Experimental report

07/04/2020

Proposal:	**CRG-2449**	**Council:**	4/2017
Title:	Crystallization of GexTe100-x amorphous films		
Research area:			

This proposal is a new proposal

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Samples: GexTe100-x with x=15, 24, 30, 37 and 48 at.%Ge
10Na2O-50V2O5-25
6B2O3-14
4P2O5
33Na2OGe2O4-47P2O5

Instrument	Requested days	Allocated days	From	To
D1B	4	2	01/04/2018	03/04/2018

Abstract:

Electrolytes and sodium all solid-state batteries (performed experiment)

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Initial Experiment: Crystallization of Ge_xTe_{100-x} amorphous films

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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 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. However, the development of all solid state battery encounters some difficulties. As a matter of fact, solid electrode/electrolyte interfaces are usually easily deteriorated during charge/discharge processes. In order to overcome this problem, we propose to develop all solid-state batteries based on the use of glasses or glass-ceramics for both the electrolyte and the electrodes. Moreover, the use of a common glass or glass ceramic network for both electrolyte and electrode could help in producing a better interface delocalization and an ideally compacted monolith. The first goal of this project is to develop an all solid-state battery that would work at high temperature (T> 200°C). It will be based on the use of oxide materials and will help in validating the concept of "monolith solid-state batteries".

In this context, we would like to investigate the crystallization process of two oxide glasses: $33Na_2O$-$20Ge_2O4$-$47P_2O_5$ (electrolyte) and $10Na_2O$-$50V_2O_5$-$25,6B_2O_3$-$14,4P_2O_5$ (electrode). The beginning of the crystallization as well as thermal stability of each crystallised phase are two important parameters when assembling a battery.

Experimental Details

Two glasses of nominal compositions $33Na_2O$-$20Ge_2O_4$-$47P_2O_5$ and $10Na_2O$-$50V_2O_5$-$25.6B_2O_3$-$14.4P_2O_5$ were prepared from 1N8 (98% purity) di-ammonium hydrogen phosphate (Sigma-Aldrich), 3N5 (99.95 % purity) sodium carbonate (Sigma-Aldrich), 2N6 (99.6 % purity) vanadium(V) oxide (Sigma-Aldrich), GeO_2 (homemade) and 5N (99.999 % purity) ammonium phosphate monobasic (Sigma-Aldrich) powders. The materials were synthesized by placing the powdered elements in stoichiometric proportions in a 90/10 Pt/Rh crucible. The batch was then heated at 5K/min up to T = 1173K / 1523K for the Na_2O-V_2O_5-B_2O_3-P_2O_5 and Na_2O-Ge_2O_4-P_2O_5 systems respectively. It was then quenched between two brass plates to obtain the glassy materials.

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 non-sealed cylindrical vanadium containers with a diameter of 8.0 mm. A standard ILL furnace (vertical top loading furnace) was used for the experiments. Neutron diffraction spectra were continuously collected on samples subjected to the following heating ramps: i) $33Na_2O$-$20Ge_2O_4$-$47P_2O_5$: from room temperature to 793K at a rate of 10K/min and then from 793K to 943K at a lower rate of 0.25K/min, and ii) $10Na_2O$-$50V_2O_5$-$25.6B_2O_3$-$14.4P_2O_5$: from room temperature to 508K at a rate of 10K/min and then from 508K to 724K at a lower rate of 0.25K/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 $33Na_2O$-$20Ge_2O_4$-$47P_2O_5$ sample, the first reflections of the crystalline phase $NaGe_2(PO_4)_3$ (rhombohedral structure, space group R-3c [1]) appear at ~ 842.15 K (Fig. 1). The four main peaks of this phase are at 2θ = 20.8°, 24.9°, 38.1° and 45.1° and the stability domain of this phase is at least until the end of the heat treatment, *i.e.* at 943K.

The $33Na_2O$-$20Ge_2O_4$-$47P_2O_5$ glass and $33Na_2O$-$20Ge_2O_4$-$47P_2O_5$ partially crystallized glass (with the $NaGe_2(PO_4)_3$ crystalline phase) present similar and rather large conductivity.(~ $10^{-4.5}$S/cm at 200°C). Owing to the stability of the $NaGe_2(PO_4)_3$ phase and the absence of any other metastable/stable phases in the whole investigated temperature domain, the $33Na_2O$-$20Ge_2O_4$-$47P_2O_5$ composition could be considered as a potential electrolyte for the development of all solid state batteries working at intermediate temperatures. In particular, the $33Na_2O$-$20Ge_2O_4$-$47P_2O_5$ glassy powder could be used to prepare a glass-ceramic composed of $NaGe_2(PO_4)_3$ crystalline phase under pressure and/or temperature. Such a glass-ceramic could be used to elaborate a monolithic battery.

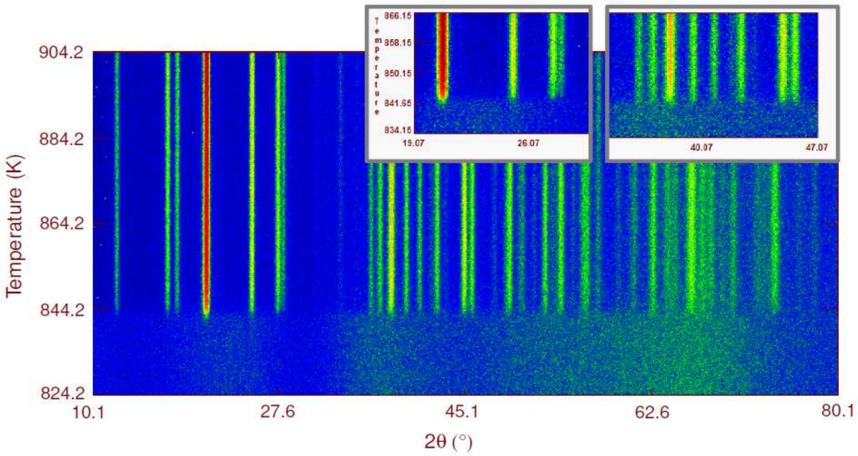

***Figure 1**: 2D plots of the powder thermodiffractograms for the $33Na_2O$-$20Ge_2O_4$-$47P_2O_5$ sample.*

Figure 2 shows the crystallization process of the $10Na_2O$-$50V_2O_5$-$25.6B_2O_3$-$14.4P_2O_5$ glass, which involves several steps. The main reflection at 2θ = 32.0° and the small reflections at 12.7°; 18.8° and 41.6° that appear at ~ 555 K could be the signature of crystalline NaV_6O_{15} phase. The thermodiffractograms also show that a second crystalline phase with two main reflections at 2θ = 20.1° and 32.7° and many minor ones appears at ~ 700 K. This second phase co-exists with the first crystalline phase, which signature, such as the peak intensity, does not change. To date, it was not possible to identify the second phase on the basis of the two main intense reflections without ambiguity.

Finally, it appeared that the investigated temperature range (room temperature - 724 K) was not large enough to reach the complete crystallization of the sample. Therefore, we cannot guarantee that other new stable/metastable phases will not appear at higher temperatures.

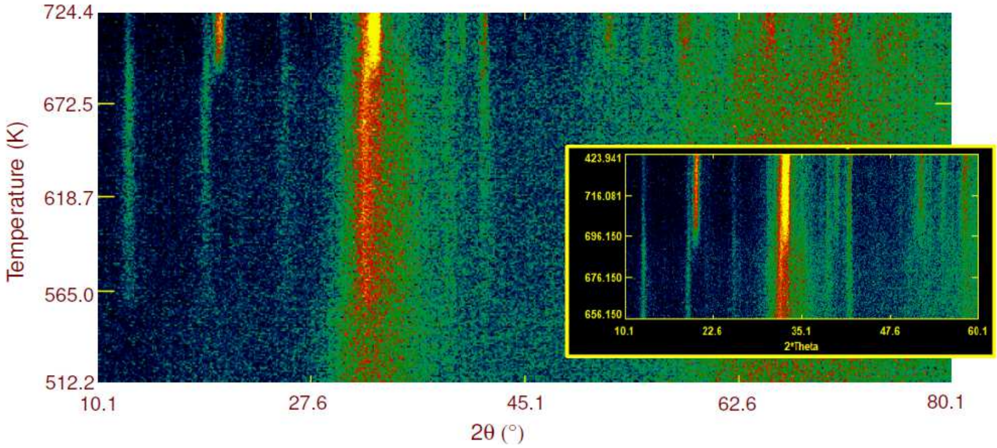

***Figure 2:** 2D plots of the powder thermodiffractogramsn for the $10Na_2O$-$50V_2O_5$-$25.6B_2O_3$-$14.4P_2O_5$ sample. In the insert is shown a magnification of the 2D mapping of the diffraction data corresponding to the beginning of the second crystalline phase.*

References

[1] L. Hagman, P. Kierkegaard, Acta Chemica Scandinavica 22 (1968) 1822-1932.