Experimental report

09/11/2023

Proposal: **6-05-1026** **Council:** 4/2020

Title: New glass-ceramics of chalcogenidematerials for electrochemical energy storage

Research area: Materials

This proposal is a new proposal

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Samples: Na_3PS_4, $Na_7P_3S_{11}$, $Na_3P_{0.62}As_{0.38}S_4$ and Na_3PSe_4

Instrument	Requested days	Allocated days	From	To
D20	5	3	26/02/2021	01/03/2021
D1B	5	0		

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-ceramics with performances in terms of conductivity and electrochemical stability that will allow the development of all-solid-state batteries working at ambient temperature and suitable for nomad application, vehicle propulsion application and domestic use to store the energy arising from intermittent source.

We propose to study Na-P-S(e) and Na-As-P-S systems by neutron thermodiffractometry. These measurements will help to identify new metastable phases which could be interesting as solid electrolytes.

New glass-ceramics of chalcogenide materials for electrochemical energy storage

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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 requires 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 different Na-based ionic conductive systems (oxide and chalcogenide glasses) 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 and probably new interesting materials as solid electrolytes.

Experimental Details

Three glasses (oxide or chalcogenide) of nominal compositions $0.25Na_2O$-$0.75GeO_4$, $Na_7P_3S_{11}$ and $0.63Na_2S$-$0.37GeS_2$ were synthesized by melt quenching technique for the oxide glass and by ball-milling technique for chalcogenide glasses.

Neutron thermodiffraction was used to study the crystallization process occurring in the glasses upon heating. The neutron diffraction experiments were performed using the D20 instrument at the Institute Laue–Langevin in Grenoble (France) with a nominal wavelength of 1.51Å. As the compositions are air sensitive due to the large amount of Na, the powered 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. In all samples, previous neutron thermodiffraction measurements were carried out for each sample in order to optimize the temperature range to be studied.

Neutron diffraction spectra were continuously collected on samples subjected to the following heating ramps: i) $0.25Na_2O$-$0.75GeO_4$: from room temperature to 403K at a rate of 10K/min and then from 403K to 623K at a lower rate of 0.2K/min, ii) $Na_7P_3S_{11}$ from room temperature to 358 K at a rate of 10K/min and then from 358 K to 423K at a lower rate of 0.2K/min, and iii) $0.63Na_2S$-$0.37GeS_2$: from room temperature to 418K at a rate of 10K/min and then from 418K to 568K at a lower rate of 0.25K/min. For all 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 $Na_7P_3S_{11}$ sample, the first reflections appear at ~ 400 K and they would be identifying by the Na_3PS_4 crystalline phase (Fig. 1). The six main peaks of this phase are at $2\theta = 31.1°, 36.1°, 44.7°, 48.5°, 55.6°$, and $58.8°$. However, their existence domain is very narrow (~ 15 K), because a second crystalline phase start to appear at 413K (see Fig. 1 - reflection at $2\theta = 32.2°$). This second phase co-exists with the first crystalline phase, which signature, such as the peak intensity, does not change. On the other hand, it appears that the investigated temperature range was not large enough to reach the complete crystallization of the sample.

These results are not very interesting for the development of a monolithic battery where the chalcogenide electrolyte (glass or glass-ceramic with a unique conductive crystalline phase) with others materials (active material and carbon) will be prepare under pressure/temperature by spark plasma sintering as in ref. [1]. The crystallization of possible new phases could change the overall conductivity of the system, modify the cycling, electrochemical stability, …

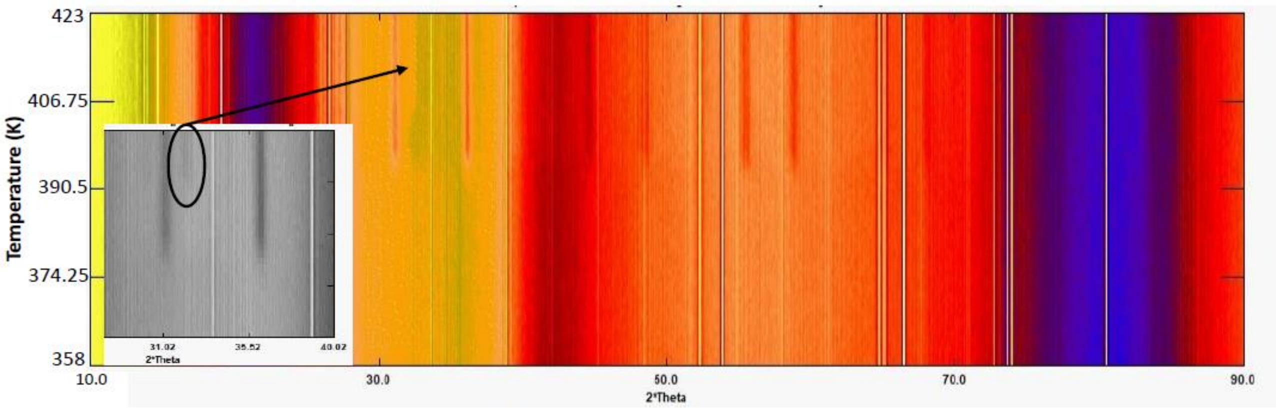

Figure 1*: 2D plots of the powder thermodiffractograms for the* $Na_7P_3S_{11}$ *sample. The strong reflections observed even before the crystallization are likely coming from the sample environment.*

Figure 2 shows the crystallization process of the $0.25Na_2O$-$0.75GeO_4$ glass. The main reflections at $2\theta = 21.7°$, 30.5°, 48.5° and 56.8° appear at ~ 457 K accompanied by low intensity peaks (31.9°, 35.3°, 36.8°, 40.6°, 44.2°, 52.9° and 56.7°). Not second crystalline phase is observed until the higher measured temperature, *i.e.*, 623 K.

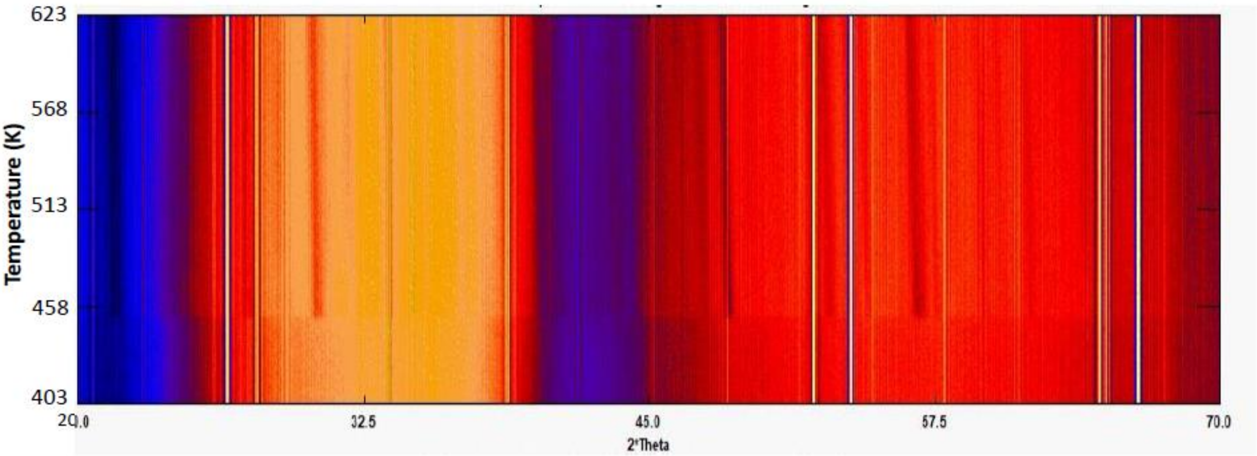

Figure 2*: 2D plots of the powder thermodiffractograms for the* $0.25Na_2O$-$0.75GeO_4$ *sample. The strong reflections observed even before the crystallization are likely coming from the sample environment.*

The crystallization process of $0.63Na_2S$-$0.37GeS_2$ glass resulted very complex with the appearance of multiple crystalline phases difficult to index. Therefore, a new glass composition $0.66Na_2S$-$0.34GeS_2$ (with a higher Na_2S content and a high conductivity [2]) has been elaborated in order to try stabilize a single crystalline phase during the crystallization. This glass was measured in the experiment EASY-852 (see experimental report).

References

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

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