Experiment report :

HC- 1862

Structure and Dynamics Of Ge $_X$ Se $_{(1-X)}$ Glasses Under Pressure : relation between atomic local order and mechanical stability.

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Results summary :

Pressure induced structural modifications in vitreous Ge_xSe_{1-x} (where $0.10 < x < 0.25$) have been investigated using X-ray absorption spectroscopy (XAS, Figure 1) along with supplementary X-ray diffraction (XRD) experiments and ab initio molecular dynamics (AIMD) simulations. All the compositions studied were observed to remain amorphous under pressure values up to 42 GPa. The Ge-Se interatomic distances extracted from XAS data show a two-step response to the applied pressure; a gradual decrease followed by an increase at around 15-20 GPa, depending on the composition. This increase could be attributed to the metallization event that can be traced with the red shift in Ge K edge energy which is also identified by the principle peak position of the structure factor (figure 2). The densification mechanisms were studied in details by means of AIMD simulations and compared to the experimental results. The evolution of bond angle distributions, neighbor distances, standard deviations, coordination numbers were obtained. Universal changes in distances and angle distributions are observed when scaled to reduced densities (figure 3).
A manuscript is in preparation

Experimental details :

XAS and XRD experiments on amorphous Ge_xSe_{1-x} (where x=10, 17, 20, 22 and 25) samples have been performed at the European Synchrotron Radiation facility at beamline BM23. High pressure conditions up to 41.4 GPa were achieved by a gas driven membrane diamond anvil cell (DAC) having conical Boehler-Almax diamonds with 300-µm- diameter. Fine pieces of samples were loaded into rhenium gaskets having 120 µm diameter hole and about 35 µm thickness. Paraffin oil was used as pressure transmitting medium in order to achieve hydrostatic condition. The applied pressure was determined through the ruby florescence method from ruby spheres placed close to the border of the hole . XAS data were collected at Ge K edge (11.1 keV) and Se K (12.66 keV) using ion chambers. The X-ray beam spot size focused on the sample was about 79 x 79 μm^2. XAS data were analyzed using the ATHENA and ARTEMIS programs of the IFFEFIT package . The EXAFS, chi(k), signal for Ge K edge was been obtained after removing the background with the by a cubic spline and then normalizing the magnitude of the oscillations to the edge jump. The chi(k) signals were fitted in k space in an interval of 3.96 to 15.2 $Å^{-1}$. The first shell contribution was isolated by selecting the a back transforming range $1 < R < 3$ Å . A Hanning window function was used for the Fourier transformations. The fitting parameters amplitude reduction factor, S^2_0, and energy mismatch, E0, were refined with initial predictions between 0.86 to 1.25 and 5 to 7, respectively. For XAS refinement of the short range structure, two methods were compared to obtain the best-fitting parameters ; in one method the first shell neighbor coordination numbers were fixed to n(GeSe) = 4 and n(SeGe) = 2 whereas in the other the coordination numbers found through ab initio calculations of amorphous Ge_xSe_{1-x} under pressure are implemented . The comparison revealed no significant differences in the σ^2 values and Ge-Se distances (i.e. for the structural parameters in the refining of Ge25Se75, when n(GeSe) is set to be equal to 4, the calculated best fit yields to R(GeSe)

=2.366(4) Å and σ^2 (GeSe) = 0.00429(3) which is identical to the case when n(GeSe) = 3.87 determined by the ab initio simulations with a 3 % difference in S^2_0). Therefore the former method has been adopted in which the coordination numbers are fixed to n(GeSe) = 4 and n(SeGe) = 2 for the XAS data refinement. XRD patterns were recorded simultaneously during the XAS experiments at each pressure point with a MAR345 detector placed at about 164 mm from the sample. A Si (111) monochromator was used to select the wavelength of 0.688 Å spanning a q vector range up to 5.68 $Å^{-1}$. The typical exposure time was set to 600 s. An empty cell measurement was performed in order to subtract the background cattering from the diamond and the air. The sample-to-detector distance and the detector tilt angles were determined by using diffraction data from a Ce2O3 standard. The FIT2D software package was used for XRD data reduction.

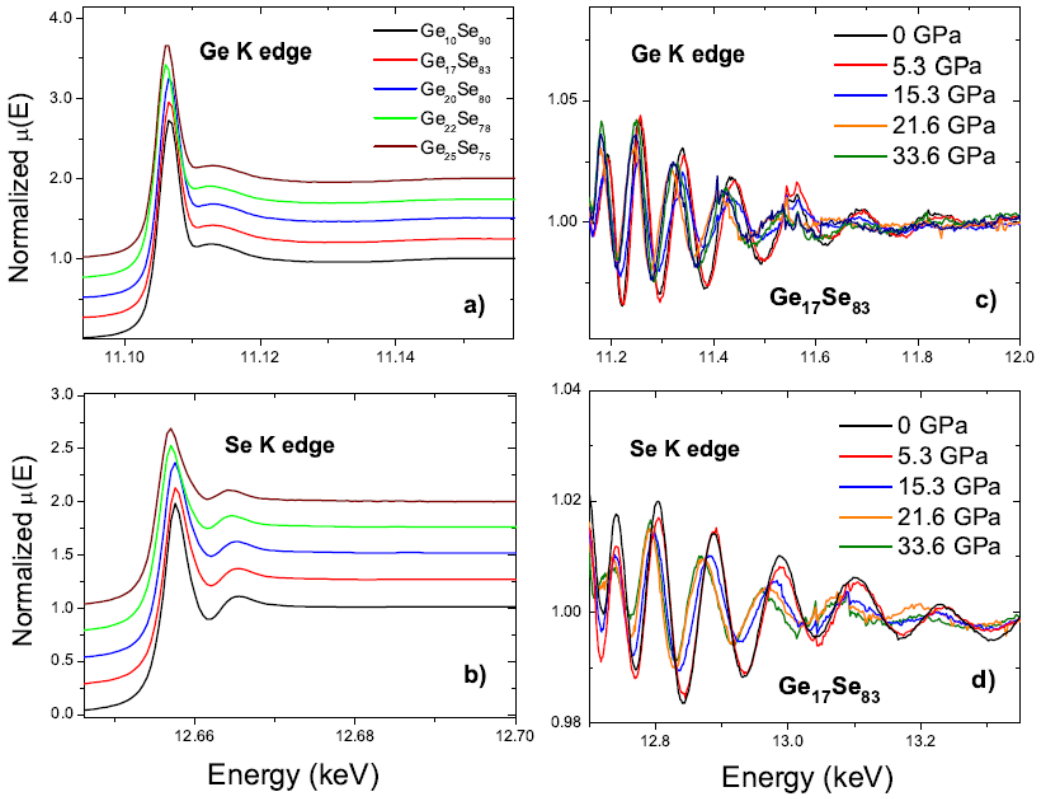

Figure 1 :
Normalized X-ray absorption spectra at the a) Ge K edge and b) at the Se K edge of amorphous Ge_xSe_{1-x} at ambient pressure. EXAFS oscillations of $Ge_{17}Se_{83}$ at the c) Ge K edge and d) at the Se K edge under selected pressure points collected using DAC.

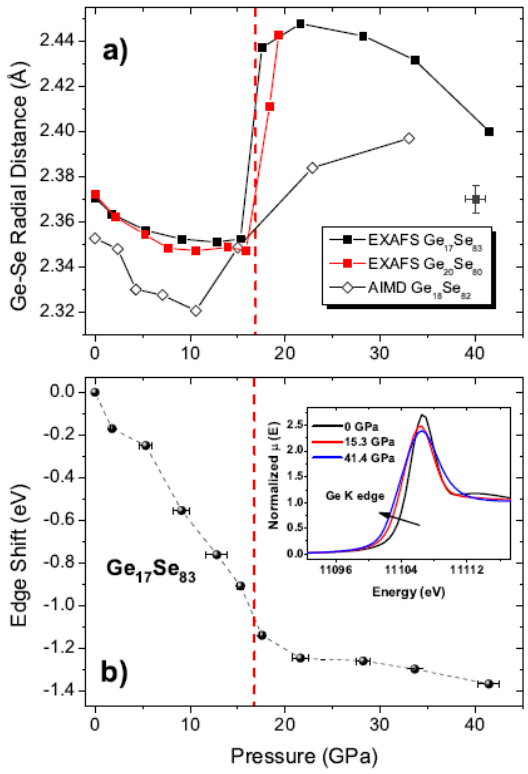

Figure 2 :
a) Evolution of the Ge-Se interatomic distance as a function of increasing pressure. The filled symbols represent $Ge_{17}Se_{83}$ (black) and $Ge_{20}Se_{80}$ (red). The open diamond symbols are AIMD results for $Ge_{18}Se_{82}$. The estimated error bars are shown separately in the graph. The red dashed line corresponds to the interception of low and high pressure regimes shown by the pressure dependency of the PP position in Fig. 1 b).
b) Energy decrease in the Ge K absorption edge position with increasing pressure of $Ge_{17}Se_{83}$. In the inset, the XANES spectra of selected pressures are compared to provide evidence for the clear edge shift.

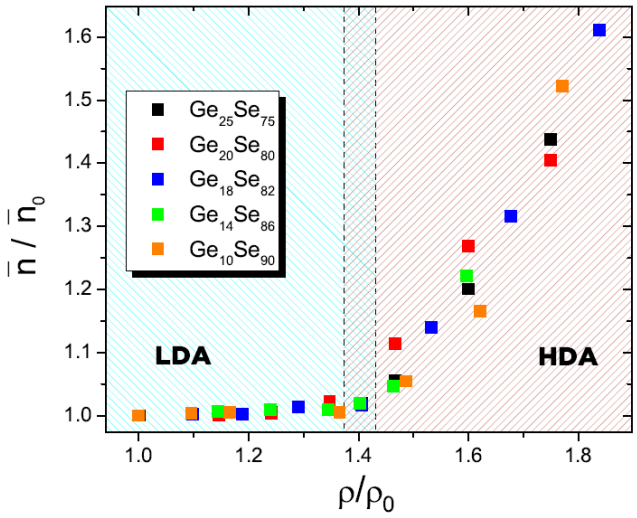

Figure 3 :
Normalized total coordination number as a function of the reduced density for the selected ompositions of Ge_xSe_{1-x} obtained from CPMD calculations. Here the y axis represents the total oordination number at a given r divided by the total coordination number at ambient pressure. A lobal behavior is clearly observed for all the ompositions with a marked increase in the coordination number starting around ρ=ρ0 = 1:4.