Ion Conducting Chalcogenide Glasses: Transport Properties, Structural Characterization and Their Applications in Solid Electrolytes

M. Kassem, M. Bokova, D. Fontanari, A. Sokolov, P. Masselin, E. Bychkov

Laboratoire de Physico-Chimie de l'Atmosphère (LPCA), EA 4493, Université du Littoral Côte d'Opale (ULCO), 59140 Dunkerque

Introduction

- Crystalline and glassy Na^+ conducting sulphide electrolytes appear to be promising materials for all-solid-state rechargeable batteries in large-scale stationary energy storage applications
- Recent interest in superionic sodium conductors was focused on specific crystal structures consisting of 3D tunnels for fast ion migration over an open space around lattice-forming polyhedra, i.e., PS_4 or SbS_4 tetrahedra with additional cationic vacancies
- In sodium sulphide vitreous alloys, functional properties depend on the short and intermediate range order in the glass network, providing the structural basis of preferential conduction pathways and thus high ionic conductivity

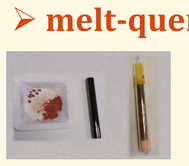
AIM:

- Understand the glass structure in the Na_2S-As_2S_3 ; Na_2S-Ga_2S_3 and Na_2S-GeS_2 systems and its relationship with other properties such as macroscopic and electrical properties.

Synthesis, Macroscopic and Electrical properties

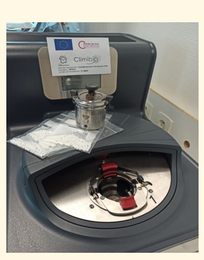
Glass synthesis

➢ melt-quenching:



✓ Silica tubes under vacuum
✓ vitreous carbon crucible

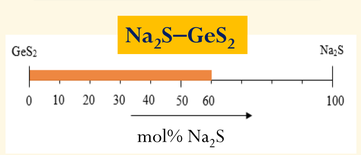
➢ mechanical milling

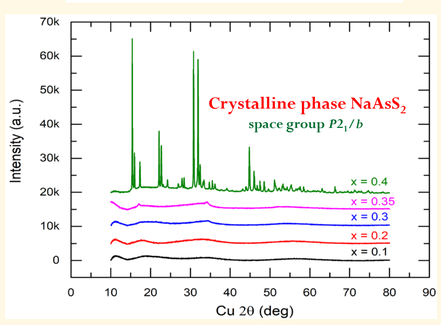


FRITSCH Pulverisette 7 premium line

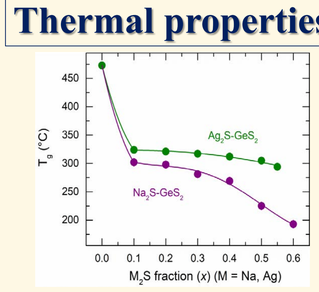
Plas-Labs Nitrogen dry-box glove box

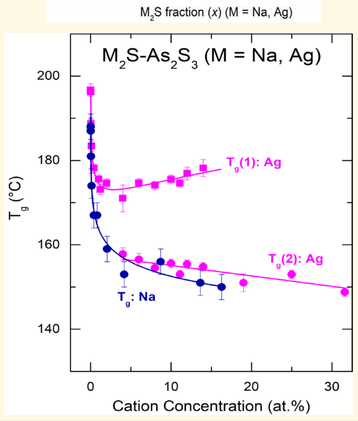
Vitreous domain



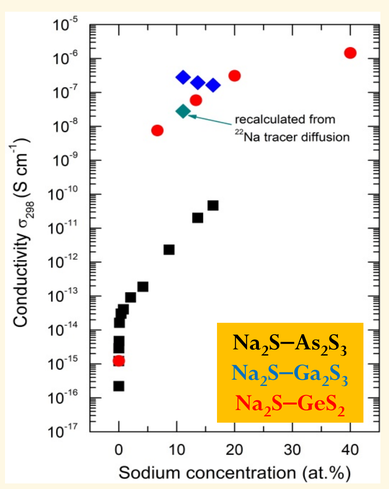


Thermal properties





Conductivity and tracer diffusion

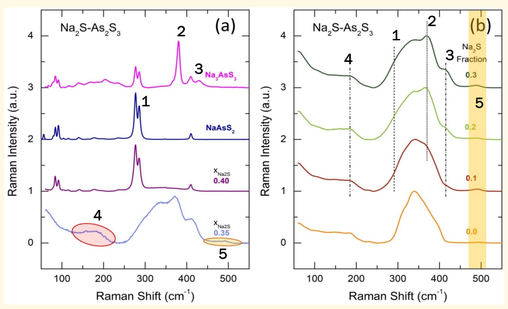


- ❑ **Conductivity of Na_2S-GeS_2 is higher than that of Na_2S-As_2S_3 (several orders of magnitude)**
- ❑ Na_2S–Ga_2S_3 : σ_{298} ↘ with mobile Na^+ content ⇒ unexpected behaviour
- ❑ Na_2S–Ga_2S_3 : $t_{Na+}H_R = 0{,}032$ ⇒ **high $\sigma_{electronic}$**
- ❑ **Traceur ^{22}Na :** the calculation of σ_i (Na_2S–Ga_2S_3) gives a conductivity value similar to that in thiogermanate system (Na_2S–GeS_2)

Tracer diffusion: I. Alekseev au V. G. Khlopin Radium Institute de St. Petersburg

Glass structure

Na_2S-As_2S_3 glasses and crystals: Raman and DFT modelling



Crystallization of monoclinic $NaAsS_2$ in glassy/crystalline composition (x = 0.4) results in a dramatic change of Raman spectra compared to the x = 0.35 composition

1 **$NaAsS_2$**

Bimodal feature at 277/286 cm^{-1} ⇒

A_1 in-phase Na-S stretching coupled As-S bending (chains)

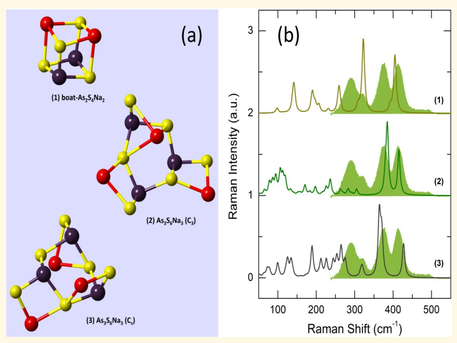
2 3 **Na_3AsS_3**

Intense peak at 380 cm^{-1} ⇒

A_1 symmetric in-phase As-S stretching in isolated ISO-AsS_3 pyramids

4 **Na-S stretching modes**

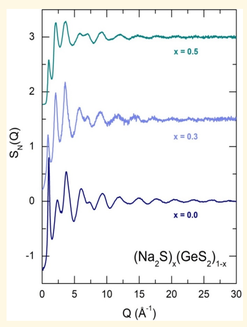
5 **S-S stretching modes**



DFT simulations of small rings involving sodium; (a) selected DFT clusters $As_mS_{2m}Na_m$: (1) edge-sharing dimer ES-$As_2S_4Na_2$ in a *boat* conformation, corner-sharing trimers $As_3S_6Na_3$ with initial (2) C_3 or (3) C_s symmetry of the central As_3S_3 ring; (b) corresponding DFT Raman spectra plotted in comparison with experimental difference spectrum for glassy $(Na_2S)_{0.35}(As_2S_3)_{0.65}$ (highlighted in green).

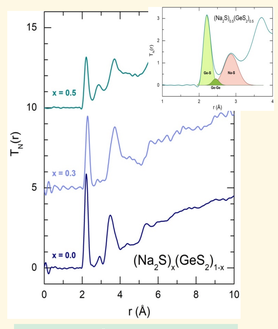
Na_2S-GeS_2: Neutron diffraction and FPMD Molecular Dynamics

Reciprocal space

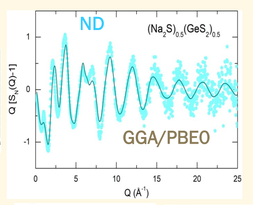


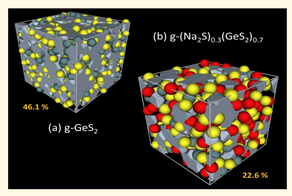
FSDP ↘
PP ↗ moves to lower Q
⇒ Expansion of the network

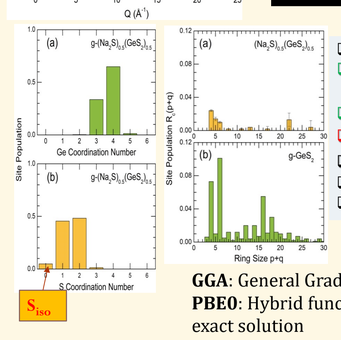
Real space



$r_{Ge\text{-}S}$ = 2.21 Å ↗ **x**
$r_{Ge\text{-}Ge}$ = 2.90 Å (ES-GeS_4) ↘ **x**
Chemical desorder χ **1-6 %** ↗ **x**
$r_{Na\text{-}S}$ = 2.8-2.9 Å







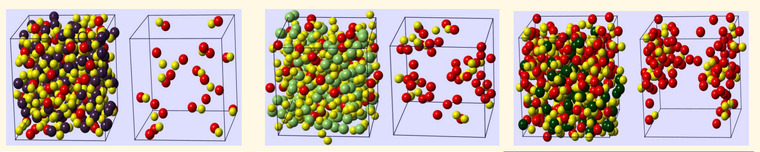
- ❑ **Tetrahedral** germanium environment ⇒ $N_{Ge\text{-}X} \approx 4$
- ❑ **Tetrahedral** sodium environment **(symmetric approximation)**

- ❑ Chemical desorder $\chi = 0.11 \pm 0.07$
- ❑ **Ge coordination:**
  ⅔ GeX_4 et ⅓ GeX_3 (X = S,Ge)
- ❑ **[S(*b*)]≈ [S(*t*)]**
- ❑ **S_{ISO} is clearly visible**
- ❑ **N_{Na-S} = 4.5 ± 0.5**
- ❑ Marked disappearance of the rings
- ❑ Reduced empty space: 22.6 vs. 46.1%

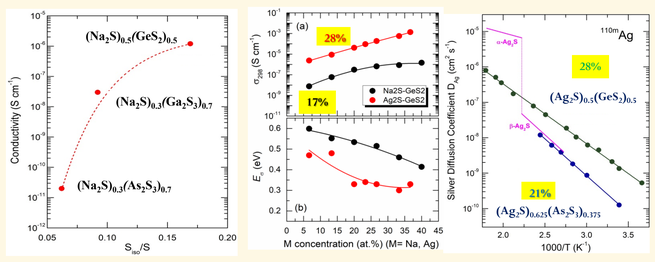
GGA: General Gradient Approximation
PBE0: Hybrid functional = PBEsol + Hartree-Fock exact solution

Structure-transport relationship

Preferential conduction pathways related to the presence of isolated sulphur



$(Na_2S)_{0.3}(As_2S_3)_{0.7}$ ⇔ **6%** S_{iso} | $(Na_2S)_{0.3}(Ga_2S_3)_{0.7}$ ⇔ **9%** S_{iso} | $(Na_2S)_{0.5}(GeS_2)_{0.5}$ ⇔ **17%** S_{iso}



Na-$S_{(iso)}$ sublattice ensures high ionic conductivity

Conclusion

The **Na_2S-As_2S_3 , Na_2S-Ga_2S_3** and **Na_2S-GeS_2** glasses and crystalline references have been synthesized and studied.

The conductivity of sodium thioarsenates and thiogermanates glasses is ionic, room temperature conductivity of Na_2S-GeS_2 is several orders of magnitude higher than that of Na_2S-As_2S_3. The conductivity nature of glassy sodium thiogallates is probably not ionic.

According to Raman studies, the identified sodium-related structural motifs in glasses only partially reflect crystalline patterns. Only about 60% of atomic species follow the thermodynamic pathway; the remaining 40% participate in the formation of structural units or structural fragments which either are not predicted by the phase diagram or appear too early with respect to a given composition.

Neutron diffraction experiments and FPMD simulations show the appearance of isolated sulphur species (sulphur without chemical bonding with glass-forming species: As, Ga, Ge) well below the compositional limits of the crystals. They are only related to sodium and the Na/S_{iso} ratio is about 2.

The binary Na_2S_{iso} units are not randomly distributed and form preferential conduction pathways. The clear correlation between the isolated sulphur fraction and the room temperature conductivity was established.

1ères journées scientifique du GdR CHALCO sur les matériaux chalcogénures et leurs applications, Dijon, 20 - 21 Juin 2022