



**DOSSIER DE CANDIDATURE
POUR THESE EN COTUTELLE
POUR LA RENTREE 2021
FINANCEMENT : BOURSE**

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26 mars 2021 au plus tard.

A la Direction de la Recherche et Valorisation

secretariat.recherche@univ-littoral.fr

Titre de la thèse: Sodium and Lithium Chalcogenide Glasses/Glass-ceramics for Battery Applications: Synthesis, Structure and Conduction pathways

Laboratoire d'accueil ULCO :

*Laboratoire de physico-chimie de l'atmosphère (LPCA) / MREI 2
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59140 Dunkerque*

Directeur de thèse ULCO : *Dr. Mohammad KASSEM (directeur de thèse)
Dr. Maria BOKOVA (co-directeur de thèse)*

Si nouveau partenariat (absent ci-dessous) merci de nous indiquer l'université d'origine, le directeur de thèse, le laboratoire, ainsi que les conditions de financement du doctorant dans le pays d'origine

☒ LIBAN – Université Libanaise (2 financements)

Pour ce dispositif, merci d'indiquer en plus :

- le nom du codirecteur étranger et le laboratoire partenaire

Pr. Joumana TOUFAILY

*Laboratoire de Matériaux, Catalyse, Environnement et Méthodes analytiques (MCEMA),
Université Libanaise / Ecole Doctorale en Sciences et Technologie / Beyrouth (LIBAN)*

- Thématique :

- (1) La qualité de l'air
- (2) Le milieu aquatique
- (3) L'obésité, la nutrition et les activités sportives,
- ☒ Les énergies propres et renouvelables**
- (5) La gestion et le traitement des déchets
- (6) L'urbanisme



☐ **LIBAN – CNRS Libanais (4 financements)**

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- (5) La gestion et le traitement des déchets
- (6) L'urbanisme

☐ **ALGERIE - Université Badji Mokhtar d'Annaba (UBMA) (2 financements)**

- Thématique :

- (1) La gestion et le traitement des déchets,
- (2) L'aménagement littoral et portuaire,
- (3) Le milieu aquatique,
- (4) La surveillance et la gestion durable des Infrastructures.

☐ **MAROC - Université Hassan II / HESTIM (UH2C) (4 financements)**

- Thématique :

- (1) Economie Gestion
- (2) Sciences et Technologies

☐ **MAROC – Université Mohammed V (4 financements)**

- Thématique :

- (1) Environnement, Milieux Littoraux Marins
- (2) Sciences et technologie
- (3) Santé
- (4) Sciences Humaines et Sociales



***LABORATOIRE D'ACCUEIL**

Nom du laboratoire d'accueil : **Laboratoire de physico-chimie de l'atmosphère (LPCA)**

Nombre de HDR dans le laboratoire : **13**

Nombre de thèses encadrées dans le laboratoire (rentrée 2020) : **19**

Durée moyenne des thèses soutenues dans le laboratoire, sur la période 2015-2020 : **3 ans**

***ENCADREMENT**

Nom, Prénom du directeur de laboratoire : **Pr. Gaël Mouret**

Nom, Prénom du directeur de thèse : **Dr. Mohammad KASSEM**

Nombre de doctorats en préparation sous la direction du directeur de thèse : **2 thèses en cotutelle**

Avis détaillé du directeur de thèse :

Cette thèse s'inscrit dans le domaine des énergies propres et renouvelables. Le projet porte sur l'étude de nouveaux matériaux de chalcogénures dopés aux ions sodium et lithium pour une application en tant qu'électrolyte solide conducteur dans les batteries tout solide. Le travail implique la synthèse de ces matériaux via 2 méthodes différentes: « melt-quenching » et « ball-milling ». Une étude intensive se concentrera sur la structure de ces matériaux et sa relation avec les voies de conduction préférentielles responsables de la conductivité ionique élevée; ce dernier est un critère essentiel pour une telle application dans les batteries. Ce sujet appartient aux thématiques nouvelles de notre équipe et celles de notre laboratoire. J'émet un avis très favorable à ce projet de thèse.

Signature du directeur de thèse

Fait à Dunkerque, le 16/03/2021
Mohammad KASSEM

Avis détaillé du directeur de laboratoire :

Ce travail aborde une problématique d'actualité et d'importance qui consiste à proposer de nouveaux électrolytes solides pour le stockage de l'énergie. L'impact sociétal de ces investigations est évident. Nos besoins en stockage seront de plus en plus importants dans les prochaines années. Le savoir-faire développé dans l'équipe d'accueil est en parfait accord avec les actions envisagées, bien qu'il s'agisse d'une nouvelle thématique, défendue et présentée lors de notre dernière évaluation HCRES. Il est de fait important de soutenir ce projet de thèse. C'est également une excellente occasion de renforcer les liens entre le Liban et le LPCA via le dispositif de cotutelle que l'unité n'a que peu utilisé. C'est sans réserve que je suis favorable au financement de ces travaux de thèse.

Signature du directeur de laboratoire

Fait à Dunkerque, le 16/03/2021
Gaël Mouret



PROJET DE THESE

Intitulé du projet de thèse : *Matériaux de chalcogénures dopés aux ions sodium et lithium pour les applications d'électrolyte solide dans les batteries: Synthèse, Structure, et voies de conduction préférentielles*

Domaine scientifique : *Chimie de Matériaux / Domaine énergie*

Résumé (1/2 page maxi.) :

La proposition de thèse actuelle porte sur le développement de nouveaux matériaux de chalcogénures dopés aux ions lithium et sodium pour une application possible en tant qu'électrolytes solides (SE) dans les batteries tout-solide. Le SE sera synthétisé en utilisant la technique classique de « melt-quenching » et celle de « ball-milling ». Un effort particulier sera consacré à l'établissement des propriétés de transport ionique des matériaux à l'aide de mesures d'impédance (conductivité électrique) et d'expériences de diffusion de traceurs. Le développement des matériaux SE repose également sur des études avancées utilisant des faisceaux de synchrotron et de neutrons intenses en plus des spectroscopies de laboratoire habituelles telles que Raman, etc. Enfin, des techniques de modélisation (par exemple RMC, DFT et AIMD) seront utilisées pour relier les propriétés « conduction – structure » des électrolytes solides.

I. Context and state-of-the art

The current French energy sources, mostly generated by (i) nuclear reactors and (ii) the burning of fossil fuels/biomass, raise serious environmental and societal concerns related to the disposal of radioactive wastes, greenhouse gas emissions, etc. As a result, the utilization of alternative energy renewable sources such as sunlight and wind power becomes attractive. However, the utilization of such intermittent sources requires the development of innovative energy storage means as batteries, which are a key technology in modern society [Erreur ! Source du renvoi introuvable.,2]. Lithium-ion batteries, for example, are now the dominant rechargeable systems in the market. They are widely used in portable electronics and are considered as the perfect candidates for electric transportation such as electric and hybrid vehicles. Sodium-ion rechargeable batteries are suitable for large-scale stationary applications such as electric grids, etc.

The future technology in the battery domain lies in the development of an all-solid-state battery configuration and the key for emerging of a viable battery is the development of a solid electrolyte (SE). Replacing the currently used flammable liquid electrolyte by a safer solid electrolyte (a) eliminates the risks related to leakage, toxicity, (b) eliminates some of the costs associated with the usual carbonate based electrolytes, and (c) eventually affects the energy and power density of the battery. Requirements of such electrolyte will be high ionic ($\sigma_i > 10^{-4} \text{ S.cm}^{-1}$) and negligible electronic conductivity ($\sigma_e < 10^{-9} \text{ S.cm}^{-1}$) at room temperature, good chemical stability, chemical compatibility with the electrodes, etc.

Among the solid electrolytes, which are of interest to our project, are the sulfide based and to lower extent the selenide based SEs. These SEs present several important benefits of high conductivity, wide electrochemical window, and appropriate mechanical properties, such as formability and elastic modulus. A shortcoming of sulfide electrolytes is its low air stability. In the literature, we find the Li solid electrolytes that are classified as (a) crystals such as $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ [3], $\text{Li}_6\text{PS}_5\text{Cl}$ [4], $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ [5] $\text{Li}_{3.833}\text{Sn}_{0.833}\text{As}_{0.166}\text{S}_4$ [6], $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$ [7], (b) glass-ceramic as $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ [8], $63\text{Li}_2\text{S}\cdot 27\text{P}_2\text{S}_5\cdot 10\text{LiBr}$ [9], $70\text{Li}_2\text{S}\cdot 30\text{P}_2\text{S}_5$ ($\text{Li}_7\text{P}_3\text{S}_{11}$) [10], and (c) glasses as $30\text{Li}_2\text{S}\cdot 26\text{B}_2\text{S}_3\cdot 44\text{LiI}$ [11], $70\text{Li}_2\text{S}\cdot 30\text{P}_2\text{S}_5$ [12], $63\text{Li}_2\text{S}\cdot 36\text{SiS}_2\cdot 1\text{Li}_3\text{PO}_4$ [13], $50\text{Li}_2\text{S}\cdot 17\text{P}_2\text{S}_5\cdot 33\text{LiBH}_4$ [14]. In a similar manner, the sodium solid electrolytes, although are far less common than their Li counterparts, are occurring in the form of crystalline tetragonal Na_3PS_4 [15], the glass ceramic cubic Na_3PS_4 [16] and $94\text{Na}_3\text{PS}_4\cdot 6\text{Na}_4\text{SiS}_4$ [17], and finally the chalcogenide glass $60\text{Na}_2\text{S}\cdot 40\text{GeS}_2$ [18]. In this category, we also find the crystalline selenide based solid electrolyte Na_3PSe_4 [19].

II. Scientific aims

The scientific aim of the current PhD project is to:

- ✓ To develop new lithium and sodium SEs based on sulfide/selenide chalcogenide glasses and glass-ceramics. It is noteworthy that the ionic conductivity of these glasses is 2 to 3 orders of magnitude higher than that of oxide glasses with the same mobile ion content [20,21].

To fabricate the sulfide/selenide electrolytes, a **screening** of a wide range of compositions will be performed. In this framework, we will rely on various combinations of Li^+/Na^+ halides and sulfides/selenides with (1) chalcogenide glasses as P_2S_5 (P_2Se_5), GeS_2 (GeSe_2), Ga_2S_3 (Ga_2Se_3), As_2S_3 (As_2Se_3), etc. and (2) with cage-like chalcogen-based molecules of A_4X_n type ($\text{A} = \text{As}, \text{P}$; $\text{X} = \text{S}, \text{Se}$; $n = 3, 7, 10$) using mechanical milling technique. In theory, the cage-like structure of the molecules to be investigated should allow (i) the incorporation of large Li^+/Na^+ ion content and (ii) the high mobility of ion Li^+/Na^+ ions within the cage structure; thus resulting in glasses with high ionic conductivity, which is the essential criterion for solid electrolytes. A schematic representation of A_4X_n ($\text{A} = \text{As}, \text{P}$; $\text{X} = \text{S}, \text{Se}$; $n = 3, 7, 10$) cage-like molecules is presented in Fig. 1. The symmetric nature of those cage-like molecules makes impossible to obtain them in an amorphous form using the classical melt-quenching technique.

It is noteworthy that, via the mechanical milling technique, Hayashi et al. succeeded in obtaining an amorphous P_4S_{10} -based solid electrolyte [16] and via this same technique, we extended the glass-forming range of the quasi-binary $(\text{AgI})_x(\text{As}_2\text{Te}_3)_{1-x}$ chalcogenide glass up to $x = 0.8$ [22]. A test sample with $\text{NaX-P}_4\text{S}_n$ composition was synthesized and a room temperature conductivity of $2 \times 10^{-5} \text{ S.cm}^{-1}$ was obtained, Fig. 2. This preliminary result validates our approach.

✓ To study the nature of conductivity pathways in the sulfide/selenide chalcogenide glasses.

For example, the sulfide pseudo-binary or 3-component systems are also useful model systems to study structural features responsible for high ionic conductivity in glassy materials, in particular, the origin of preferential conduction pathways in superionic glasses. Our recent ND and HE-XRD studies, and DFT modeling of analogous $\text{Ag}_2\text{S-GeS}_2$ and $\text{Ag}_2\text{S-As}_2\text{S}_3$ systems have shown that preferential conduction pathways are formed by isolated sulfur species S_{iso} , i.e., sulfur atoms without direct bonding to germanium or arsenic atoms [23]. The S_{iso} species are connected only to silver and the $\text{Ag}/\text{S}_{\text{iso}}$ ratio is about 2. This situation is usual in $\text{Ag}_2\text{S-}$

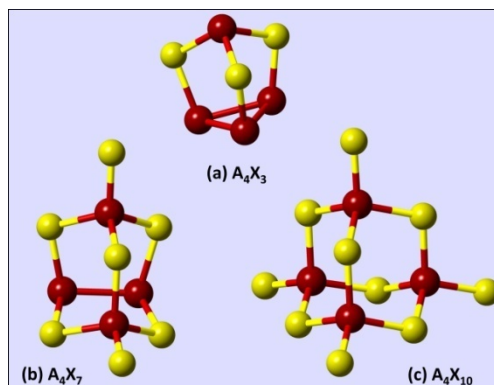


Fig. 1. Schematic representation of cage-like molecules. (a) A_4X_3 , (b) A_4X_7 , and (c) A_4X_{10}

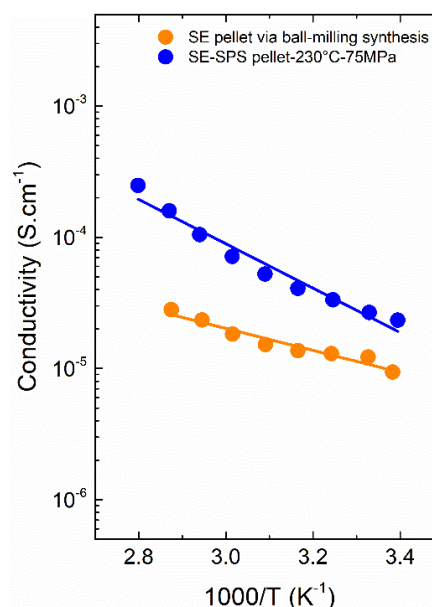


Fig. 2. Electric conductivity of sodium doped cage-like chalcogen-based molecules in the system $\text{NaX-P}_4\text{S}_n$

GeS₂ crystals when $[Ag_2S]/[GeS_2] > 2$ (Fig. 3). In argyrodite, $Ag_8GeS_6 = 4Ag_2S-1GeS_2$, one third of sulfur species are isolated from germanium and bound only to silver. In Ag_2S-GeS_2 glasses, the S_{iso} species appear far below the stoichiometric limit $[Ag_2S]/[GeS_2] = 2$ for crystals. The $(Ag_2S)_{0.45}(GeS_2)_{0.55}$ glass contains already 20% of S_{iso} , in contrast to $Ag_2GeS_3 = 1Ag_2S-1GeS_2$ crystal without S_{iso} . The S_{iso} species with connected Ag form preferential conduction pathways expanded throughout the simulation box and providing high ionic conductivity in vitreous silver thiogermanates (Fig. 4). The question appears whether similar situation exists in Li_2S/Na_2S-GeS_2 and other lithium/sodium ion-conducting glassy system and how Li^+/Na^+ ionic conductivity is related to the structural features in lithium/sodium thiogermanate, thiogallate or thioarsenate glasses.

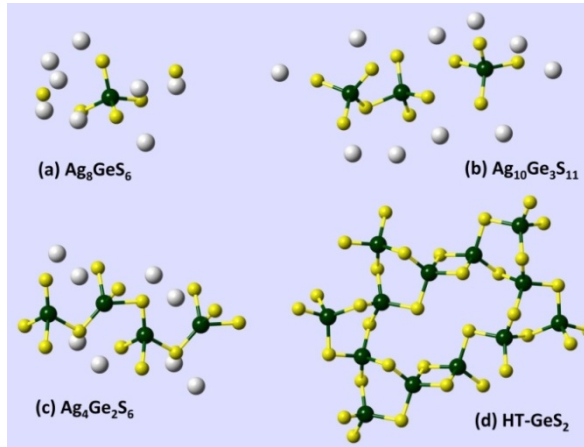


Fig. 3. Known crystalline compounds in the Ag_2S-GeS_2 system: (a) Ag_8GeS_6 , (b) $Ag_{10}Ge_3S_{11}$, (c) $Ag_4Ge_2S_6$, (d) HT- GeS_2 . The S_{iso} species appear at $[Ag_2S]/[GeS_2] > 2$.

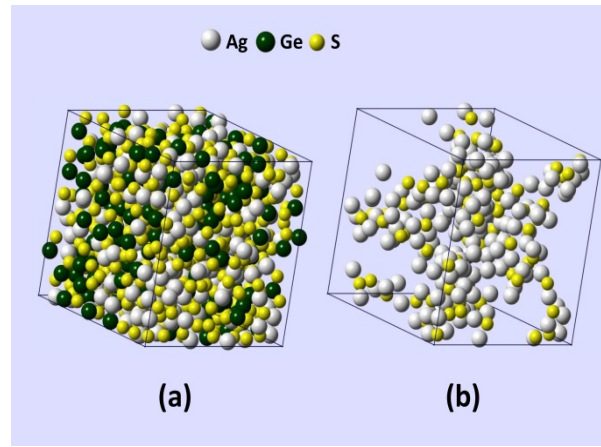


Fig. 4. DFT simulation box for a $(Ag_2S)_{0.45}(GeS_2)_{0.55}$ glass: (a) the entire box containing 1020 Ag, Ge, and S atoms, (b) a conduction pathway formed by S_{iso} species.

III. Methodology–Expected results

The development of the new Li^+/Na^+ chalcogenide glasses/glass-ceramics must go through a rigorous methodology in order to determine the occurring relationships between composition, structure, and transport properties (ionic and/or electronic). Understanding the correlation between all these characteristics and properties represents a crucial step towards acquiring the knowledge necessary for the continuous improvement of such materials. The research project can be divided into several parts:

III.1 Synthesis and macroscopic characterization of glasses/glass-ceramics

After a necessary bibliographical work, the new systems for each of the two alkali metals will be studied in order to determine the vitreous domains. The chalcogenides will be synthesized via the two techniques available to us in the LPCA laboratory and which are (i) melt-quenching and (ii) mechanical milling. Laboratory x-ray diffraction identification will be used to identify the glassy domain. The macroscopic properties include densities and the characteristic temperatures (glass transition T_g , crystallization T_x , and melting T_m) analyzed by using DSC.

III.2 Structural and electrical characterization of glasses/glass-ceramics

The structure and transport in materials is a well-developed activity in our research group and is one of the strengths of our team [21-33]. Our materials destined to solid electrolyte application are mostly amorphous. The lack of symmetry and periodicity of these compounds renders the structural characterization via the Rietveld-type structural methods inappropriate. The only possible solution is the use of direct structural and spectroscopic methods on 3G synchrotron radiation facilities and spallation/reactor neutron sources. The high-energy X-ray diffraction and pulsed neutron scattering represent ideal techniques. They allow revealing the short and medium range order correlations of the materials. To this end, proposals will be systematically written and submitted to ILL (FR), SNS (USA), APS (USA), and SPRING8 (JP) to ask for beam time. In particular, at ILL we expect to use the diffractometer for liquids and amorphous systems D4 and the SANS/WANS diffractometer D16. We estimate around 10 days/year of beam time on each instrument. Other types of laboratory structural (Mössbauer spectroscopy, Raman, XPS, etc.) and textural analysis techniques (SEM, etc) will also be used to obtain additional information. This fundamental research is essential as the structure of materials determines their corresponding properties (electrical, optical, etc.).

Also a special effort will be devoted to the study of transport properties of the synthesized materials. This can be accomplished through the combination of different analysis techniques as the complex impedance spectroscopy, the Wagner polarization method, and the radioactive tracer diffusion method. First, the complex impedance spectroscopy allows us to have information on the electrical properties of materials such that the total conductivity. However, it does not allow differentiating between ionic and electronic components of conductivity. To this end, we could employ two other complementary techniques (i) the Wagner method that allows us to measure the residual electronic conductivity and (ii) the radioactive tracer diffusion method, a very powerful experimental technique destined for studying the phenomena of ionic transport in solids. So the combination of these three techniques gives us the ability to unambiguously determine the ionic and electronic conductivity contributions. To summarize, we seek to:

- establish the ion transport properties of glasses using ac impedance measurements and ^{22}Na tracer diffusion experiments (V.G. Khlopin Radium Institute–Russia)
- reveal the short and intermediate range order in the SE using synchrotron and neutron facilities, Mössbauer and Raman spectroscopy, etc.

III.3 Modelling of glasses/glass-ceramics

The *ab initio* molecular dynamics AIMD simulations will be carried using the CP2K 5.0 program package and Born-Oppenheimer approach. The initial random configurations will be created and optimized using RMC++ code to obtain a good agreement with experimental diffraction results. Despite good agreement with the experiment, the RMC models usually yield a metallic density of states and a large number of three-fold rings. Consequently, further structural optimization will be carried out based on local minima in the energy surface determined by DFT calculations using the GGA exchange-correlation



functional PBEsol or some hybrid functionals and the consecutive basis sets SZV, DZVP and TZVP. Further AIMD simulations will include sample annealing above T_g for 30-50 ps, cooling and final modeling over 50-100 ps at room temperature. The simulations will be done using access to the HPC resources of IDRIS under the allocation 2018-A0050910639 made by GENCI (Grand Équipement National de Calcul Intensif).

IV. Description of the main phases and timetable

Our team will first focus on the fundamental studies that are essential in the proposed project. The described project will rely heavily on national and international collaborations for all characterization studies, including:

- Laboratoire de Matériaux, Catalyse, Environnement et Méthodes analytiques (MCEMA-CHAMSI), Beirut (Lebanon)
- ISIS Facility for neutron diffraction, UK
- Diamond facility for HE-XRD diffraction, UK
- Advanced Photon Source (APS), Chicago (USA)
- Spring-8 at Osaka (JAPON)

The work, related to collaborations with our colleagues from MCEMA-CHAMSI (Beirut), will begin after a, estimated period of 6 months, i.e., after the synthesis of a part of the materials by our team. They will be mainly involved in the macroscopic characterization part and also in Raman measurements.

PhD duration = 36 months	
0-3 months	Bibliographical work, training on synthesis techniques
2-24 months	Materials synthesis and macroscopic characterization: XRD, density, DSC, conductivity and radioactive tracer diffusion measurements
3-24 months	Structural characterization: HEXRD, ND, Raman, etc.
16-30 months	Materials modeling
30-36 months	PhD writing

V. References

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