Usage Report for Fiscal Year 2021

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

Flexible network structure of multicomponent oxide systems is at the heart of many glassy materials with functional properties. The *PbO-SiO*$_2$*, MgO-SiO*$_2$*, CaO-SiO*$_2$*, CaO-Al2O3-SiO2* glasses, and melts are of significant interest to many technologically important fields and applications, including geology, glass science, metallurgical process, nuclear waste storage. In particular, SiO_2, CaO and Al_2O_3 oxides are the main components of synthetic refining slags. The composition and properties of slags directly affects smelting products. Because of their important application, the microstructure of SiO_2, PbO-SiO_2, MgO-SiO_2, CaO-SiO_2 and CaO-Al_2O_3-SiO_2 melts have been studied extensively for a long time. As we have known, the structure of SiO_2 consists of tetrahedra SiO_4 that connects each other forming continuous random tetrahedral network in three-dimensional space. As metal oxides such as Na_2O*, CaO, MgO, and Al2O3…* are added into silica, the *-Si-O-Si-O-* network is broken and form non-bridging oxygen (*NBO*). The metal ions tend to incorporate into -Si-O-Si-O- network through $[NBO]^-$, therefore, they act as network modifiers that are thought to weaken the -Si-O-Si-O- network and influence transport properties. In CaO-Al_2O_3-SiO_2 system (the Al_2O_3 is an intermediate oxide), the Al^{3+} ions tend to replace the Si^{4+} sites forming tetrahedra AlO_4 with negative charge ($[AlO_4]^-$). Ca^{2+} ions tend to locate near the $[AlO_4]^-$. In this case, Ca^{2+} ions play the role of charge balancing where one Ca^{2+} compensates two tetrahedra $[AlO_4]^-$. The concentration of $[NBO]^-$ and $[AlO_4]^-$ in PbO-SiO_2, MgO-SiO_2, CaO-SiO_2, *CaO-Al2O3-SiO2* glasses and melts are strongly dependent on temperature, pressure and composition. Structural characteristics and the relationships between network structures and corresponding properties of oxide melts is the key data for improving the properties and designing new materials. Controlling the structure based on fabrication technology conditions and/ or composition will help to create materials with the desired properties. This is also the purpose of this project.

2. Specific usage status of the system and calculation method

Molecular Dynamics and Monte-Carlo simulation, topological analysis, structure recognition and visualization methods are applied to clarify the structure and properties of oxide melts.

3. Result

- Structural phase transition and densification mechanism in lead silicate melt (Pb_2SiO_4) is investigated by molecular dynamics simulation, topological analysis, structure recognition and visualization methods are applied to clarify structural characteristics of models. The investigation results have been submitted for publication on Phase Transitions Journal.
- Local structure environment and network structure of multicomponent oxide systems [CaO-SiO_2 (brief as CS) and CaO-Al_2O_3-SiO_2 (brief as CAS)] at 3500 K are investigated by molecular dynamics simulation (MDS). The investigation results have been submitted for publication on Bulletin of Materials Science Journal

4. Conclusion

Structure of Pb_2SiO_4 system consists of three phases: SiO_4, SiO_5 and SiO_6 ones. Under compression, it tends to transform from SiO_4 to SiO_6 phase via SiO_5. The topology and size of basic structure units is identical, not dependent on pressure. At low pressure, the SiO_x units tend to connect to each other via corner-sharing bonds. However, at high pressure, they tend to connect each other via corner-sharing, edge-sharing and face-sharing bonds. The incorporation mechanism of Pb^{2+} ions into glassy network is via negative species. At low pressure, Pb^{2+} ions have the role of network modifier. However, at high pressure, they have the roles of both network modifier and charge belance. In Pb_2SiO_4 system, there is existence of Pb-rich and Si-rich regions. These reveal the microphase separation. The microphase separation dereases as pressure increases. The densification mechanism in Pb_2SiO_4 is via the increase of coordination number and the rearrangement of glassy network. The polymerization increases with pressure. Intermediate range order is stronly dependent on pressure.

The network structure of CAS melt consists of two types of networks: *-Si-O-Si-* and *-Al-O-Al-* networks. The -Si-O-Si-O- network is the main one in the CAS system. The Al^{3+} ions tend incorporates into -Si-O-Si-O- network forming mixture network. The Al^{3+} ions have the same role as Si^{4+} ions in the network. The distribution of Al^{3+} ions in the silicate network is not uniform. The Ca^{2+} cations tend to incorporate into *-T-O-T-* network via negative charge species of $[NBO]^-$, $[AlO_4]^-$. It also reveals that the Ca^{2+} cations are mainly distributed in the *-Al-O-Al-* network and in the bondary between *-Si-O-Al* and *-Al-O-Al-* networks. So, the distribution of Ca^{2+} cations in CAS system is not uniform. The boundaries between subnets are the *Ca*-rich regions. The regions inside the large *-Si-O-Si-O-* network are the *Ca*-poor regions (micro-phase separation phenomenon).

The incorporation mechanism of Ca^{2+} cations into glassy network can be applied to design functional materials in nuclear waste storage, glass science, and metallurgical process.

5. Schedule and prospect for the future

In next time, we will focus functional material based on network forming materials with application in nuclear waste storage and bioative-materials.

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

Fiscal Year 2021 List of Publications Resulting from the Use of the supercomputer

No publication