Synthesis and characterization of glass and crystalline compositions in the $(Na_2Se)_x(As_2Se_3)_{1-x}$ chalcogenide system

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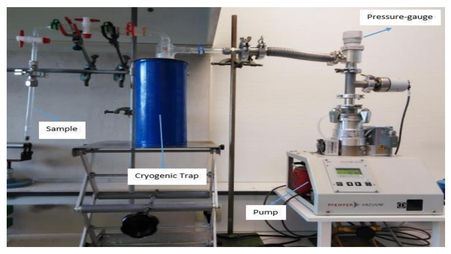
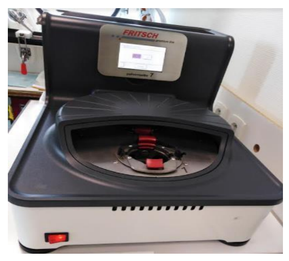
1 Introduction

- Enduring enigma surrounding the dissimilarities in ionic conductivity between glasses and crystals with the same chemical composition.
- Superionic sodium crystal conductors have three-dimensional tunnels, allowing for rapid ion migration through an unobstructed space around lattice-forming polyhedral, e.g. PX_4 or SbX_4 tetrahedra (X = S, Se), that possess additional cationic vacancies.
- The functional characteristics of sodium vitreous alloys are heavily influenced by the order present in the glass network at short and intermediate ranges, which provide the foundation for preferential conduction pathways and facilitates the high ionic.

2 Experimental Procedure





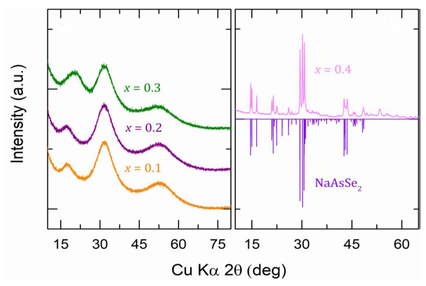
Melt quenching technique

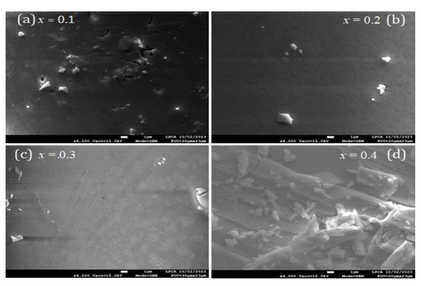
- ✓ **Starting materials**: Na, Se, and As_2Se_3 **sealed up** in silica tube **under vacuum**
- ✓ **Heated slowly in furnace** up to 700°C, **quenched** in cold water

Mechanical Milling Technique

- ✓ A planetary micro-mill Pulverisette 7 premium line (Fritsch GmbH, Germany) with zirconia jar and ZrO_2 grinding balls.

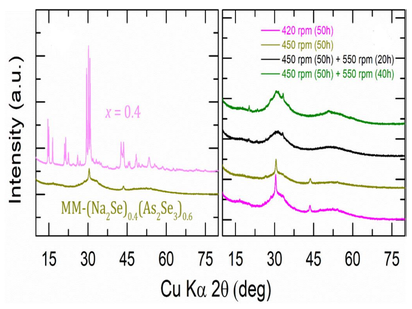
3 Vitreous Domain and Surafce morphology

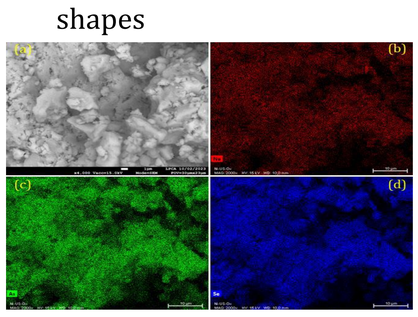




- ✓ x = 0.1, 0.2 and 0.3 : amorphous
- ✓ x = 0.4 is crystalline : orthorhombic $NaAsSe_2$

- ✓ x = 0.1 : homogenous
- ✓ $x \geq 0.2$: phase separation
- ✓ x = 0.4 : structures of various shapes





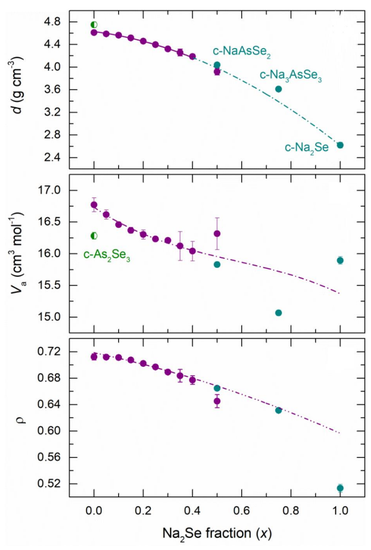
MM-$(Na_2Se)_{0.4}(As_2Se_3)_{0.6}$

- ✓ x = 0.4 samples milled at additional 550 rpm for 20h and 40h are majority amorphous : Glass Ceramic

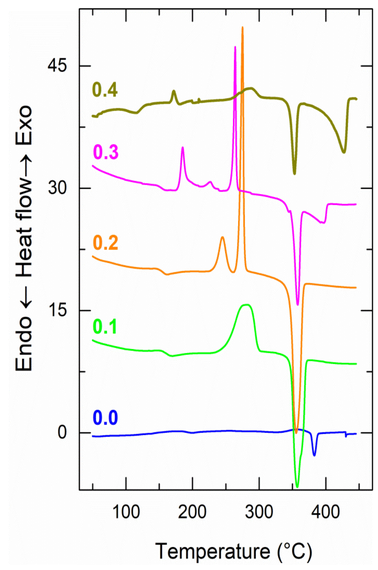
- ✓ nano and micro sizes particles
- ✓ Na, As and Se are uniformly scattered

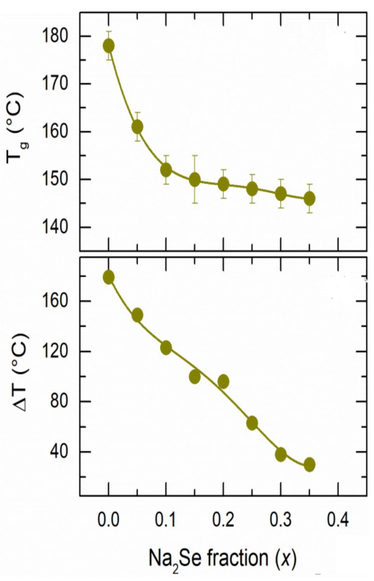
4 Macroscopic Properties

Density



Thermal Properties

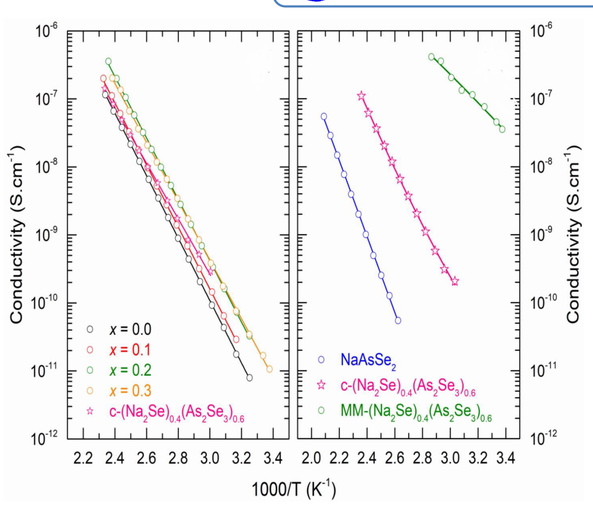


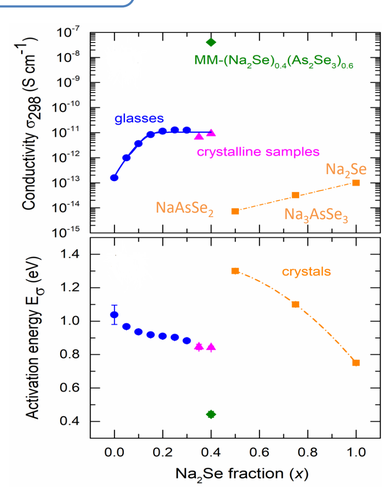


- ✓ **Density** decreased with x
- ✓ **Mean anomic volume Va** decrease : Denser packing
- ✓ ***Glass packing density P*** decrease : less compact g-As_2Se_3 network

- ✓ One Tg : Homogeneity in contrary to SEM results
- ✓ Tg decrease : Depolymerization of the host glass
- ✓ ΔT decrease : Diminished glass stability

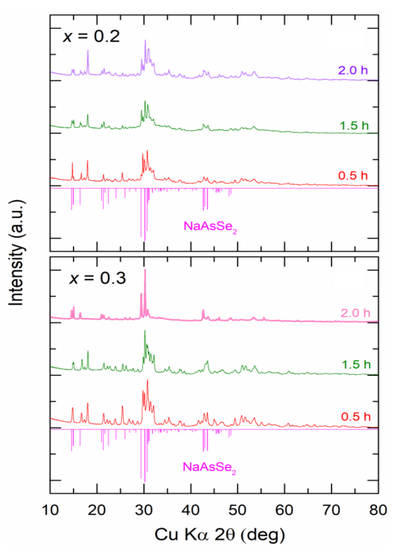
5 Electrical Properties

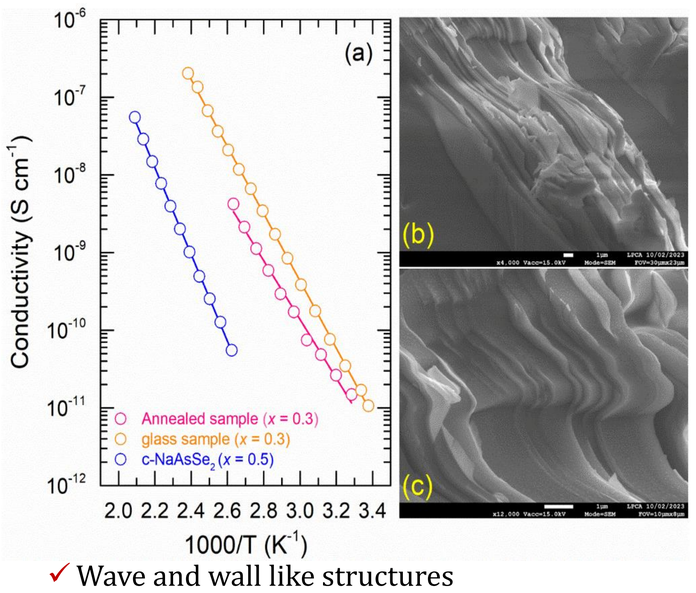




- ✓ **Arrhenius-type behaviour:** $\sigma = \sigma_0 T^{-1} \exp(-E_\sigma/kT)$
- ✓ 2 domains for glasses :
  - $0.0 \leq x \leq 0.2$: σ_{298} increases with x
  - $0.2 \leq x \leq 0.4$: σ_{298} remains invariant (inhomogeneity of the samples)
- ✓ **MM-$(Na_2Se)_{0.4}(As_2Se_3)_{0.6}$** : 4 order of magnitude increase in conductivity with lowest E_σ

6 Effect of annealing on Electrical conductivity





- ✓ x = 0.3 annealed for 2h using Microwave : $NaAsSe_2$ crystal phase

- ✓ Wave and wall like structures
- ✓ Decrease in conductivity compared to the glass counterpart

7 Conclusion

- The glass forming region is limited.
- The Tg decrease suggests depolymerization of the host network.
- The **MM-$(Na_2Se)_{0.4}(As_2Se_3)_{0.6}$** exhibited an astonishing 4 orders of magnitude increase in conductivity at room temperature.

8 Perspective

- Deciphering the glass structure :
  - Raman modelling
  - High Energy X-Ray Diffraction
  - Neutron Diffraction