

Project Title:

Structure and properties of oxide melts

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1. Background and purpose of the project, relationship of the project with other projects

The structure of multicomponent oxide glass system based on SiO₂, B₂O₃, Al₂O₃, P₂O₅ network forming oxide has been studied extensively by different techniques within last decades. Experiment and simulation results showed that structure of silicate and aluminosilicate glasses has appropriate mechanical-, physical- and chemical-properties to immobilize and isolate nuclear wastes from the biosphere. As alkali oxides (alkaline-earth oxides) are added into aluminosilicate glass, some properties of the glass system (melting temperature, electrical conductivity, thermal conductivity, thermal expansion coefficient ...) will be improved and the [NBO]⁻ bonds are also generated in network structure. In nuclear waste glasses, the elements in nuclear waste tend to bind to the [NBO]⁻ and form the bonds: *R-NBO-T*, *R'-NBO-T*, *RE-NBO-T* and *An-NBO-T* (*T* is Si, B; *R* and *R'* are the alkali and alkaline-earth metals, *RE* is the rare earth elements, *An* is the elements in actinide series). Capability of nuclear waste immobilization in the glassy network will increase as [NBO]⁻ concentration increases. Research results show that [NBO]⁻ bonds and [BO₄]⁻, [AlO₄]⁻ units will be generated in the glass network structure as CaO is added to B₂O₃-SiO₂, Al₂O₃-B₂O₃-SiO₂. At low CaO concentration, Ca⁺ cations tend to be close to the [BO₄]⁻, [AlO₄]⁻ units and they have role of charge-balance. Conversely, at higher CaO concentrations, the Ca⁺ cations tend to be closer to the [NBO]⁻ and they act as the network-modifier.

Multi-component glass systems based on SiO₂, Al₂O₃ are typical glass groups containing two types of network forming elements. In addition, the local environment of the alkali and alkali-earth cations in the multicomponent oxide glass systems based on SiO₂-Al₂O₃ has not yet been well understood. So, it is necessary to get more researches on the

structure of the glass systems based on SiO₂, Al₂O₃. Besides, Multi-component glass systems based on P₂O₅, SiO₂, B₂O₃ and Al₂O₃ network forming oxides are also the typical bioactive glass systems.

Investigating the structure of multicomponent oxide glass based on SiO₂, B₂O₃, Al₂O₃, P₂O₅ network forming oxides will help optimized structure to improve desirable properties of nuclear waste storage materials and bioactive materials. Information on these issues is difficult to trace directly by experiment and ones usually apply molecular dynamics simulations. Therefore, present project is devoted to giving some new insight into the structure of the above multicomponent oxide glass system.

2. Specific usage status of the system and calculation method

Molecular dynamics simulation, topology analysis, cluster analysis, simplex analysis and density fluctuation method as well as recognition and Visualization methods are applied to clarify the structure and properties of multicomponent-oxide glass systems: SiO₂; CaO-Al₂O₃-SiO₂; Na₂O-B₂O₃-SiO₂; CaO-P₂O₅-SiO₂.

3. Result

The structure of SiO₂ and CaO-Al₂O₃-SiO₂ system under high pressure has been clarified. The investigation results have been published on 02 papers

4. Conclusion

Network structure of amorphous SiO₂ at 500K in the 0-100 GPa pressure range comprises basic structural units of SiO₄, SiO₅ and SiO₆. At low pressure, most of structural units are SiO₄. Under compression, there is a transformation from tetrahedral- to octahedral-network through SiO₅ units. The concentration of SiO₅ get maximum at around 10-15 GPa. At high pressure, most of structural units are SiO₆. The

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concentration of SiO_6 units is over 95 % at pressure beyond 20 GPa. The transformation from SiO_4 to SiO_6 under compression is accompanied by the transition from OSi_2 -linkage to OSi_3 -linkage. In the 0-20 GPa pressure range, the Si-O bond length increases with pressure. At pressure beyond 20 GPa, the Si-O bond length decreases with pressure. The O-O bond length decreases with pressure in the considered pressure range (0-100 GPa). The increase of Si-O bond length as well as the decreases of O-O bond length under compression is due to the decrease of O-Si-O bond angle. The first Si-Si peak splitting under compression relates to the two kinds of Si-O-Si bond angle (95° and 135°) due to the forming of OSi_3 linkages. The structure of silica consists of three phase: SiO_4 -, SiO_5 - and SiO_6 -phases. At pressure beyond 20 GPa, most of basic structural units are SiO_6 forming SiO_6 -cluster (SiO_6 -phases) and they tend to arrange orderly, forming stishovite crystalline. The silica glass will tend to transform to crystalline under high pressure. This is supported by the fact that many materials tend to form crystal structure under compression. Maybe this is also one of many reasons that explains why the materials in the inner-core of the earth (where the pressure is very high) have the crystalline structure.

The network structure of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ melt consists of two types of networks: -Si-O- and -Al-O- networks. The -Si-O- network is built from SiO_x units and the -Al-O- network is built from AlO_x units. The topology of AlO_x units is more sensitive with pressure in comparison to SiO_x ones. The topology of SiO_x is almost not change, meanwhile the topology of AlO_x is slightly distorted under compression.

In general, the degree of polymerization of -T-O- network increases with pressure. The mixture between -Al-O- and -Si-O- networks also increases with pressure. Investigation result shows the existence of -Si-O-Si- subnets beside the -O-Al-O- subnets with chain- or tree-shape. This reveals the structural and compositional heterogeneities that is the origin of microphase separation in CAS system.

The Ca^{2+} cations tend to incorporate into -T-O- network via negative charge species of $[\text{NBO}]^-$, $[\text{TO}_x]^-$. However, the Ca^{2+} cations are mainly distributed in the -Al-O- network and in the boundary between -Si-O- and -Al-O- networks. So, the distribution of Ca^{2+} cations in CAS system is not uniform.

The boundaries between -Si-O- and -Al-O- networks are the Ca -rich regions. The regions inside SiO_x -clusters are the Ca -poor regions.

The number of O-Al_3 triclusters is very small (only several ones) at ambient pressure and it increases gradually with pressure. At 40 GPa, the number of O-Al_3 triclusters is about several tens. This demonstrates that the aluminum avoidance principle is also exhibited in CAS system.

The densification mechanism of CAS system is due to: 1/ the SRO change of Ca and Al atoms; 2/ the change of IRO that relates to the decrease of the T-O-T bond angles and T-T distances (T=Al, Si).

The incorporation mechanism of Ca^{2+} cations into -T-O- network can be applied as a good solution for immobilization of hazardous wastes (industrial and nuclear wastes) in network structure of multicomponent glass systems.

5. Schedule and prospect for the future

In next time, we will focus on the structural investigation of $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$; $\text{CaO-P}_2\text{O}_5\text{-SiO}_2$. These are typical groups of nuclear waste storage materials and bioactive-materials with many good properties.

6. If no job was executed, specify the reason.

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Fiscal Year 2019 List of Publications Resulting from the Use of the supercomputer

- [1] Nguyen Thu Nhan, Giap Thi Thuy Trang, Toshiaki Iitaka and Nguyen Van Hong, Crystallization of amorphous silica under compression, *Can. J. Phys.* 97: 1133–1139 (2019) [dx.doi.org/10.1139/cjp-2018-0432](https://doi.org/10.1139/cjp-2018-0432)
- [2] Nguyen Van Hong, Nguyen Thi Thanh Ha, Pham Khac Hung, Toshiaki Iitaka, Pressure-induced structural change of CaO–Al₂O₃–SiO₂ melt: Insight from molecular dynamics simulation, *journal of Materials Chemistry and Physics*, [Vol. 236](#), 1 October 2019, 121839, <https://doi.org/10.1016/j.matchemphys.2019.121839>.