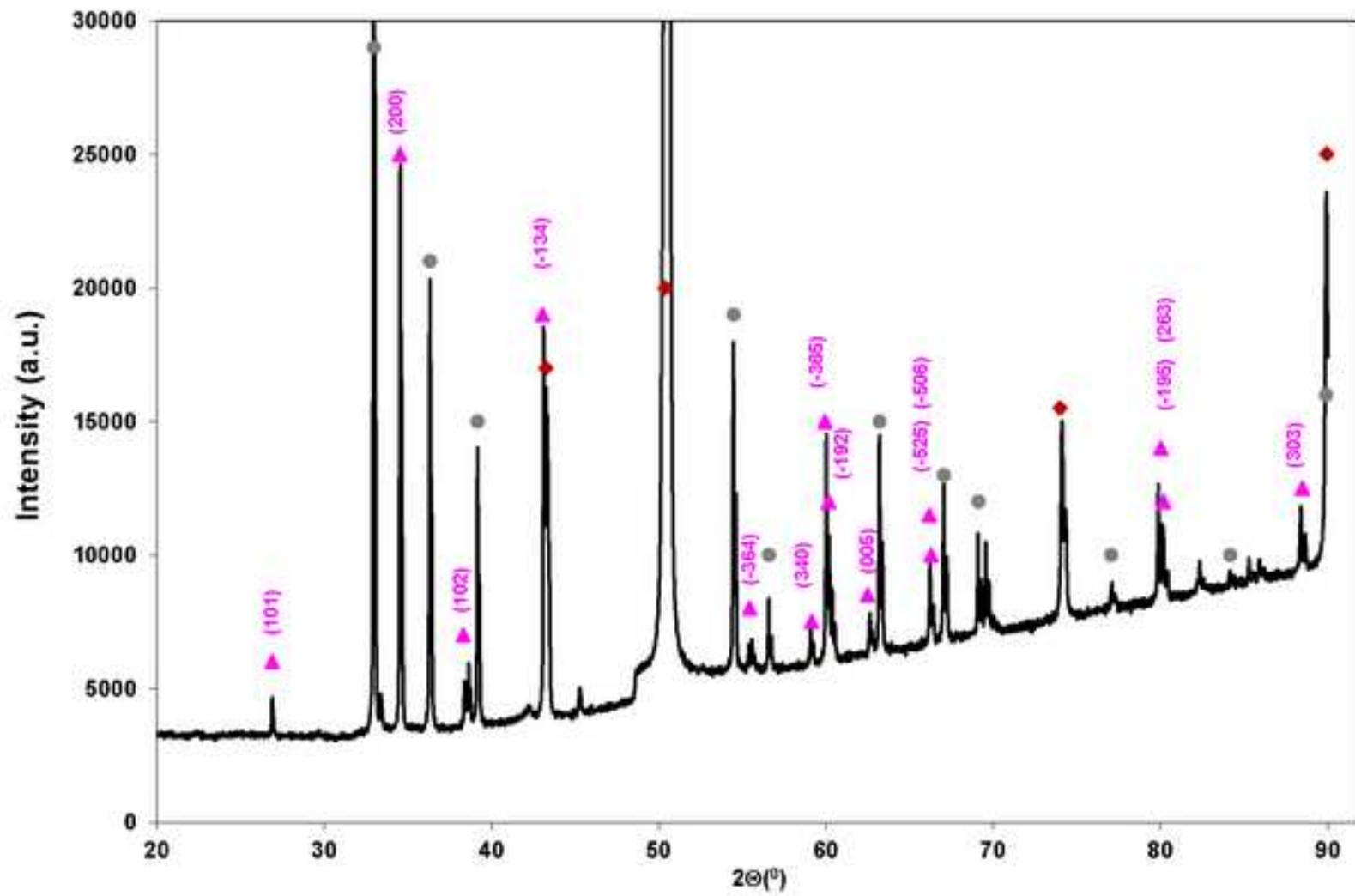


Figure 19 a

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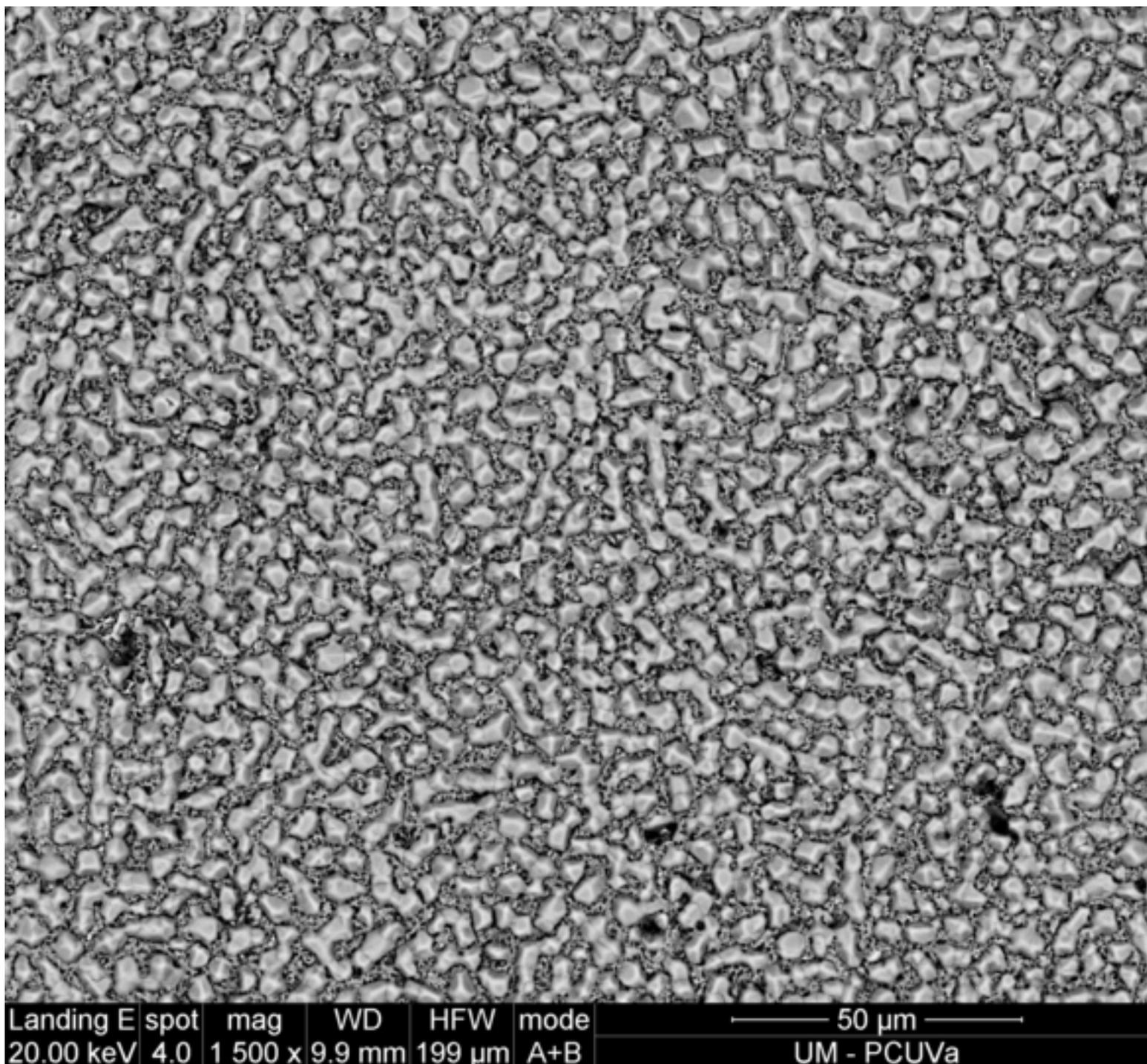


Figure 19 b  
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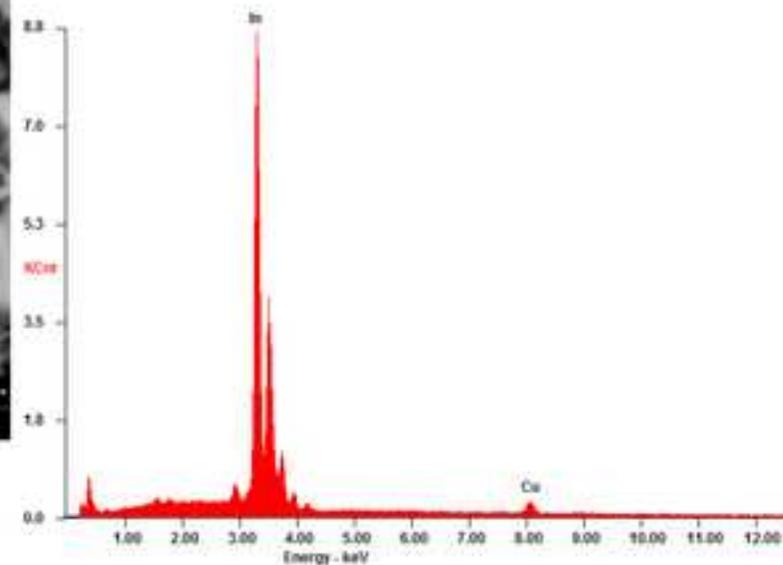
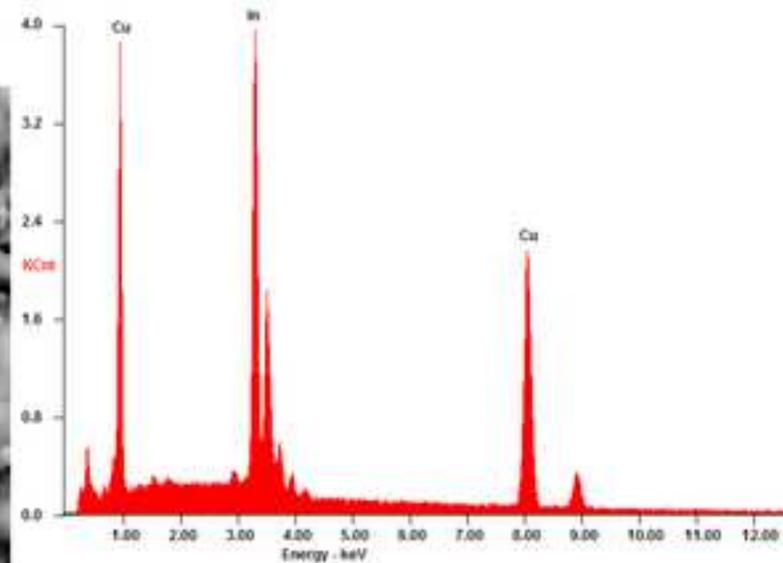
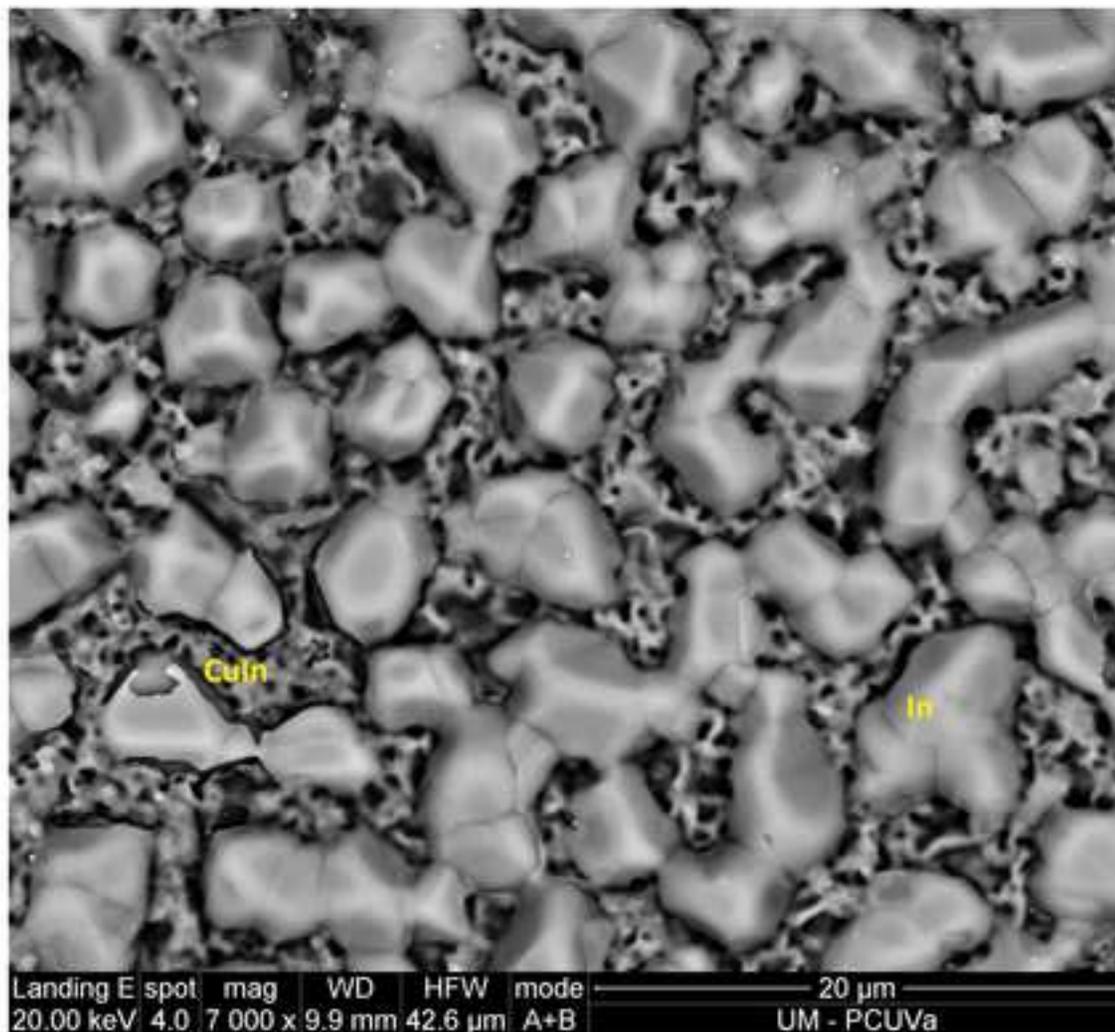


Figure 20

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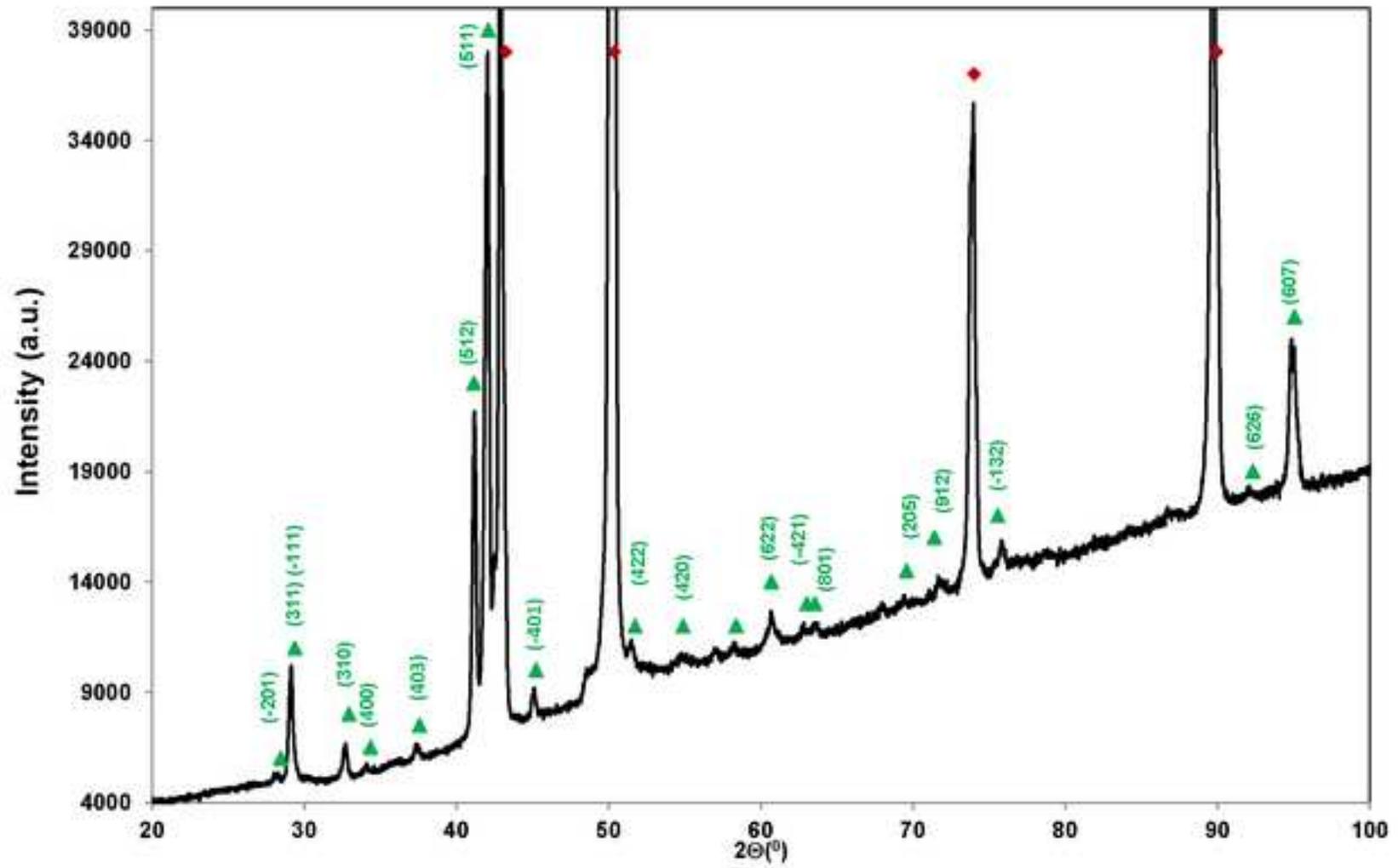


Figure 21

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