50 years of the Institute of High Pressure Physics Polish Academy of Sciences

'RoadMaP' X-PressMatter Lab: Soft Matter, Food & Glasses under Pressure

Anniversary Symposium „Unipress 50”

Glassy materials for electrodes in new generation batteries. The impact of High Pressure & Temperature transformation

Sylwester J Rzoska, Aleksander Szpakiewicz-Szatan, Szymon Starzonek, Aleksandra Drozd-Rzoska and Michał Bućkowski

X-PressMatter Lab: Innovation Park in Celestynów, IHPP PAS: Park Innowacyjny IWC PAN w Celestynowie

(*) The cooperation with Jerzy E. Garbarczyk group, Faculty of Physics, Warsaw University of Technology (WUT)

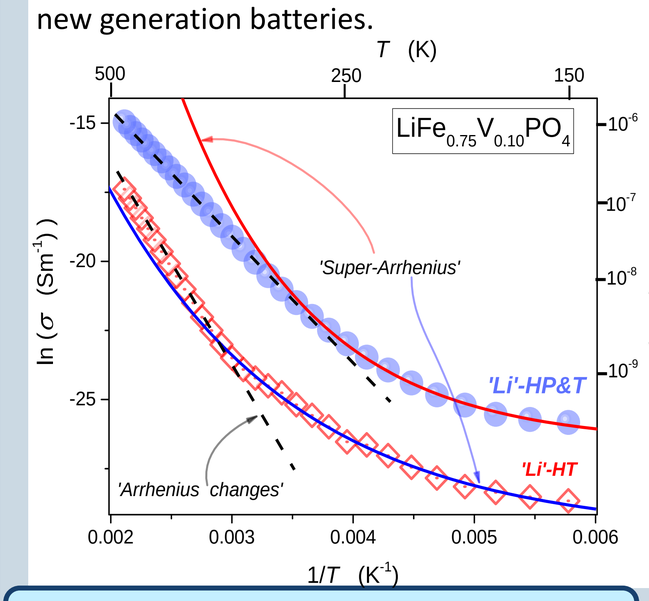
High Pressure Treatment - introduction

According to DARPA agency (USA), high compressing can increase the number of useful materials 10x, often with exotic, even breakthrough, features. Unfortunately, it requires pressures of the order of the Earth's Core (~ 350 GPa) matched with extreme temperatures, and possible amounts are limited to micrograms. After decompressing, the unusual properties disappear. Decades of work on obtaining the exceptional material in normal conditions and in larger quantities begin. Successful or not.

The situation for solid amorphous glasses is qualitatively different. HP&T annealing (‘aging’) several degrees below the glass temperature (T_g) for about an hour at pressure of only ~ 1GPa can yield unusual properties preserved after decompressing. In IHPP PAS there are HP&T processors operating up to P ~ <2.2 GPa, for T <1600°C and volumes even V ~ 1 L. All the limitations mentioned above disappear.

The first studies of this type were acquired out in cooperation with Profs. Morten Smedskjaer (Aalborg Univ. Denmark), John C. Mauro (Corning Glass, Penn State Univ, USA) for 'display’-focused silicate and oxide glasses. Record surface hardness and densification close to 20% were obtained [1].

This poster demonstrates the application of this concept to glass composite electrodes for new generation batteries.

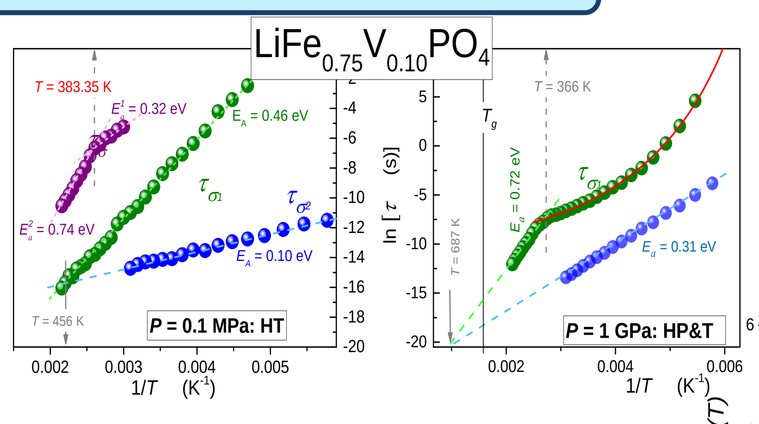


DC electric conductivity in basic amorphous glass and after High Pressure – High Temperature (HP&T) treatment, associated with nanocrystallization within glass matrix in the supercooled liquid state above the glass temperature T_g and the subsequent 1 h annealing 10 K below T_g , in the solid glass. [2,3]

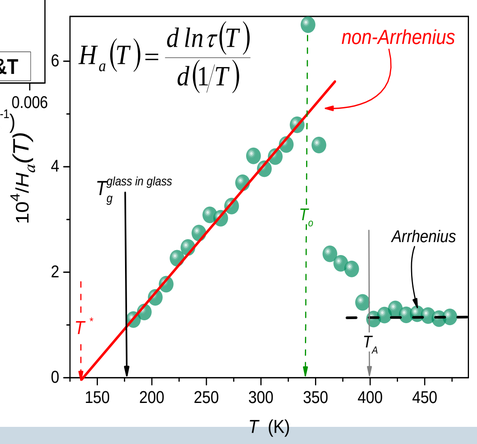
The comparison for nanocrystallites formation under atmospheric pressure, using only temperature is shown.

Note: the application level for $\sigma > 10^{-6}$ Sm^{-1}

Apparent activation enthalpy



HP&T treatment reduces the number of relaxation processes and yields the SA process. It is the non-evidenced (so far) ‘**hoping glass in solid glass matrix**’. [3]



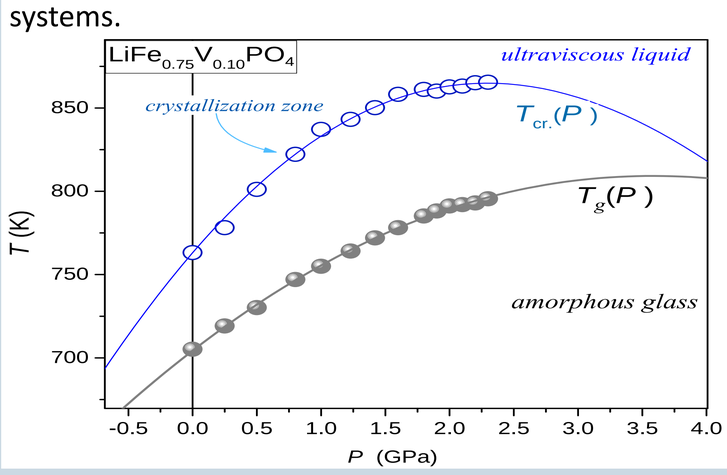
Changes in the apparent activation enthalpy $H_a(T)$ show that dynamics follow the ‘critical&activation’ model relation, derived 3 years ago in X-PressMatter [3, 4]:

$$\tau(T) = \tau_0 \left(t^{-1} exp t\right)^{\Omega} \qquad t = \left(T - T^*\right)/T$$

Lithium-iron-phosphate ($LiFePO_4$)

Lithium-iron-phosphate ($LiFePO_4$) with olivine structure are widely implemented for cathodes in new generation batteries since J.B. Goodenough (Nobel Prize 2019) drew attention to its high theoretical electrochemical capacity. The relatively low electronic conductivity is overcome by carbon additives, structural modifications, doping… A decade ago, Garbarczyk’s et al. (WUT) developed the novel concept to improve conductivity via the appearance of nanocrystallites within the amorphous glass matrix. It was first implemented for $LiFe_{0.75}V_{0.10}PO_4$ glass, where a short heating above the glass temperature created nanocrystallites, preserved due to subsequent quench thermal quench to ambient conditions. The unique (homo)-composite been created, in which electric conductivity is supported via hoping between nanocrystallites, as suggest the classic Mott’s model.

The last 5 years coop between WUT and IHPP PAS teams showed that HP&T transformation can qualitatively boost the desired properties ($LiFePO_4$) glass based systems.



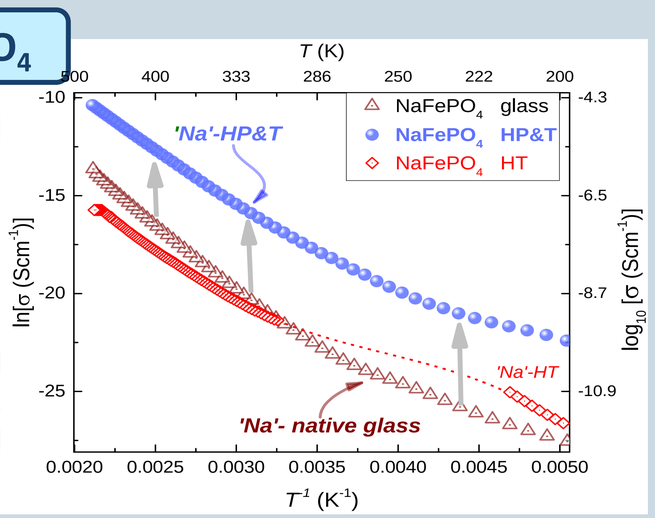
A phase diagram was established showing the (unusual - with maximum) evolution of glass temperature (supercooled liquid, amorphous glass) and crystallization zone above T_g, which made it possible to plan the experiment of creating nanocrystallites in glass matrix, and the permanent boost of electric conductivity. [2,3]

Future: $LiFePO_4$ → $NaFePO_4$

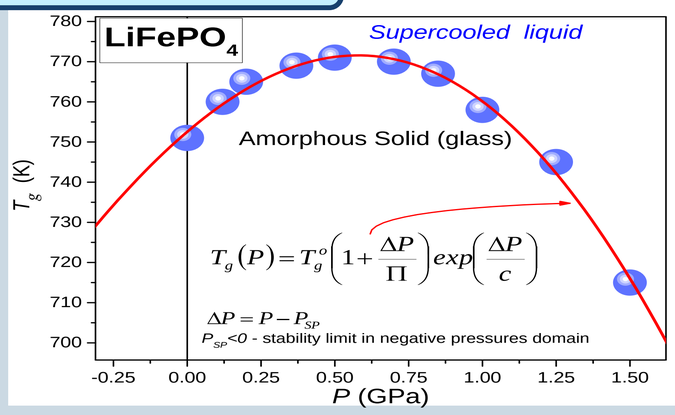
Very recently, the sodium-based parallel of $LiFePO_4$ has been tested in the same way as above. [5]

Electric conductivity reaches 10^{-4} Scm^{-1}, i.e. it is located well within the applications domain!)

Note that Lithium is expensive and available in such countries as China, Russia or Bolivia. Sodium is cheap and available everywhere.



Further studies



$$T_g(P) = T_g^o\left(1 + \frac{\Delta P}{\Pi}\right) exp\left(\frac{\Delta P}{c}\right)$$

$\Delta P = P - P_{SP}$

P_{SP}<0 - stability limit in negative pressures domain

For further studies on glassy $LiFePO_4$, the *P-T* phase diagram is essential. It has been determined recently. [6]

It shows unique maximum of $T_g(P)$. *This is in fact the first ever explicit evidence of such phenomenon.*

The portrayal is possible due to relation given in the Figure, worked out in X-PressMatter Lab. [7]

References

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