

2nd International Workshop on Challenges of Atomistic Simulations of Glasses and Amorphous Materials

Wuhan, China

June 22-24, 2015



Lake View Garden Hotel Wuhan

Conference website:

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International Commission on Glass (ICG)

Conference Program

Date	Time	Event/Presentation
June 21	7:00 pm	Reception at Lakeview Garden Hotel Wuhan
June 22	8:40 am	Opening remarks
		Session 1: Simulations of oxide glasses (1), Chair: Jincheng Du
	9:00 am	<i>Alastair Cormack</i> “ <i>In silico</i> silicate glass formation process”
	9:40 am	<i>Akira Takada</i> “Comparative study on glass structure between SiO ₂ , B ₂ O ₃ , P ₂ O ₅ systems by computer simulations”
	10:20 am	Coffee break (conference photo)
	10:50 am	<i>Guillaume Ferlat</i> “Numerical exploration of the phase diagram of B ₂ O ₃ : challenges and progresses”
	11:30 am	<i>Simona Ispas</i> “Atomistic modeling of complex borosilicate glasses”
	12:10 pm	Lunch
		Session 2: Simulations of oxide glasses (2), Chair: Alastair Cormack
	1:40 pm	<i>Maria Christina Menziani</i> “Modeling unconventional bioactive glasses”
	2:20 pm	<i>Junko Habasaki</i> “MD simulations of glass transition in ionic liquids”
	3:00 pm	Coffee break
	3:30 pm	<i>Hiroiyuki Inoue</i> “Structure and physical properties of La ₄ Ti ₉ O ₂₄ glasses”
	4:10 pm	<i>Alfonso Pedone</i> “Molecular dynamics simulations of the uniaxial tensile tests of silica based glasses: from bulk to nanowires”
	6:00 pm	Dinner
June 23		Session 3: Simulations of phase changing materials, Chair: Xiujian Zhao
	8:40 am	<i>Jean-Yves Raty</i> “Ageing mechanism in amorphous phase change materials”
	9:20 am	<i>Jaakko Akola</i> “Crystallization of the prototype phase-change material Ge ₂ Sb ₂ Te ₅ : density functional theory”
	10:00 am	Coffee break
	10:30 am	<i>Carlo Massobrio</i> “What to learn about disordered chalcogenides by using first principles molecular dynamics”
	11:10 am	<i>Neng Li</i> “High pressure induced phase transformations of berlinite glasses”
	12:00 pm	Lunch
		Session 4: Simulations of chalcogenide glasses, Chair: Carlo Massobrio
	1:30 pm	<i>Eric Furet</i> “On the structure of chalcogenide glasses using solid state NMR and molecular dynamics simulations”
	2:10 pm	<i>Guido Ori</i> “Structure and properties of glassy chalcogenide surfaces”
	2:50 pm	<i>Haizheng Tao</i> “Structural investigation of glasses based on Raman scattering and <i>ab initio</i> calculations”
	3:30 pm	Coffee break
	4:00 pm	Round table discussion: challenges and future of atomistic simulations and ICG TC27 road map
	6:00 pm	Conference banquet

June 24		Session 5: Simulations of porous amorphous materials, <i>Chair: Alastair Cormack</i>
	8:30 am	<i>Beniot Coasne</i> , “Molecular modeling of gas adsorption in bulk and porous silica”
	9:10 am	<i>Jincheng Du</i> “Molecular dynamics simulations of the structure and mechanical properties of nanoporous silica and organosilicate glasses”
	9:50 am	Closing remarks
	10:00 am	Tour of Wuhan University of Technology
	12:00 pm	Lunch at Garden View Hotel Wuhan
	1:30 pm	City tour of Wuhan

List of Invited Speakers

- Benoit Coasne, MIT, USA
- Alastair Cormack, Alfred University, USA
- Guillaume Ferlat, UPMC, France
- Jincheng Du, University of North Texas, USA
- Jean-Yves Raty, Université de Liège, Belgium
- Jaakko Akola, Tampere University of Technology, Finland
- Carlo Massobrio, Institut de Physique et Chimie des Matériaux de Strasbourg, France
- Hiroyuki Inoue, University of Tokyo, Japan
- Akira Takada, Asahi Glass Inc., Japan
- Habasaki Junko, Tokyo Institute of Technology, Japan
- Maria Christina Menziani, University of Modena and Reggio Emilia, Italy
- Alfonso Pedone, University of Modena and Reggio Emilia, Italy
- Simona Ispas, University of Montpellier 2, France
- Guido Ori, Institut de Physique et Chimie des Matériaux de Strasbourg, France
- Eric Furet, University Renné 1, France
- Neng Li, Wuhan University of Technology, China
- Haizheng Tao, Wuhan University of Technology, China
- Seungwu Han, Seoul National University, Korea

***In Silico* Silicate Glass Formation Processes**

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Finding the optimal formation process for silicate glasses in atomistic computer simulations is still more of an art than a science. The standard approach, to start with a disordered structure, disorder it further by heating at a high temperature and then “cool” it down to room temperature, at some nominal rate, usually as slow as possible, is not, in fact, guaranteed to produce a defect-free structure. Furthermore, what appears to work for some compositions may not work for others. In addition, the same process used on different system sizes will result in different structures. These points assume greater significance as the availability of increased computer power enables the routine use of (much) larger system sizes, or much longer run times, than were practical a decade ago.

In this presentation, we will discuss the role of thermal history on the *in silico* formed silicate glass structures, including post-formation annealing. This latter exercise is an attempt to ameliorate fictive temperature effects, in a fashion similar to that undertaken experimentally. We note that, underlying all of this, is the question of what exactly is the temperature of the simulated glass. A related question is whether it is possible in MD simulations to effect changes in the effective internal (or configurational) temperature of the simulated glass, which would be reflected in changes in such structural properties as the Q^n distribution.

Comparative study on glass structure between SiO₂, B₂O₃, and P₂O₅ systems by computer simulation

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Three prototype systems of glass, SiO₂, B₂O₃, and P₂O₅, have their peculiar structural features. The structural motif of SiO₂ is a tetrahedral SiO₄ unit, however, the network comprised of such structural units involves several anomalous properties in SiO₂ glass. It is believed that the boroxol rings (B₃O₆ units) are principal structural units in B₂O₃ glass. Similar super-structural units are thought to exist in many borate systems. The structural motif of P₂O₅ is tetrahedral unit in the same way as SiO₂, however, the number of connection around the PO₄ unit is three in the same was as B₂O₃ due to the existence of terminal O atoms.

In this study, structures of crystals and glasses between B₂O₃, P₂O₅ and SiO₂ are analyzed by computer simulations. First, the difference between crystal and glass is investigated on each system. Next, the structures of three systems are compared. Structures are studied in terms of coordination number, clustering, and packing. Finally, the future direction of structural modeling on these complex glass systems by computer simulation is discussed.

Numerical exploration of the phase diagram of B₂O₃: challenges and progresses

Guillaume Ferlat

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As a network-forming system made of low-coordinated units, B₂O₃ is a good candidate for structural transitions as a function of density. Thus, one expects a phase-diagram as rich as that of silica or water. Along this line, we have recently predicted from first-principles a wealth of new crystalline polymorphs [1]. Further, in the glassy phase, there has been numerous experimental and numerical studies showing unambiguously polyamorphic transitions under pressure between low- and high-coordinated phases [2]. Evidences of a similar transition in the liquid state have also been reported although the data are much more scarce. After a brief review of these works, we will focus on investigations of the liquid phase from first-principles. In addition to the expected high density transition, we will present hints of another transition occurring at low density [3]. This transition which involves changes in the medium-range order but not in the short-range one, bears similarities with the glass transition in B₂O₃ and possibly with the LDA-HDA liquid-liquid transition in water. This transition is likely connected to the underlying crystalline polymorphism [1]. Incidentally, we took advantage of the structural changes occurring in this part of the phase-diagram to produce new models of B₂O₃ glass, much realistic than those obtained from the ordinary quench-from-the-(ambient)-melt technique. In order to investigate more extensively these transitions, empirical potentials calibrated from first-principles and benchmarked against experimental data have been devised [2,4]. Preliminary results from these on-going efforts will be presented.

References:

- [1] G. Ferlat, A.P. Seitsonen, M. Lazzeri, F. Mauri, *Nature Materials*, 11, 925 (2012).
- [2] A. Zeidler et al., *Phys. Rev. B*, 90, 024206 (2014).
- [3] G. Ferlat, chapter 14, in "Frontiers and challenges in molecular dynamics simulations of structurally disordered materials: from network glasses to phase change memory alloys", Eds C. Massobrio, J. Du, P. S. Salmon, M. Bernasconi, Springer (2015).
- [4] O. Alderman et al., in preparation.

What to learn about disordered chalcogenides by using first-principles molecular dynamics

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We have been producing a consistent effort to model the properties of chalcogenides at the atomic scale by using the most accurate first-principles tool within the framework of density functional theory. In order to achieve a comprehensive picture accounting for both methodological issues and physico-chemical properties, we have explored several research lines, encompassing: *a*) the real space fingerprints of intermediate range order and their manifestation in $\text{Ge}_x\text{Se}_{(1-x)}$ glasses and liquids; *b*) the impact of exchange-correlation functionals on the description of bonding and the interplay with the atomic structure; *c*) the changes in the nature of structural motifs with the relative Ge-Se concentration within the $\text{Ge}_x\text{Se}_{(1-x)}$ family; *d*) the effect of pressure on the structural properties of glassy GeSe_2 and GeSe_4 ; *e*) the impact of the dispersion forces on the structural properties of glassy GeTe_4 and *f*) (as an extension to ternary systems, of interest in the area of phase change memory device materials) a description of the structure of glassy $\text{Ga}_4\text{Sb}_6\text{Te}_3$.

The talk will review these achievements by stressing the predictive power inherent in our approach and its capability to complement and enrich structural information.

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Density-driven defect-mediated network collapse of GeSe_2 glass.

K. Wezka, A. Bouzid, K.J. Pizzey, P.S. Salmon, A. Zeidler, S. Klotz, H.E. Fischer, C.L. Bull, M.G. Tucker, M. Boero, S. Le Roux, C. Tugène, C. Massobrio, **Phys. Rev. B** **90**, 054206 (2014)

First principles molecular dynamics study of glassy GeSe_2 : atomic structure and bonding properties

M. Celino, S. Le Roux, G. Ori, B. Coasne, A. Bouzid, M. Boero, C. Massobrio, **Phys. Rev. B** **88**, 174201 (2013)

Structural properties of glassy Ge_2Se_3 from first-principles molecular dynamics, S. Le Roux, A. Bouzid, M. Boero, C. Massobrio, **Phys. Rev. B** **86**, 224201 (2012).

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Structural properties of liquid Ge_2Se_3 : a first-principles study, S. Le Roux, A. Zeidler, P.S. Salmon, M. Boero, M. Micoulaut, C. Massobrio, **Phys. Rev. B** **84**, 134203 (2011).

Atomistic modelling of complex borosilicate glasses

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We have carried out *ab initio* or combined classical and *ab initio* molecular dynamics (MD) simulations in order to investigate the structural and vibrational properties of several borosilicate glasses. We have considered rather simple ternary compositions with varying SiO₂, B₂O₃ or Na₂O concentrations, or more complex compositions containing equally CaO, Al₂O₃ or MgO. The *ab initio* calculations have been carried out within the density functional theory framework as implemented in the VASP code. The classical MD simulations were carried out using different effective pair potentials.

We have studied the local structure of the various structural units, and in particular we have focused on the structures around the boron atoms and how these are embedded into the network. We have investigated how the Na atoms are distributed around the ^[3]B triangles and ^[4]B tetrahedra. Furthermore, we have found that the Na distribution associated to a BO₄ tetrahedron is different from that corresponding to a SiO₄ tetrahedron in that the former gives rise to a distribution that is significantly more structured.

The vibrational properties have been equally studied within the *ab initio* approach, and we have identified the contributions of the various species as well as those of the local structural units. We have also calculated the dielectric function $\epsilon(\omega)$ as well as the absorption spectra. The latter are in good quantitative agreement with experimental data .

The results obtained in this work confirm that the atomistic simulations, in particular the *ab initio* ones, give access to a better understanding of complex borosilicate glasses since their structural and vibrational properties can be extracted with a good accuracy and compare very well to experimental data.

Modelling unconventional bioactive glasses

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A survey of the structure-property relationships of bioactive glasses doped with unconventional elements is presented in this talk.

I will show, based on our research experiences, that a deep understanding of the glass structure can only be obtained by means of sound atomic scale computer simulations. The acquisition of this knowledge is mandatory for the design of glasses with new or improved therapeutic benefits, such as bone regeneration, bactericidal action, vascularization.

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- 3) Malavasi et al. Study of the structural role of gallium and aluminum in 45S5 bioactive glasses by molecular dynamics simulations, J. Phys. Chem. B, 2013, 117, 4142-4150

Molecular Dynamics Simulation of Glass Transition in an Ionic Liquid: Topological Aspect of Infinitive Networks in a Fragile System

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The typical ionic liquid, 1-ethyl-3-methyl imidazolium nitrate (EMIM-NO₃) was examined by molecular dynamics simulations of an all-atomistic model to show the characteristics of networks of cages and/or bonds in the course of vitrification of this fragile glass-former. The system shows changes of dynamics at two characteristic temperatures, T_B (or T_c) and T_g , the glass transition temperature, found in other fragile glass forming liquids [K. L. Ngai and J. Habasaki, J. Chem. Phys. 141, 114502 (2014)]. The glass transition temperature, T_g , is characterized by the saturation of the total number of “bonds”, N_B , and the corresponding decrease in degree of freedom, $F=[(3N-6)-N_B]$, of the system consisting of N particles. Similar behavior holds for the other ion-ion pairs. Therefore, as an alternative to conventional approach, the dynamics of glass transition can be interpreted conceptually by rigidity percolation.

Before saturation occurring at T_g , the number of bonds shows a remarkable change at around T_B . This temperature is associated with the disappearance of the loosely packed coordination polyhedra of anions around cation (or vice versa), related to the loss of geometrical degree of freedom, f_g , of each coordination polyhedron, which can be defined by $f_g=[(3N_v-6)-N_b]$, where $3N_v$ is the degree of freedom of N_v vertices of the polyhedron and N_b is number of fictive bonds. The packing of polyhedra is characterized by the soft percolation of cages, which allows further changes with decreasing temperature.

Structure and physical properties of $\text{La}_4\text{Ti}_9\text{O}_{24}$ glass

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The $\text{La}_4\text{Ti}_9\text{O}_{24}$ glass can be prepared only by using container-less processing, such as gas levitation furnace. The glass shows high refractive index, such as 2.29. The high refractive index of the glass shows the high packing density of atoms and high ionicity of the chemical bonds around oxygen atoms.

Molecular dynamics simulation of $\text{La}_4\text{Ti}_9\text{O}_{24}$ glass has been carried out using empirical potential. The interatomic potential functions were Born-Mayer type. The effective charges were used. There were 400 La atoms, 900 Ti atom and 2400 O atoms in the unit cell. The size of the unit cell was 35.78 \AA of cube. The density of the structural models was set at 4.97 g/cm^3 . The initial random configurations of the atoms was equilibrated at 4000 K for 20 ps, and then cooled to 293 K for 200 ps. Five structural models were prepared from the different initial random configuration. The simulation reproduced the total correlation function obtained from x-ray and neutron diffractions. The values of R_x factor for x-ray and neutron correlation functions, which are proposed by A. C. Wright, were 3.4% and 4.5%, respectively.

The cutoffs for Ti-O and La-O are 2.6 \AA and 3.2 \AA and the coordination numbers of Al and La were 5.6 and 8.7, respectively. There were corner, edge and face sharing linkages between TiO_n polyhedral. The fraction of edge sharing linkage was more than 20%. There were threefold and fourfold coordinated oxygen atoms by the Ti atoms. The fraction of threefold coordinated oxygen atoms were more than 20%. It was found that the network constructed by Ti-O bonds in the glass shows different characteristics from the conventional random network of the glasses.

The full-potential linear augmented plane wave method, as implemented in Wien2k code, was applied to perform first-principles calculation. The exchange-correlation potential was calculated using the generalized gradient approximation (GGA). For the structural models obtained from the classical molecular dynamics simulation, the imaginary part of the dielectric function $\varepsilon_2(\omega)$ was calculated from the electronic band structure. The real part $\varepsilon_1(\omega)$ of the dielectric function was extracted from the imaginary part using the Kramers-Kronig relations. The refractive index $n(\omega)$ can be calculated from the both dielectric functions, $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$. The calculated refractive index at 587 nm was 2.54. This value was larger than 2.29 obtained experimentally.

Molecular dynamics simulations of the uniaxial tensile tests of silica based glasses: from bulk to nanowires.

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Silica-based glasses are of great importance in various technological fields ranging from fiber optic wave guides, laser optics for initiating fusion reactions, containers for radioactive waste, and biomedical applications. Despite the great number of properties and functionalities that can be easily conferred to glassy materials by changing composition and/or processing technologies their poor mechanical properties has always been considered as the main limitation to application with high levels of tensile stress.[1]

Therefore, the understanding of fracture mechanism and intrinsic strength of silicate glasses is of crucial importance to design new ultrastrong materials for addressing new social challenges in energy, medicine and communication systems.

In this communication, I will show how MD simulations can be employed to understand the effect of the system size, strain rate, the presence of nanometric defects and the composition on the mechanical properties and the fracture mechanism of SiO_2 and $20\text{Na}_2\text{O} \cdot 80\text{SiO}_2$ bulk glasses and nanowires.

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Aging Mechanisms in Amorphous Phase Change Materials

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Aging phenomena are common to all amorphous structures, but of special importance in phase change materials (PCM) since it impedes the realization of multi-level memories. Different interpretations have been proposed, but we focus here on the structural relaxation of amorphous GeTe, chosen because it is the simplest system that is representative of the wider class of GST alloys, lying along the GeTe-Sb₂Te₃ composition line of the GeSbTe phase diagram.

A first problem is that directly generating an amorphous structure by quenching a liquid using Density Functional Theory (DFT) based Molecular Dynamics leads to one sample with a small number of atom (typically a few hundreds), and, hence of small number of atomic environments. Here we sample a large number of local atomic environments, corresponding to different bonding schemes, by chemically substituting different alloys, selected to favor different local atomic structures. This enables spanning a larger fraction of the configuration space relevant to aging.

A second aspect is that GST alloys are known to display complex bonding mechanisms, for which the simple chemist's "octet-rule" does not apply, leading a long series of controversies, concerning in particular the local structure around Ge atoms. We overcome this problem by using state of the art non local DFT-MD, including the so-called van der Waals corrections. This leads to more clearly defined environments that are thoroughly analyzed.

We can then identify their fingerprints in the available structural experimental data and assess the stability of these local environments to obtain information of the driving forces leading to the structural relaxation. The calculated electronic properties nicely match the most recent photothermal deflection spectroscopy experiments that are presented here.

Our results support a model of the amorphous phase and its time evolution that involves an evolution of the local (chemical) order towards that of the crystal (by getting rid of homopolar bonds), and an evolution of its electronic properties that drift away from those of the crystal, driven by an increase of the Peierls-like distortion of the local environments in the amorphous, as compared to the crystal [1].

[1] J.Y Raty, W. Zhang, J. Luckas, C. Chen, R. Mazzarello, C. Bichara and M. Wuttig, *submitted*.

Crystallization of the prototype phase-change material Ge₂Sb₂Te₅: Density functional study

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Phase-change materials are ubiquitous in the world of rewritable optical storage media (DVD-RW and Blu-ray Disc), and they are being applied in new nonvolatile memory applications (PRAM). Nanosized bits in a thin polycrystalline layer are switched reversibly and extremely rapidly between amorphous and crystalline states by laser irradiation or resistive heating. Crystallization of amorphous bits is the time-limiting process in the write/erase cycle and has been the subject of much speculation. We have studied the process in amorphous Ge₂Sb₂Te₅ (GST) using four extensive (460 atoms, up to 5 ns) density functional/molecular dynamics simulations at 600 K. This phase change material is a rare system where crystallization can be simulated without adjustable parameters over the physically relevant nanosecond time scale. Crystallization is accompanied by an increase in the number of "ABAB squares" (A: Ge, Sb; B: Te), percolation, and the occurrence of low-frequency localized vibration modes. A sample with a history of order crystallizes completely in 1.2 ns, but ordering in others was less complete, even after 5 ns and can lead to more than one crystalline cluster, i.e. a polycrystalline material. The amorphous starting structures without "memory" display phases (>1 ns) with sub-critical nuclei (10-50 atoms) ranging from nearly-cubical blocks to strings of ABAB squares and AB bonds extending across the cell. Percolation initiates the rapid phase of crystallization and is coupled to the directional p-type bonding in metastable GST, providing insight for the nuclei-nuclei interactions in real samples. Cavities play a crucial role, and the final ordered structure is distorted face-centered-cubic with a sublattice containing predominantly Te atoms. These extremely extensive calculations demonstrate that much shorter simulations on smaller samples can lead to qualitatively incorrect findings.

Reference:

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High Pressure Induced Phase Transformation of Berlinite Glass

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We have investigated the mechanism of phase transitions from crystalline to amorphous of berlinite (AlPO_4) with 72 atoms and periodic boundary conditions. This supercell model is systematically densified up to a pressure of 80 GPa using ab initio constant pressure technique. By assessing a full spectrum of properties including atomic structure, bonding characteristics, effective charges, bond order values, electron density of states, localization of wave functions, elastic and mechanical properties, and interband optical absorption at each pressure, we reveal the pertinent details on the structural, mechanical and optical characteristics of the glass model under pressure. They all confirm the central theme that crystalline to amorphous phase transformation (CAPT) happens with the pressure around 20 GPa. This performance is similar with the amorphous silica glass densification under high pressure.^{1, 2} Moreover, the aluminum atom displacements are bigger than that of phosphorus atom with increasing pressure, and the number of five coordination aluminum atoms also increasing with pressure. The phase transformation roots from the change of Al-O and P-O bonding from a mixture of ionic and covalent nature at low pressure to a highly covalent bonding under high pressure. In addition, the calculated theoretical refractive index of the glass model as a function of the pressure is reported for the first time and in good agreement with the available experimental data. This work will opens a way to explain the driving force of pressure-induced phase transitions of berlinite (AlPO_4) from the atomic scale.

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On the Structure of the Chalcogenides Glasses using Solid-State NMR and Molecular Dynamics Simulations

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During the last decades, the chalcogenide glasses have attracted considerable interest from the scientific community due to the wide spectrum of physical properties exhibited.¹ Some of these materials are notably known for reversible amorphous-to-crystal transitions induced by laser irradiation,² such as the prototypical phase-change glass Ge₂₂Sb₂₂Te₅₆ that has been employed for optical data storage, or non-volatile memories.³

Another fundamental aspect of the chalcogenide glasses is related to their large infrared transparency windows that extend far beyond the two atmospheric bands (3-5 μm and 8-12 μm - Figure 1) and cover the vibrational signatures of most of the molecules. Such features have opened up the way to various photonic-related applications, such as remote sensing/*in vivo* investigations by *fiber evanescent wave spectroscopy* or low cost thermal imaging.³ Indeed until recently, only polycrystalline ZnSe or single crystal Ge were commonly used to fabricate IR lenses transparent in the second atmospheric window.

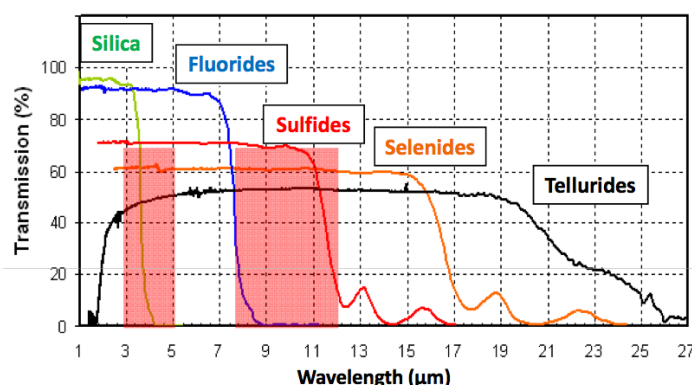


Fig.1. Typical transmittance spectra of silica, fluorides and chalcogenides bulk glasses.
The atmospheric transparency windows are depicted by colored orange boxes

Despite their intrinsic qualities, the atomic-scale structure of these materials remains to a large extent unknown, therefore precluding the rationalization and subsequent optimization of both their synthesis and optical, thermal, mechanical or electrical properties.

In this context, we wish to present results of recent investigations that we have carried out on glasses in the Ge-Te and Ge-Te-Se systems, by combining solid-state NMR measurements and NMR parameters calculations on *in silico* samples produced by molecular dynamics simulations.⁴

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Structure and Properties of Glassy Chalcogenide Surfaces: An Atomic Scale Modeling Approach

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Amorphous porous chalcogenides are receiving increasing attention as efficient sorbents for environmental remediation from gaseous and water waste media.^[1-2] However, little is (still) known about the surface properties of glassy chalcogenides due to the complexity of their disordered nature. In this context, computational approaches represent a valuable tool to investigate these systems at the atomic scale on the base of an accurate description of their ionic-covalent bonding chemistry.

In this work, I will show how both first-principles and classical atomistic simulations can be used to develop and investigate the properties of glassy chalcogenide surfaces. Several chemistries will be considered within the germanium sulphide and selenide families. In a first step, first-principles molecular dynamics is used to develop, at finite temperature, a realistic model of these materials with emphasis on their surface chemistry.^[3-4] A detailed account of the structure of the surface models is given in terms of pair correlation functions, structure factors and chemical order. A particular attention is then focused on the comparison between the surface and bulk counterpart in terms of chemical bonding. In a second step, Monte Carlo simulations are employed to investigate the surface adsorption properties of these materials. I will show how the realistic details of the surface chemistry drastically affect the adsorption of various fluids and their mixtures.

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Structural investigation of glasses based on Raman scattering and *ab-initio* calculations

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ABSTRACT

In contrast to diffraction methods, which deal with the coherence lengths of about 150 –200 nm, only very few unit cells of a definite structure are required for Raman scattering identification. This allows the micro-structural analysis of amorphous materials. However, until the vibrational properties of glasses are better understood in terms of their structure and bonding, vibrational spectroscopy can not be rigorously used as a tool for probing their detailed molecular structure. In this report, based on the *ab-initio* calculations of normal Raman mode, combined with group theory analysis, we revealed the subtle evolution of local nearest neighbor connectivity of structural units in glasses, indicating the high sensitivity of Raman scattering to structural change in glasses.

Keyword: glasses, structure, *ab initio* calculations

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Molecular Modeling of Gas Adsorption in Bulk and Porous Silica

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Adsorption in amorphous porous solids such as silica glasses is at the heart of important applications: catalysis, energy, environment, etc. From a computational point of view, understanding the adsorption and transport of fluids in such complex amorphous materials requires developing realistic models. In this work, I will show how a multiscale strategy, using both first principles and classical atomistic simulations, can be used to develop and investigate the properties of such amorphous surfaces [1]. The surface properties of these materials can then be assessed by simulating small angle scattering, adsorption isotherms, etc. using classical approaches. I will show how the realistic details of the surface chemistry drastically affects the adsorption of various fluids such as water, carbon dioxide, methane, hydrogen and their mixtures. Finally, I will also consider the specific case of He and Ne adsorption in dense amorphous silica when subjected to high pressures [2]. I will show that a generalized poromechanical approach, describing the elastic properties of microporous materials upon adsorption, can be applied successfully to silica glass in which the free volume exists only at the subnanometer scale.

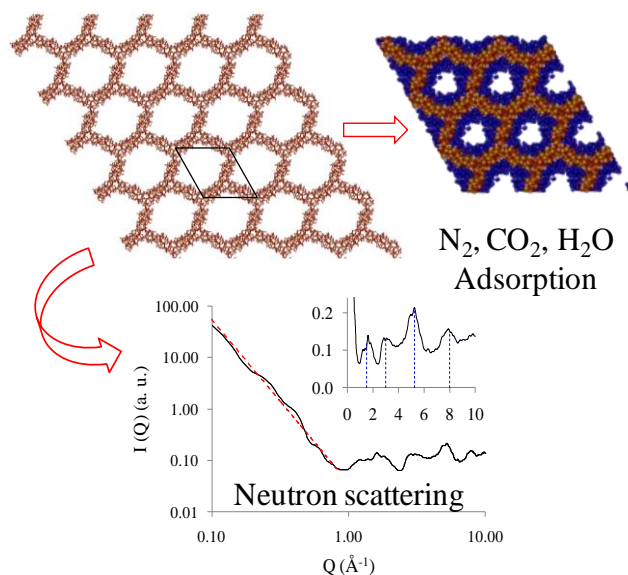


Fig. 1. Atomistic model of micelle-templated mesoporous silicas: Structural, morphological and N₂, CO₂, H₂O adsorption properties. Structural, morphological and adsorption properties of porous silica. The structure and morphology of a realistic model of MCM-41 mesoporous silicas are determined by simulating neutron scattering, X-ray diffraction, electronic microscopy and by calculating chord length distributions, surface area, porous volume, etc. N₂, CO₂ and H₂O adsorption are simulated and compared with experimental data and theoretical models of adsorption in nanopores.

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Molecular dynamics simulations of the structure and mechanical properties of nanoporous silica and organosilicate glasses

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Nanoporous silica and silicate glasses find applications as catalyst support, hydrogen storage, gas separation, and insulating materials. The porous structures with organic component (hybrid organic-inorganic materials or organosilicate glasses (OSG)) also find applications as low-k dielectrics in Integrated Circuit (IC) devices of microelectronics. Understanding the atomic and microstructure of nanoporous silica and their relationship to properties such as mechanical behaviors are thus of great technological and scientific interest. In this paper, nanoporous silica and silicate glasses with 30-70% porosity were developed using two molecular dynamics (MD) simulation protocols to obtain structures with dissimilar pore morphologies. Short and medium range structural characteristics including bond angle distributions and pair distribution functions were analyzed and found to be consistent with experimental results. OSG structures were simulated using ReaxFF. Surface area to volume ratio and pore microstructures were characterized and compared with experimental observations. Mechanical properties including elastic, shear and bulk moduli of these nanoporous silica systems were calculated and their change as a function of porosity was compared with experimental data and theoretical models. It was found that the elastic modulus of porous silica with 50% porosity is 5-14 GPa which is consistent with experimental results. The elastic moduli – porosity relationship was fitted by exponential and power functions, and analysis of coefficients was performed to obtain microstructure characteristics of the simulated nanoporous silica structures. This work confirms that two distinct nanoporous silica microstructures are generated with MD simulations which result in variations in mechanical properties and highlight the importance of selecting a nanoporous silica simulation method which approximates experimental systems.

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Defects and impurities in amorphous semiconducting oxides

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Ultra-definition, large-area displays with three-dimensional visual effects represent megatrend in the current/future display industry. On the hardware level, such a “dream” display requires faster pixel switching and higher driving current, which in turn necessitate thin-film transistors (TFTs) with high mobility of 30~50 cm²/V·s. The traditional *a*-Si TFT performs far below than this requirement and amorphous semiconducting oxides (ASOs) such as In-Ga-Zn-O are poised to enable the high-mobility TFTs. However, the device instabilities under various stress conditions such as voltage, temperature, and light become the main hurdle against the massive commercialization of the AOS-based TFTs. Therefore, the microscopic understanding on the device instability is highly demanded at this moment.

In this presentation, I will summarize our recent *ab initio* calculations on the source of instability in ASO, mainly focusing on the defects and impurities introduced during the thin-film growth. To explain various instability sources, we calculated the absorption spectrum of ASO, the interface between ASO and SiO₂ [2], and the oxygen vacancies [3]. In addition, through the combined study with experiments, we investigated the device instability more directly [4] and proposed how to improve the stability. [5,6]

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Notes:

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