Usage Report for Fiscal Year 2017

**Project Title:**

# Structure and properties of materials in the deep earth and planets

**Name:**
John Sak Tse
Tsutomu Kawatsu
Le The Anh
○Toshiaki Iitaka

**Laboratory at RIKEN:**
Computational Astrophysics Laboratory

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## 1. Background and purpose of the research.

The computational facility was used on two independent research projects: [a] Structure and dynamics of molten and glass Basalt at high pressure and [b] First Principles prediction on the thermal conductivity of minerals and semiconducting thermoelectric materials.

[a] Structure and dynamics of molten and glass Basalt at high pressure.

Silicate liquids play a vital part at all stages of deep Earth evolution, ranging from early stage on the core and crust formation to the present-day volcanic activity. Quantitative modeling of the dynamical processes in the Earth mantle will require detail knowledge of the structures and transport properties (e.g. viscosity and thermal conductivity) in liquid silicates at the pressures and temperatures in the Earth's interior. In particular, the densities of silicate mineral melts are the most important parameters as they are the primary factors controlling the evolution of magmas in the Earth mantle. Not until recently, reliable measurements of the density and the structure of a liquid at high pressure have been hampered by experimental difficulties. Basalt is an igneous rock formed from the lava and a key component of the magmas. Basalt is mainly a mixture of quartz and feldspar. In this study, a model basalt consisting of Ca, Al and Mg silicates close to the eutectic composition of 36 mol% anorthite and 64 mol% diopside ($Ca_{22}Mg_{14}Al_{16}Si_{44}O_{144}$) was used. Canonical (NVT) MD calculations ere performed on the melt at 2200- 3300K and the quenched glass between 10 – 60 GPa. Apart from the density and structure, important parameters such as the bulk modulus and average sound velocity, viscosity, diffusion coefficient and the phonon density of states were calculated.

[b] First Principles prediction on the thermal conductivity of minerals and semiconducting thermoelectric materials.

The thermal conductivity is an important thermophysical property of a material. Indeed, it is the fundamental quantity governing the performance of thermoelectric devices. The maximum efficiency for power generation and cooling is determined by the dimensionless figure of merit (ZT), which is proportional to the Seebeck coefficient and the electrical conductivity but inversely proportional to the thermal conductivity. Therefore, thermal conductivity is a critical parameter to be optimized. Equally importantly, knowledge of relevant minerals' thermal conductivity elevated pressure and temperature is sine qua non for understanding the rate of core heat loss and the Earth's evolution. However, direct measurement of thermal conductivity under these We implemented an efficient computational scheme for estimating lattice thermal conductivities of

ordered and disordered solids using an efficient scheme based on the Einstein relationship of the energy moment, sampled from first-principles Born-Oppenheimer molecular dynamics employing Density Functional Theory. The performance and accuracy of this method is validated through calculations for selected examples, including MgO at elevated temperatures and pressures, as well as the potential efficient thermoelectric materials of doped Si46 and CoSb3 semiconductors.

## 2. Specific usage status of the system and calculation method

*Ab-initio* Molecular dynamics simulation was carried out on basalt. Initially, the model systems were equilibrated at the desirable pressure and temepratures using isobaric-isothermal molecular dynamics (NPT) calculations. This was followed by canonical ensemble constant volume and constant temperature (NVT) calculations. The reason for using the canonical ensemble is because we wish to compute the viscosity of the melt from the fluctuations of the strain using the Green-Kubo method. All the simulations were done using the VASP program. The electron orbitals were expanded in the plane wave basis set and the Perdew-Burke–Ernzerhof (PBE) functional was used. The kinetic energy cutoff of the plane wave was 400 eV. It was found that the inclusion of the Ca 2s and 2p orbitals in the valence shell was important for SCF convergence, The stoichiometry of the basaltic material studied included 22 atoms of calcium, 14 atoms of magnesium, 16 atoms of aluminium, 44 atoms of silicon and 148 atoms of oxygen. The total number of atoms in the unit cell was 244. Owing to the large size of the unit cell and computational limitations, we ran all the simulations employed one *k*-point (Γ) for Brillouin Zone sampling. For basalt melt, simulations were performed at 0, 18, 23, 38, 50, 62, 68 and 82 GPa and 2200 K, similar to the experimental conditions. MD calculations on the quenched glass was performed using NVT MD at 300 K by adjusting the dimensions of the model to reproduce the corresponding pressures. The time step pf 2.0 fs was used for the integration of the equation of motions All AIMD simulations were performed for at least 50 ps.

For DFT thermal conductivity calculations on MgO, pure and Te-doped $CoSb_3$ and $Ba_8Si_{46}$ using the projected-augmented wave (PAW) potentials and a plane-wave basis within the framework of the generalized-gradient approximation, employing the PBE exchange-correlation functional. The Vienna *ab initio* simulation package (VASP) was used for all electronic and first-principles Born-Oppenheimer molecular-dynamics calculations in the canonical (NVT) ensemble. For all cases, the integration time step was 2 fs. Additional calculations on MgO were performed using Vanderbilt ultra-soft pseudopotentials,and the results were compared with those obtained by PAW potentials. The supercell models used for the MD calculations were generated by replicating the respective primitive cells. or MgO most calculations were performed on a 4×4×4 supercell. To test the convergence on the system size, a smaller 3×3×3 and a larger 5×5×5 supercell of MgO were also studied. For pristine and Te-doped CoSb3,29 and Ba8Si46 2×2×2 supercells were used resulting in 256 atoms for the former and 432 atoms for the latter. Integration in the Brillouin zone was sampled by the Γ point. A trajectory consisted of 30,000 – 60,000 MD time steps (i.e. 60 – 120 ps) after thermal equilibration wasmally required for thermal-conductivity calculations.

## 3. Result

A brief summary and highlights of the results are presented below.

The pressure-volume relation of basaltic melt is shown in Fig. 1.. A distinct discontinuity close to 35 GPa was observed. The theoretical prediction agrees very well with experimental

observations The break in the EOS curve is a clear indication of the structural change at 35 GPa. This can be ascribed to the change in the nearest neighbor environment in Si and Al from tetrahedral to octahedral.

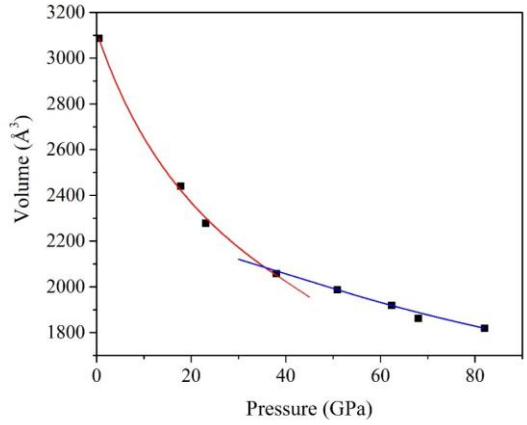


Fig. 1 P-V EOS of molten

The structural change is also reflected in the abrupt change in the sound velocity as shown in Fig. 2.

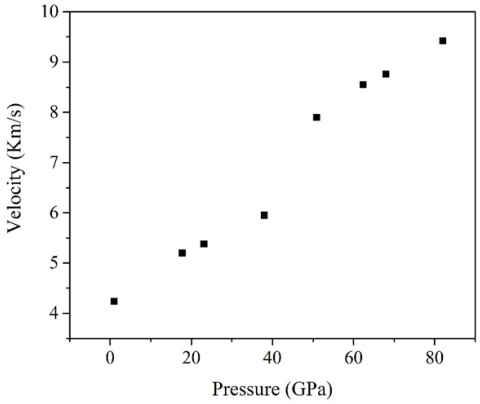


Fig. 2 Pressure evolution of the velocity of sound

It is also found that the structural similarities between high pressure silicon and oxygen coordination for glass and melt are striking. It becomes evident that the Si atoms are 4 fold coordinated with respect to oxygen atoms at ambient pressure to form $SiO_4$ tetrahedrons. On being compressed, till approximately 18 GPa, the coordination number of silicon atoms remains 4. However, above 20 GPa, the coordination number increases at the cost of the four-fold coordination. A mixture of four and five-fold coordination species become prevalent. This trend of mixed coordination is seen till approximately 38 GPa when at pressures close to 38 GPa, the four-fold coordination gets replaced by six-fold coordination. After 38 GPa, the number of nearest oxygen neighbors of silicon becomes six completely, thus completing the first order structural phase transition of the melt from four to six-old coordination, which is expected when compared to other silicate melts.

The most striking example om the tjermal conductivity calculations is typified by the results on pristine and Ba doped $Si_{46}$, a semiconductor clathrate. Previously, crystalline silicon and silicon clathrates of types I ($Si_{46}$) and II ($Si_{136}$) structures were used to validate the Einstein-MD method for thermal-conductivity calculation Here, we studied the effect of Ba doping modelled by a 2×2×2 replicated supercell of type I silicon clathrate consisting of 368 Si with both the small and large cavities filled completely by 32 Ba atoms ($Ba_8Si_{46}$) at ambient pressure. MD calculations were performed at 80 and 300 K. The results for the Ba-filled and empty $Si_{46}$ reported previously are depicted in Fig. 3

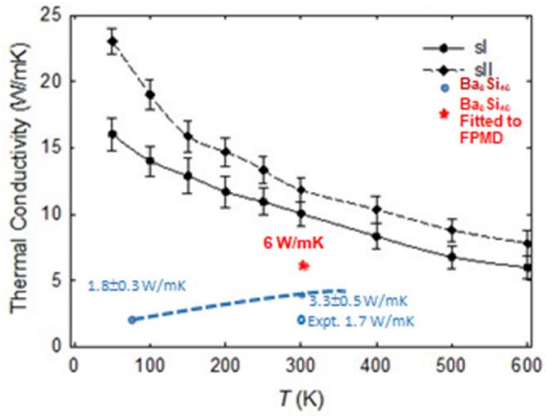


Fig. 3

Thermal conductivity of types I ($Si_{46=}$) and II ($Si_{136}$) empty Si clathrates and lattice thermal conductivity of $Ba_8Si_{46=}$ (this work). The red

star denotes the lattice thermal conductivity of $Ba_8Si$=16 calculated from Green-Kubo heat-flux autocorrelation formula from a molecular-dynamics calculation wherein the interatomic potential has been fitted to first-principles calculations

The calculated lattice components to the thermal conductivities of Ba8Si46 at 80 and 300 K are 1.8 × 0.3 W/m/K and 3.3 ×0.5 W/m/K, respectively. The calculations reproduced correctly the glass-like behavior of the thermal conductivity, with conductivity of the Ba-filled clathrate is lower than the empty clathrate and pure silicon.

Another powerful test on the accuracy of our implantation is the calculations on the thermal conductivity of MgO at high pressures at 300 K. The results using the 4×4×4 supercell model are reported in Fig.4

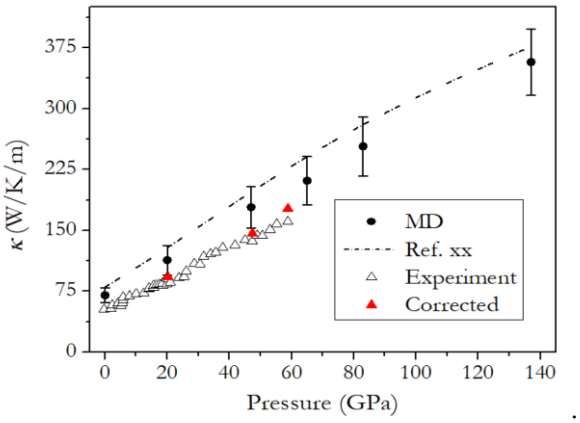


Fig. 4 Comparison of theoretical and experimental thermal conductivity of MgO as a function of pressure at 300 K. The experimental data are represented by open triangles with the filled red triangles corrected for the heat capacity. The dot-dash line is computed from the theoretical calculated thermal conductivities using cubic anharmonic force constants fitted to an analytical function

The thermal conductivities are found to increase with increasing pressure. At 137 GPa, the thermal conductivity of 357 ± 41 W/m/K is almost five times larger than the ambient-pressure value of 70.3 ± 8.9 W/m/K. Apparently, the thermal conductivities are overestimated somewhat by the theory and the deviation with experiment becomes larger with increasing pressure. This discrepancy is puzzling, as there is no obvious reason that the MD method should perform less well under increasing pressure. A probable reason is that measured quantity in the experiment was derived from the thermal diffusivity and then converted to thermal conductivity by multiplying the estimated heat capacity. However, the heat capacity at constant pressure is not known and cannot be measured directly and therefore, estimated from the knowledge of the equation of state and other elastic properties from literature data. We found the estimation was very poor as compared to the calculated heat capacity at constant pressure (Cp) from quasi-harmonic (QHA) lattice dynamics. If the "experimental" thermal conductivities were corrected by scaling with the appropriate (QHA/empirical) Cp ratios, the absolute magnitudes increased bringing the experimental results in better agreement with the theoretical Einstein-MD values.

## 4. Conclusion

We used *ab initio* molecular dynamics method to study the structural and transport properties of basalt melt and glass under the mantle conditions. Structural changes were observed in both cases, For the melt, the compressibility and transport properties have been computed and compared with experiments, A structural change from 4- to 6-coordiantion Si-O was found in both the melt and the glass. The compute diffraction patterns are in good agreement with observation and this give us confidence on the predicted structural change and the

interpretation on the experimental findings in particular on the high pressure densities of silicate melts which are one of the most much sought after properties because density is the primary factor controlling the evolution of magmas at the Earth mantle. In addition, we have also computed the viscosities of the melts at different pressure. This information will help to explain the transplort of magmas in the Earth,

The computational algorithm presented here is valid for solids: the convection contribution to thermal conduction is neglected Comparing to current and widely-used methods based on the Boltzmann transport equation and relaxation times computed from anharmonic force constants or derived from MD trajectories through calculation of the intermediate scattering functions, the present method is more suitable and efficient to study both low-symmetry crystal, positionally-disordered and amorphous solids, The present MD method can be applied to high temperature where high-order anharmonic effects certainly cannot be neglected if accuracy is desired. The method introduced in this study will become the method of choice in the near future due to anticipated advances in more efficient algorithms for linear-scaling electronic structure calculations and increasing computing power.

## 5. Schedule and prospect for the future

The computational part of the two projects had been completed. We are analyzing the computational results on basalt and the plan is to have a paper ready for submission in the early summer. The investigation on the performance of our computational scheme for efficient and accurate prediction of the thermal conductivity has been completed and a paper is already submitted for publication.

**Fiscal Year 2017 List of Publications Resulting from the Use of the supercomputer**

**[Oral presentation at an international symposium]**

I **J.S. Tse,** N.J. English and **T. Iitaka**, Thermal Conductivity of Thermoelectric Materials, The International Conference on Materials for Advanced Technologies ICMAT-2017, Singapore. (Invited)