Pressure induced amorphization of molecular crystals: SnI_4 and GeI_4

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Background

Pressure induced amorphisation (PIA) has been observed in various materials; the mechanism of the order-disorder transition can differ. It can imply coordination change, like in GeO_2 [1] or in nano-anatase [2] ($nTiO_2$). Ta_2O_5 nanowires undergo an irreversible PIA at 19 GPa [3] connected to the breaking of some of the octahedral interconnections preserving the nanowire shape accompanied by a reduction of resistivity of an order of magnitude.
For molecular crystals like benzene [4] or thiophene [5], an irreversible PIA is observed and a highly reticulated polymer is formed. AX_4 molecular compounds where A= Sn or Ge and I = Cl, Br, I exhibit also reversible PIA [6,7], observed for GeI_4 and SnI_4 is accompanied by metallization. The mechanism proposed to explain the phase transformation is a charge transfer from intramolecular bonds (Sn-I) to intermolecular bonds (I-I). At ambient pressure these compounds crystallize in a cubic structure with SnI_4 molecules interacting through Van der Waals forces. At high pressure, charge transfer leads to the creation of Sn-I-I-Sn-I chains [8] and conductivity increases. Such mechanism can effectively explain the amorphisation and the metallization, but it has not been fully demonstrated due to the lack of crystallographic information.

Methods

Thanks to the advent of nano polycrystalline diamonds [9] usable in diamond anvil cells we could combine EXAFS and XRD measurements to establish the mechanism of PIA in SnI_4 without suffering from strong diamond diffraction peaks using a scanning EXAFS beamline (SAMBA, Synchrotron SOLEIL) to obtain successively Sn and I K edge spectra at pressures up to 27 GPa and XRD on the same setup. Reverse Monte Carlo [9] and traditional EXAFS analysis have been applied and XRD data has been used to provide lattice parameters and detect phase transitions.

Results and discussion

XRD data indicate a progressive amorphisation that takes place above 15 GPa. EXAFS reveals a more complex picture where Sn-I compression is followed by expansion and splitting in two sub shells. RMC EXAFS fitting via the EvAX code [9] was used to analyse the complex coordination scheme around the iodine atoms. From radial distribution functions we observe the approach of I atoms of different SnI_4 tetrahedrons and the formation of I-I bonds. Between 10 and 15 GPa we observe a redistribution of the number of intra and inter I-I bonds until they become equivalent, while Sn-I and I-I distributions remain different even after amorphisation.

Conclusions

Our results are in agreement with the percolation model of Pasternak and Taylor [7], and provide a new understanding on this process of amorphisation. SnI_4 results will be compared to those recently obtained on the isomorphic GeI_4.

References

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