Experimental report

08/11/2023

Proposal:	**EASY-852**	**Council:**	10/2020

Title: Investigation of highly conducting Na+ rich electrolytes by crystallization of thiogermanate glasses

Research area: Materials

This proposal is a new proposal

Main proposer: **Andrea Alejandra PIARRISTEGUY**

Experimental team:

Local contacts: Vivian NASSIF

Samples: 0.66Na2S-0.34GeS2

Instrument	Requested days	Allocated days	From	To
D1B	12	12	29/03/2021	30/03/2021

Abstract:

A carbon-free renewable energy future requires that next generation electrochemical energy storage systems be developed. Even as successful as the present lithium batteries have been, their dependence on flammable liquid electrolytes require that new battery systems be developed. Safer all-solid-state batteries which would not suffer from leakage, volatilization, or flammability could be an alternative. The development of all-solid-state sodium batteries should not be overlooked either. Sodium is indeed among the most abundant of all elements and significantly cheaper than lithium. The aim of the project is to identify Na+ conducting chalcogenide glass and/or glass-ceramics with performances in terms of conductivity and electrochemical stability that will allow the development of all-solid-state batteries working at ambient temperature.

We propose to study a new 0.66Na2S-0.34GeS2 conducting chalcogenide glass by neutron thermodiffractometry. These measurements will help to identify eventual phase transitions, occurrence of metastable phases that could exist on small temperature intervals as well as possible decompositions.

Investigation of highly conducting Na^+ rich electrolytes by crystallization of thiogermanate glasses

A.A. Piarristeguy[1], R. Escalier[1], V. Nassif[2,3], G. J. Cuello[4], A. Pradel[1]

[1]ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France
[2]Université Grenoble Alpes, Grenoble, France
[3]CNRS, Institut Néel, Grenoble, France
[4]Institut Laue Langevin, 6 rue Jules Horowitz, BP 156, F-38042 Grenoble, France

Abstract

A carbon-free renewable energy future requires that next generation electrochemical energy storage systems be developed. Even as successful as the present lithium batteries have been, their dependence on flammable liquid electrolytes require that new battery systems be developed. Safer all-solid-state batteries which would not suffer from leakage, volatilization, or flammability could be an alternative. The development of all-solid-state sodium batteries should not be overlooked either. Sodium is indeed among the most abundant of all elements and significantly cheaper than lithium. The aim of the project is to identify Na+ conducting chalcogenide glass and/or glass-ceramics with performances in terms of conductivity and electrochemical stability that will allow the development of all-solid-state batteries working at ambient temperature.

We propose to study a new $0.66Na_2S\text{-}0.34GeS_2$ *conducting chalcogenide glass by neutron thermodiffractometry. These measurements will help to identify eventual phase transitions, occurrence of metastable phases that could exist on small temperature intervals as well as possible decompositions.*

This experiment (EASY-852 – 12h) is the continuation of the crystallization study on $Na_2S\text{-}GeS_2$ glasses corresponding to the proposal 6-05-1026.

Experimental Details

In order to stabilize a single phase during the crystallization of $Na_2S\text{-}GeS_2$ glasses with a high Na_2S content and a high conductivity, a new glass composition $0.66Na_2S\text{-}0.34GeS_2$ has been elaborated.

The ball-milling technique was used to synthesize the $0.66Na_2S\text{-}0.34GeS_2$ glass. Stoichiometric ratios of the Na_2S (Sigma-Aldrich) and GeS_2 (precursor prepared in the laboratory) reagents were intimately mixed in a mortar and pestle and placed in a 20-mL ZrO_2 ball-milling jar along with 80 (diameter = 5 mm) ZrO_2 balls. The batch weighed 3 g, with a ball-to-powder weight ratio of 11/1. The jars were placed in a planetary ball mill (Pulverisette 7 Premium Line, Fritsch) in an argon atmosphere in a glove box to reduce oxidation. The synthesis of this sample was done in three steps. We started at $0.60Na_2S\text{-}0.40GeS_2$ composition, and by addition of Na_2S, we went to $0.63Na_2S\text{-}0.37GeS_2$ and then to $0.66Na_2S\text{-}0.34GeS_2$. 12 rotation cycles of 3 h (36 h of milling) at 510 rpm were scheduled with break and milling the block between each cycle. After every two cycles, a small amount of the powder (0.1 g) has been taken out in order to verify the amorphous nature by x-ray diffraction (XRD).

Neutron thermodiffraction was used to study the crystallization process occurring in the glasses upon heating. The neutron diffraction experiments were performed using the D1B instrument at the Institute Laue–Langevin in Grenoble (France) with a nominal wavelength of 1.28Å. The samples were placed in a cylindrical silica container (6 mm inner diameter and 1 mm thick) sealed under secondary vacuum (10^{-5} mbar). A standard ILL furnace (vertical top loading furnace) was used for the experiments. Neutron diffraction spectra were continuously collected on the amorphous samples subjected to the following heating ramps: i) from room temperature to 513K at a rate of 10K/min and then from 513K to 623K at a lower rate of 0.2K/min. For the cooling process, the furnace was simply switched off to allow the samples to reach room temperature in ‘free fall’.

Results

In the thermodiffractograms of the $0.66Na_2S\text{-}0.34GeS_2$ sample, the first reflections appear at ~ 502 K and they would be identifying by the Na_4GeS_4 crystalline phase (Fig. 1). The five main peaks of this phase are at $2\theta = 21.8°$, 23.4°, 25.9°, 26.7°, and 35.0° and the stability domain of this phase is at least until the end of the heat treatment, *i.e.* at 623K.

On the other hand, it appears that the investigated temperature range (room temperature - 623 K) was not large enough to reach the complete crystallization of the sample.

Figure 2 shows the neutron diffractogram for the highest temperature, *i.e.*, 623K. We observe that there is an important contribution comes from the silica container. For the next experiments, corresponding to hygroscopic samples, a reduction of the tube wall thickness will be necessary in order to improve the quality of the measurement.

The $0.66Na_2S$-$0.34GeS_2$ glass presents a large conductivity (~10^{-4} S/cm at room temperature) [1], which could be considered as a potential electrolyte for the development of all solid-state batteries working at ambient temperatures. In particular, the crystallization of a single phase in a very wide range of temperatures (~300K) will allow (if we obtain a higher conductivity for this glass-ceramic with the Na_4GeS_4 crystalline phase) to use $0.66Na_2S$-$0.34GeS_2$ glassy powder to prepare a glass-ceramic composed of Na_4GeS_4 crystalline phase under pressure by spark plasma sintering as in ref. [2] in order to elaborate a monolithic battery.

Nevertheless, with these first analyses, we cannot guarantee that other secondary phases are also present.

***Figure 1**: 2D plots of the powder thermodiffractograms for the $0.66Na_2S$-$0.34Ge\ S_2$ sample.*

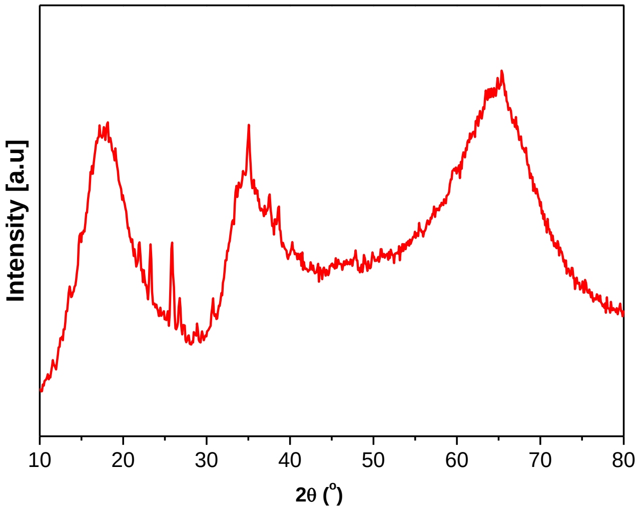

***Figure 2**: Powder neutron diffractogram for the $0.66Na_2S$-$0.34Ge\ S_2$ sample at 623K.*

References

[1] M. Micoulaut, A. Piarristeguy, O. Masson, L.-M. Poitras, R. Escalier, A. Kachmar, A. Pradel, PRB 108, (2023) 144205.

[2] F. Lalère, J.B. Leriche, M. Courty, S. Boulineau, V. Viallet, C. Masquelier, V. Seznec , Journal of Power Sources 247 (2014) 975-980.