Project Title:

Materials properties under extreme conditions: Understanding planets in depth

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MOxSiO2 oxides (here M is Pb, Al, Mg, Ca or Na) have received a great attention from materials science communities for long times, because they have certain specific properties such as high mechanical strength, special optical absorptions, corrosion and abrasion resistance... These materials are also important for geosciences because the MOxSiO2 systems are the simplest (two-component oxide) approximation to the composition of the Earth's mantle, and ultramafic and mafic liquids. These oxides are also known as the glass-forming material due to that their structure is built by basic units which randomly distribute in the space and link to each other by common oxygen. Further, the majority of basic units are SiO4 tetrahedra and a number of other types like SiOm and MOn also present in the system. The structure as well as many properties of MOxSiO2 oxides strongly depends on concentrations of MOx. For example, the absorption of x-rays of PbOSiO2 significantly increased when the concentration of PbO is greater than 30 mol%. In the case of Al2O3SiO2 the material has high melting temperature (2000K) and its mechanical property is significantly improved in comparison with the pure SiO2. The physics-chemical properties of CaSiO3 demonstrated a good likeness with human bone, so it is widely used in the treatment of bone-related diseases. Thus, detail knowledge about the network structure when MOx is added into the oxide system is very important to understanding the glass-forming oxide. One among interesting directions of recent studies is to clarify how the units SiO4 spatially distribute when the concentration MOx varies, and what role other type units (defect-units) plays. These issues are very difficult to trace directly by experiment and ones usually apply the simulation at the atomic level. Recently, the spatial distribution of defect-units as well as their equilibrated concentration has been studied intensively; however the opinions about this problem are still controversial. Therefore, more studies need to treat mention issues. Especially, the coexistence of microscopic regions with different network structure is so far understood and represents a challenge for physicists. The present project is devoted to give some new insight into the above mentioned problem. In particular, we focus on the thermodynamics of defect-units and the technique to detect them. Besides the techniques such as the topology and cluster analysis, simplexes approach…, the recognition and visualization methods are developed in order to identify different types of network structure.

Adding MOx into SiO2 system significantly changes the structure and many properties of silicates. This also causes new physics effects. So the simulation of structure and dynamics in MOxSiO2 could give new insight into the atomistic mechanism as well as behavior of phenomena observed experimentally in glass-forming materials. In our last study (Appl. Phys. Lett. 102, 191908 (2013)) we found that defect-units in certain oxide systems tend to group together into a cluster (see Fig.3). This is main reason causing the polyamorphism and dynamical heterogeneity which are widely debated in last years. However, the cluster of defect-units is found in models of 2000-3000 atoms, so the size as well as the lifetime of it remains a problem requesting further study. Advances in experimental studies as well as simulation techniques enable to solve two important problems of glass-forming oxides: 1/ thermodynamic

basis of the defect-rich and defect-poor regions; 2/ the size and lifetime of such regions as the temperature, pressure and MOx concentration varies. Successful resolving above mention problems allows to determining the conditions when the liquid-liquid phase transition occurs and can be measured by experiments.

Some results:

1/ Structure of network-forming liquids SiO2 is formed from five order-parameters and comprises two phases (two-state model): low density and high density phases. The structure of low density phase is formed from the SiO4 basic structural units and OSi2 linkage. Conversely, the structure of high density phase is formed from the SiO5 and SiO6 basic structural units, and OSi3 linkage. The structure of model is heterogeneous and tends to separate into low and high density regions. The size of low and high density regions depend strongly on pressure. The density of model at certain pressure can be determined via fraction of OSiy linkages in the network structure of model.

2/ Structural organization of liquid MgSiO3 consists of SiOx (x=4, 5, 6) and MgOn (n=3÷9) units. At low pressure most of SiOx units is SiO4. These SiOx units are linked each other via BO forming Si-O network. At low pressure, Si-O network is broken into subnets with a lot of NBO and Mg atoms incorporate into Si-O network mainly via NBO forming Mg-O-Si, Mg2-O-Si, Mg3-O-Si linkages. At high pressure, the number of NBO decrease, the Si-O network tend to expend whole model (the number of Si-O subnetworks decrease) and Mg atoms incorporate into Si-O network via both BO and NBO form Mg3-O-Si, Mg4-O-Si, Mg-O-Si2, Mg2-O-Si2, Mg3-O-Si2, Mg-O-Si3, Mg2-O-Si3 linkages. It also exists a small part of free oxygens and Mg atoms link to free oxygens forming O-Mgy¬ (y=2÷5) linkages. these O-Mgy¬ linkages is not uniformly distributed in model but they tend forming cluster of O-Mgy. This results in Mg-rich regions. It also have a small fraction of oxygen atoms that is only linked to Si atoms forming O-Siy (y=2÷5) linkages. These O-Siy linkages also tend to cluster forming Si-rich regions. This is the origin of microphase-separation and is evidence of compositional heterogeneity. Besides as pressure increases, the fraction of SiO4 deceases while the fraction of SiO5 and SiO6 increases. The fraction of SiO5 gets maximum value (54%) at pressure about 15 GPa. The size and shape of SiO4, SiO5 and SiO6 units are not dependent on compression. The distribution of SiOx units is not uniform but it tend to form clusters of SiO4, SiO5, SiO6. This results in structural heterogeneity and is origin of polyamorphism. The heterogeneity of structure and composition is the causes of dynamical heterogeneity + In near future, models of MOxSiO2 (with size from 3000-10000 atoms) at liquid and amorphous state will be constructed by Molecular Dynamics Method. New technique will be developed to analysis structural and dynamical characteristics consisting of: i/ Identify defect-rich and defect-poor regions on base of cluster analysis, simplex and the density fluctuations; ii/ Determine the size and lifetime of defect-rich and defect-poor regions under different conditions of temperature, pressure and MOx concentration; iii/ Apply visualization techniques to clarify defect-unit regions; iv/ Determine thermodynamic expression for the clustering of defect-units.

Fiscal Year 2015　List of Publications Resulting from the Use of the supercomputer

[Publication]

Luyen Thi San et al., “Structural organization, micro-phase separation and polyamorphism of liquid MgSiO3 under compression”, European Physics Journal B (accepted).

Toshiaki Iitaka et al., "Pressure-induced dissociation of water molecules in ice VII", Scientific Reports 5, 12551 (2015).
(http://www.nature.com/articles/srep12551)