Experimental report

16/11/2016

Proposal: **6-05-948** **Council:** 4/2014

Title: Crystallisation of chalcogenide materials for electrochemical energy storage

Research area: Materials

This proposal is a new proposal

Main proposer: **Andrea Alejandra PIARRISTEGUY**

Experimental team: Andrea Alejandra PIARRISTEGUY

Local contacts: Gabriel Julio CUELLO
Vivian NASSIF

Samples: As_2Te_3
Na_3PS_4
Na_4GeS_4
$Na_6Ge_2S_7$
$AsTe_3$
$Cu_{15}As_{20}Te_{65}$

Instrument	Requested days	Allocated days	From	To
D1B	4	4	04/12/2014	08/12/2014

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 sulfide glasses and 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-Ge-S and Na-P-S systems by neutron thermodiffractometry. These measurements will help to identify new metastable phases which could be interesting as solid electrolytes.

Crystallisation of chalcogenide materials for energy storage

A.A. Piarristeguy[1], V. Nassif[2,3], G. J. Cuello[4], J.B. Vaney[1,5], C. Candolfi[5], M. Ribes[1], A. Pradel[1]

[1]Institut Charles Gerhardt (ICG), UMR 5253 CNRS-Université Montpellier 2, 2 place E. Bataillon, F-34095 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.
[5]Institut Jean Lamour (IJL), UMR 7198 CNRS-Université de Lorraine, France.

Abstract

The search for efficient thermoelectric compounds has witnessed a resurgence of interest over the last two decades. These materials must meet two conflicting requirements: the thermal transport should mimic that of a glass while the electrical properties should be those of crystalline solids. One possible strategy resides in choosing materials which show inherent low thermal conductivity values. Amorphous compounds are then a natural choice since they feature the lowest thermal conductivity values among known solids. Yet, their high electrical resistivity prevented so far to achieve high thermoelectric performance. We recently initiated a study on the $Cu_xAs_{40-x}Te_{60}$ *system with the aim at tuning the electrical resistivity through varying the Cu concentration and controlled growing of highly conducting crystalline phases within the glass matrix. Preliminary results show that this is indeed the case opening up new possibilities to reach higher thermoelectric efficiency. In this context, we would like to investigate in more detail the stabilization of metastable and/or unreported crystalline phases in the Cu-As-Te system, which could exhibit interesting thermoelectric properties.*

Experimental Details

Three samples of compositions As_2Te_3, $AsTe_3$, $Cu_{15}As_{20}Te_{65}$ were prepared from 5N5 (99.9995% purity) copper (Sigma-Aldrich) pellets, 4N5 (99.995% purity) tellurium (5NPlus), 4N (99.99% purity) arsenic (Goodfellow) and 4N selenium (Sigma-Aldrich) powders. Different preparation techniques, as melt quenching or twin roller quenching, were used depending of the composition (for more details of sample preparation refer to Refs. [1, 2]. Neutron thermodiffraction was used to study the crystallization process occurring in the glasses upon heating ($AsTe_3$ and $Cu_{15}As_{20}Te_{65}$) and to identify the low-temperature crystal structure in As_2Te_3 crystalline sample. The neutron diffraction experiments were performed using the D1B instrument at the Institut Laue–Langevin in Grenoble (France) with a nominal wavelength of 2.52Å. The samples were placed in non-sealed cylindrical vanadium containers with an inner diameter of 7.6 mm, under helium exchange gas. For As_2Te_3 sample, a standard ILL cryofurnace and its control system allowed to perform cooling ramps at a rate of about 3.8 K/min from 300 K down to 20 K, with annealing steps of about 1-2 h at 300, 190, 120 and 20 K. For $AsTe_3$ and $Cu_{15}As_{20}Te_{65}$ samples, neutron diffraction spectra were continuously collected using a standard ILL furnace (vertical top loading furnace) on samples subjected to the following heating ramps: from room temperature to 363K at a rate of 5 K/min and then from 363 K to 473 K at a lower rate of 0.1 K/min.

Results

*As_2Te_3

Figure 1(a) shows the neutron powder data for β-As_2Te_3 between 10° and 60° at 298 K and 20 K. A rapid examination of the thermodiffractograms, shown in the inset of Fig. 1(a), led to the conclusion that only **one structural transition from β-As_2Te_3 to an unknown structure occurs around 200 K (structural transition β→ β')**, close to the temperature onset seen in transport and calorimetric experiments [3].

The combination of the X-ray and neutron diffraction measurements at 20 K allowed us to index a primitive monoclinic unit cell (phase β′-As_2Te_3) with a = 6.982(1) Å, b = 16.187(1) Å, c = 10.232(1) Å, and β = 103.47(1)°. This final unit cell is not only a monoclinic distortion of the 300 K hexagonal unit cell but also a superstructure with a $b_m = 4_{ah}$ modulation (see Ref. [3] for more details). In both patterns (X-ray and neutron), additional reflections with temperature independent intensities were ascribed to AsTe (0.5% mass) and arselonith As_2O_3 (0.1% mass). In neutron powder diffraction patterns (Figure 1(b)), As_2O_5 (0.1% mass) could also be detected while very weak peaks remained unindexed. Claudetite-As_2O_3 was envisaged as an extra secondary phase to index these remaining peaks, but its occurrence could not be firmly established. Systematic extinctions ((0k0), k odd) led to the choice of centrosymmetric P21/m as the space group. (See Ref. [3] for more details).

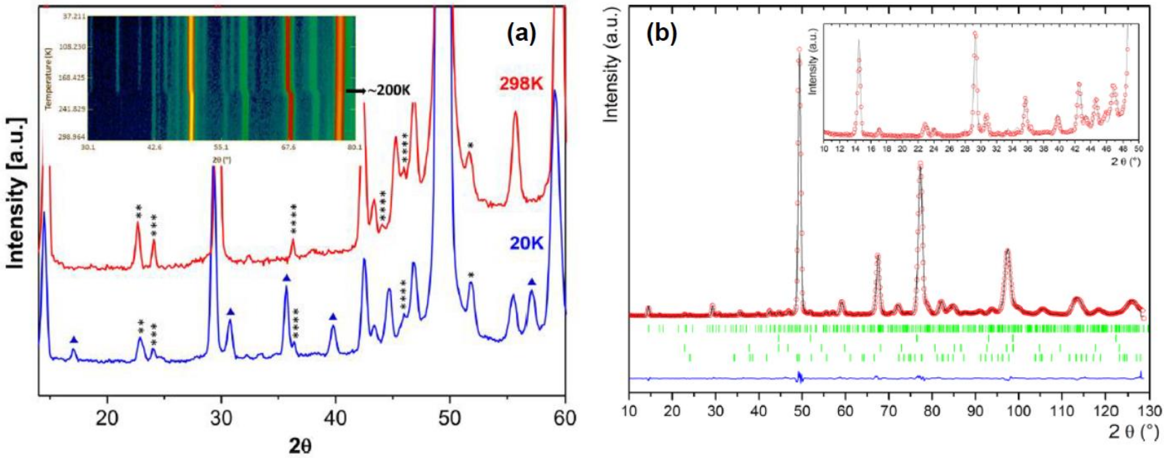

Figure 1**: (a) Neutron powder data for β-As_2Te_3 between 10° and 60° at 298 K and 20 K. Inset: 2D plot of the whole thermodiffraction data for β-As_2Te_3. (*, AsTe; **, As_2O_3 (arselonith); ***, As_2O_5; *, unidentified impurities; ▲, unindexed modulated reflections when using a base-centered monoclinic unit cell with a = 6.984 Å, b = 4.049 Å, c = 10.238 Å, β = 103.45°). (b) Experimental neutron pattern for β′-As_2Te_3 at 20 K and its Rietveld analyses. The open red circles are the experimental data. The black line is the calculated pattern. The bottom blue line is the difference, and the green ticks stand for the Bragg reflections of β′-As_2Te_3 (first row) and secondary phases AsTe (second row), arselonith As_2O_3 (third row), and As_2O_5 (fourth row). The fit to the weak intensity lines in the low angle region can be seen in the inset.*

*$Cu_{15}As_{20}Te_{65}$

Figure 2 shows the crystallization process for the glass $Cu_{15}As_{20}Te_{65}$ that involves several steps. At about 394 K, a first crystalline phase corresponding to $AsTe_3$ appears; this **phase has not been reported before.** The three main peaks are at 2θ = 48.0°; 65.4° and 75.1° and have relative intensities of 100%, 35% and 34%, respectively. These intensities increase with temperature up to about 445 K and then decrease until the end of the thermal treatment, at ~ 465 K. The thermodiffractograms also show a second metastable crystalline phase appearing at ~ 430 K, thus the $AsTe_3$ phase is the unique present phase over a temperature range of ~ 36 K. The most intense reflections of this second phase (2θ = 52.1°; 58.8° and 77.8°) do not correspond to any of the crystalline phases α-As_2Te_3, β-As_2Te_3, Te or AsTe. We also observe that this second phase does not have any effect on the crystalline phase $AsTe_3$ (for example, no changes in the peak intensity) and the temperature at which it starts disappearing corresponds to the crystallization temperature of the other crystalline phases (~ 470 K) (see Fig. 2).

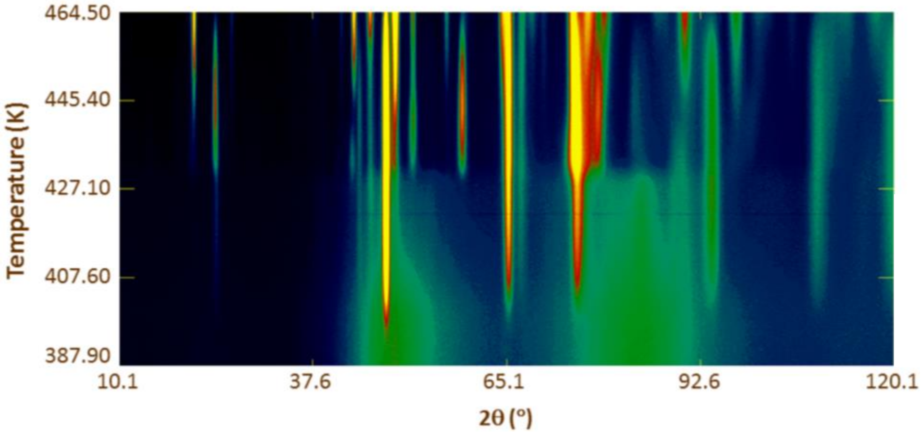

***Figure 2**: 2D plot of the powder thermodiffraction data collected between 10° and 120° as a function of temperature for the $Cu_{15}As_{20}Te_{65}$ sample.*

References

[1] J. B. Vaney, A.A. Piarristeguy, A. Pradel, E. Alleno, B. Lenoir, C. Candolfi, A. Dauscher, A.P. Gonçalves, E.B. Lopes, G. Delaizir, J. Monnier, C. Godart; "*Thermal stability and thermoelectric properties of $Cu_xAs_{40-x}Te_{60-y}Se_y$ semiconducting glasses*", Journal of Solid State Chemistry 203 (2013) 212–217.

[2] J. B. Vaney, G. Delaizir, E. Alleno, O. Rouleau, A.A. Piarristeguy, J. Monnier, C. Godart, M. Ribes, R. Escalier, A. Pradel, A. Gonçalves, E. B. Lopes, G. J. Cuello, P. Ziolkowski, E. Müller, C. Candolfi, A. Dauscher, B. Lenoir ; "*A comprehensive study of the crystallization of Cu-As-Te glasses: microstructure and thermoelectric properties*", Journal of Materials Chemistry A 1 (2013) 8190-8200.

[3] C. Morin, S. Corallini, J. Carreaud, J. B. Vaney, G. Delaizir, J. C. Crivello, E.B. Lopes, A. A. Piarristeguy, J. Monnier, C. Candolfi, V. Nassif, G. Cuello, A. Pradel, A. P. Goncalves, B. Lenoir, E. Alleno; "*Polymorphism in thermoelectric As_2Te_3*", Inorganic Chemistry 54 (2015) 9936-9947.