AB INITIO SIMULATIONS OF AMORPHOUS GeO_2 UNDER PRESSURE: A FIRST SEARCH FOR PHASE TRANSITIONS

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ABSTRACT. A series of *Ab-initio* molecular simulations oriented to get a first qualitative picture have been performed on amorphous GeO_2 at room temperature, submitted to increasing hydrostatic pressure up to 20GPa and released back to 0GPa. Unlike for pure Ge, simulations for GeO_2 show no pressure–induced low-density to high–density phase transition (LDA-HDA) in this pressures range: a result in line with preliminary experimental measurements that encourages for further investigations.

1 Introduction

During the last years –due to higher charges mobility and lower operating voltage– germanium gained increasing consideration for use in new energy-saving solid state devices, stimulating the interest of many scientists for further investigations of its properties. Amorphous Germanium and Germania (a-Ge, a-GeO_2) are among the disordered substances showing glass polymorphism or polyamorphism, a natural phenomenon yielding numerous interesting implications in various scientific fields (chemistry, material science, geology, etc) [1–9]. Glass polymorphism can manifest itself in different substances both in their liquid and glassy states, inducing changes in local structures, density and conduction properties, among others. In particular, evidence of glass polymorphism was recently found and studied in fourfold coordinated systems like amorphous Si (a-Si) ([10, 11] and Ge (a-Ge) [9, 12]. In such substances, pressure can induce low-density (LDA) to high-density (HDA) amorphous states transitions, resulting in new properties of these materials, possibly useful for technological applications. Such transformations and properties are usually studied by high-pressure experiments and Molecular Dynamics (MD) simulations. Careful investigations have been carried out including x-ray absorption spectroscopy (XAS) and Raman scattering experiments; nevertheless –since important aspects of the structural changes associated with LDA-HDA transitions are still to be assessed– advanced MD simulations are performed to clarify this transformation [9, 12–23]. A complete series of *ab-initio* Car-Parrinello MD simulations (CPMD) [24–26] for a system consisting in 125 Ge atoms was presented and illustrated, showing how high pressure induced an irreversible LDA-HDA transition around 10GPa, in close adherence to experimental results [17, 18, 23]. The results of CPMD simulations for GeO_2 (80 Ge and 160 O atoms) in the range 0-4000K were subsequently presented, showing how GeO_2 simulations resulted more challenging than Ge ones under various aspects [19–21, 27]. In particular, we found Goedecker's potentials (GOE) [28], requiring larger computing resources and power than

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Martin-Trueller's (M-T) ones [29], led to closer agreement with experimental data (M-T gave shorter distances), the differences attributed to the sole potential for oxygen (all potentials were downloaded from CPMD official distribution site): a discrepancy we intend to investigate on. Nevertheless, both GOE and M-T were in good qualitative agreement in the whole range 0-4000K. This encouraged us to continue and complete a first simulations cycle using Martin-Trueller's potentials to study the behavior of amorphous solid-state GeO_2 under pressure, while slower Goedecker simulations were in progress.

2 Computational resources

The calculations were performed using the facilities and services available at the ENEA GRID infrastructure (Italy). Molecular Dynamics simulations have been carried out using CPMD v3.15.3 running on CRESCO4 cluster. 800GB of disk storage has been granted on the PFS file system.

3 Simulations details

Our starting point was constituted by liquid GeO_2 at 4000K consisting in 240 atoms contained in a cubic simulation box of edge 15.602Å to give a density ρ= 3.66 gr/cm^3. The simulations were performed using CPMD software, describing the self consistent evolution of the electronic structure within the frame of density functional theory. A generalized gradient approximation (BLYP-GGA) was adopted for the exchange and correlation part of the total energy [30,31] together with norm conserving pseudopotentials using the Troullier-Martins parametrization in the Kleinman-Bylander separable form for the core-valence interactions [29]. The electronic wave functions were expanded in plane waves up to a kinetic energy cutoff of 90 Ry. A value of 400a.u. was used for the fictitious electronic mass, 1000 cm^{-1} and 10000 cm^{-1} for the characteristic frequencies of ions and electrons, respectively, and 3a.u. (0.072 fs) for the time-step. The initial system was quenched down to 300K and relaxed at an initial pressure of 0Pa; it subsequently was submitted to increasing pressures up to 20GPa and directly relaxed back to 0Pa. Pressures were applied via the Parrinello-Rahman method [32], by steps of 2GPa. At each stage the atomic system was equilibrated according to the criterion that all the physical quantities converged. Thermostatting was obtained by Nosé-Hoover chain thermostats [26,33,34] set on ions and electronic degrees of freedom.

4 Results

A comparison of the volumes evolutions with pressure is reported in Fig. 1 for Ge [18] and GeO_2: it clearly shows that, unlike Ge, GeO_2 undergoes no LDA-HDA transformation (its volume decreases linearly with pressure, whilst Ge shows a deep volume drop). Furthermore while the density change induced by pressure on Ge have a permanent nature, it results reversible for GeO_2. The same behavior is observed in pair distribution, nearest neighbors distribution and structure functions, as depicted in Fig. 2,3.

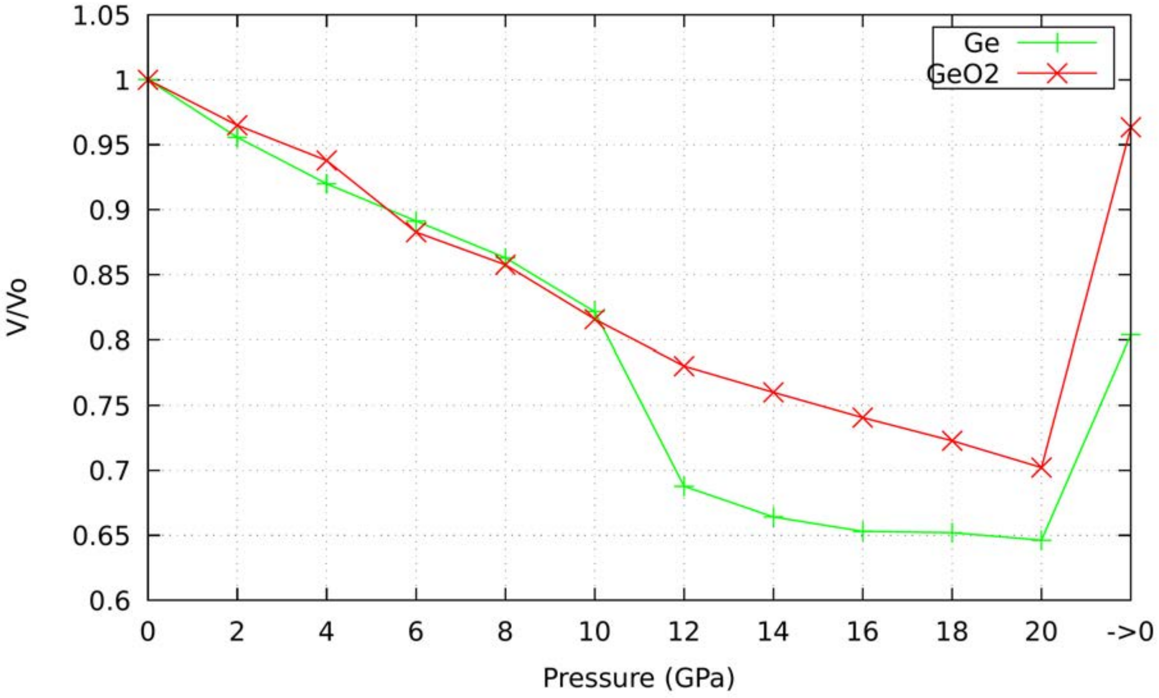
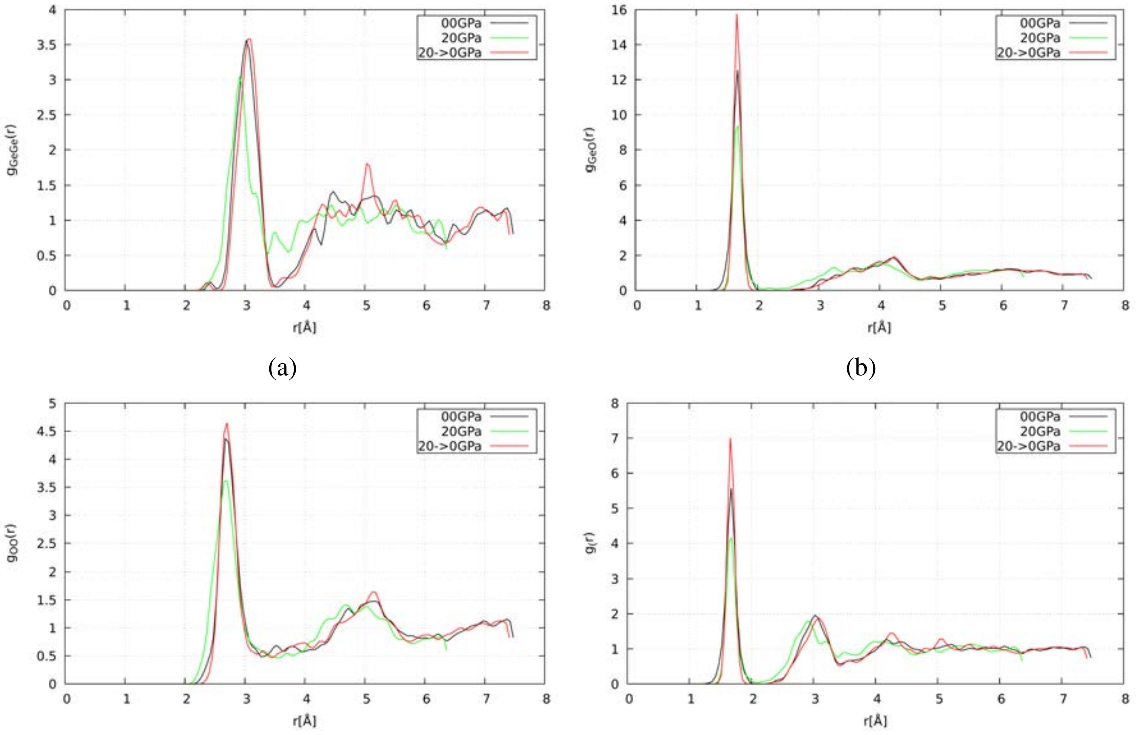


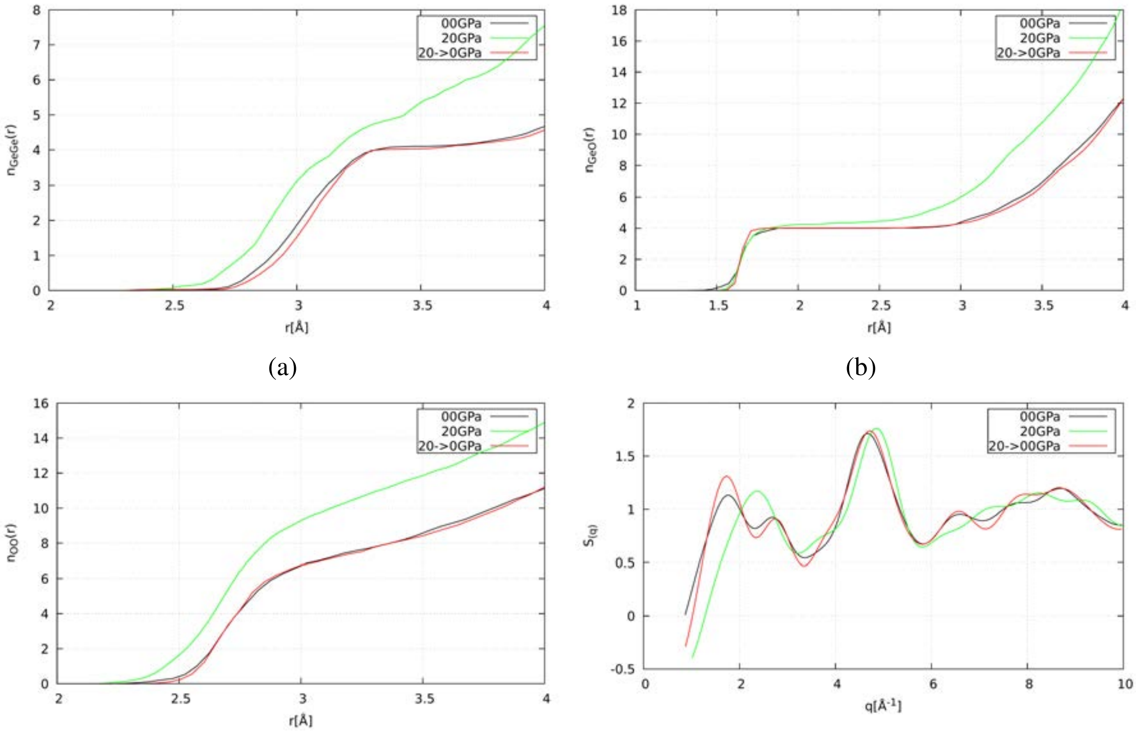
Figure 1: Evolution of Ge and GeO_2 volumes with pressure. →0 indicates the final 0Pa pressure.



(a) (b)

(c) (d)

Figure 2: Pair (a-c) and total (d) distribution functions at 0, 20 and 20 → 0 GPa for GeO_2



(a) (b)

(c) (d)

Figure 3: Nearest neighbors (a-c) and structure (d) functions at 0, 20 and 20→0 GPa for GeO_2

5 Conclusions

A preliminary study on amorphous GeO_2 under pressure in the range 0-20GPa was performed by a series of *ab-initio* Car-Parrinello molecular dynamics simulations using CPMD software. For a first qualitative exploration, faster norm conserving Troullier-Martins pseudo-potentials in the Kleinman-Bylander form were used. In contrast with both experimental and simulations results obtained for Ge, GeO_2 shows no LDA-HDA transition in the 0-20GPa range. This result is in line with experimental measurements carried out up to 10GPa by our group. Finally, while the structural changes induced by pressure in Ge are permanent, pressure effects GeO_2 are not retained when the system is released back to 0GPa.

References

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