Supplementary Information

Temperature-Dependent Properties of Molten Li$_2$BeF$_4$ Salt Using Ab Initio Molecular Dynamics

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1. Computational Methods

The electronic structure, interatomic bonding, and optical properties are calculated by using the first principles Orthogonalized linear combination of atomic orbitals (OLCAO) method. This is a DFT based method within local density approximation (LDA) and is found very efficient for the electronic structure study for crystalline to amorphous and liquids systems$^{1-5}$. The implementation of localized atomic orbitals in the basis expansion enables us to quantify the charge transfer and interatomic bonding via effective charge $Q^*$ on each atom and bond order (BO) value between pairs of atom $\rho_{\alpha \beta}$ using the Mulliken scheme$^{6,7}$

$$Q^*_\alpha = \sum_i \sum_{n, occ} \sum_{j , \beta} C_{i \alpha}^* n C_{j \beta}^n S_{i \alpha, j \beta}$$

(1)

$$\rho_{\alpha \beta} = \sum_n \sum_{occ} C_{i \alpha}^* n C_{j \beta}^n S_{i \alpha, j \beta}$$

(2)

Where $S_{i \alpha j \beta}$ is the overlap matrix between the basis Bloch sums of the orbital index (i, j) and atomic specification ($\alpha$, $\beta$). N is the band index, i, j are the orbital quantum numbers and $C_{j \beta}$ is the eigenvector coefficient.

From the calculated value of $Q^*$, the charge transfer between the ions due to atomic interaction can be quantified in terms of partial charge (PC). It is defined as the deviation of $Q^*$ from the charge of neutral atom $Q^0$ and is given by $\Delta Q = Q^0 - Q^*$. As the PC gives the quantity of charge transfer in atomic interaction, a positive PC value implies loss, and a negative PC value implies the gain of electronic charge. The BO value obtained from equation (2) gives the direct quantitative measure of bond strength between a pair of atoms. The sum of all BO values in the system is the total BO (TBO). TBO density (TBOD) defined as $TBOD = \frac{TBO}{Cell\ Volume}$ is a quantum mechanically calculated parameter. It is a single quantum mechanical metric useful for assessing the internal cohesion and strength in a material.$^8$ Higher the TBOD value indicates the material is internally
strong. The use of TBOD to characterize the internal strength of a material and to correlate it with the calculated physical properties is a novel and highly appealing concept.

The density of states (DOS) $G(E)$ gives the number of electron states per unit energy in the material. DOS can be defined as

$$G(E) = \frac{\Omega}{(2\pi)^3} \int dE \frac{1}{|E|} \left( \frac{dS}{dE} \right)$$

where $\Omega$ is volume of the unit cell, $S$ is the overlap matrix, and the integral is over the constant energy surface in Brillouin Zone (BZ). The total DOS can be resolved into partial DOS (PDOS) for atoms and orbitals.

OLCAO is suitable to calculate the linear optical properties within the random phase approximation of inter-band optical transition theory. The inter-band optical properties of the simulated glasses are calculated in the form of a frequency-dependent complex dielectric function $\varepsilon(\hbar\omega) = \varepsilon_1(\hbar\omega) + i\varepsilon_2(\hbar\omega)$. The imaginary and real parts, $\varepsilon_1(\hbar\omega)$ and $\varepsilon_2(\hbar\omega)$ respectively, are obtained from equations:

$$\varepsilon_2(\hbar\omega) = \frac{e^2}{\pi \hbar^2} \int d^3 r \sum_{n,l} \left| \left[ \psi_n^* (k,r) \right] - i\hbar \nabla \psi_n (k,r) \right|^2 \times f_i^l(k) \left[ 1 - f_i^l(k) \right] \delta \left[ E_n(k) - E_i(k) - \hbar\omega \right]$$

$$\varepsilon_1(\hbar\omega) = 1 + \frac{2P}{\pi} \int_0^{\infty} \frac{\varepsilon_2^r(\hbar\omega)}{s^2 - \omega^2} ds$$

where $l$ and $n$ represent the occupied and unoccupied states respectively, and $f_i^l(k)$, $f_i^n(k)$ are the Fermi distribution functions. From the value of $\varepsilon_1$ at the zero frequency, the refractive index $n$ is obtained using expression $n = \sqrt{\varepsilon_1(0)}$.

The energy loss function (ELF) $F(\omega)$ is calculated from the imaginary part of $(1/\varepsilon)$ as

$$F(\omega) = \text{Im}(\frac{1}{\varepsilon(\omega)}) = \frac{\varepsilon_2(\omega)}{\varepsilon_1(\omega) + \varepsilon_2(\omega)}$$

We calculated the mechanical properties based on stress vs strain relation, a similar approach adopted in our previous calculation. A small strain of ±0.25% is applied to each independent strain element of the FliBe cell to obtain stress data $\sigma_i$. The deformed structures are optimized at constant volume. From the calculated six stress component $\sigma_i$, the elastic tensor $C_{ij}$ are collected for applied strain $\varepsilon_j$ solving the following equation: $\sigma_i = \sum_j^6 C_{ij} \varepsilon_j$. From $C_{ij}$, the compliance tensor $S_{ij}$ are obtained. From the values of $C_{ij}$ and $S_{ij}$, we can get the bulk mechanical parameters, the Young’s modulus (E), bulk modulus (K), shear modulus (G) and Poisson’s ratio $\eta$ applying the Voigt-Reuss-Hill approximation for polycrystals. The Voigt’s approach gives the upper
limit of bulk modulus $K_{\text{Voight}}$ and shear modulus $G_{\text{Voight}}$ while Reuss approximation gives the lower limit of bulk modulus $K_{\text{Reuss}}$ and shear modulus $G_{\text{Reuss}}$

$$K_{\text{Voight}} = \frac{1}{9}(C_{11} + C_{22} + C_{33}) + \frac{2}{9}(C_{12} + C_{13} + C_{23})$$  \hspace{1cm} (7)

$$G_{\text{Voight}} = \frac{1}{15}(C_{11} + C_{22} + C_{33} - C_{12} - C_{13} - C_{23}) + \frac{1}{5}(C_{44} + C_{55} + C_{66})$$  \hspace{1cm} (8)

$$K_{\text{Reuss}} = \frac{1}{(S_{11} + S_{22} + S_{33}) + 2(S_{12} + S_{13} + S_{23})}$$  \hspace{1cm} (9)

$$G_{\text{Reuss}} = \frac{15}{4(S_{11} + S_{22} + S_{33}) - 4(S_{12} + S_{13} + S_{23}) + 3(S_{44} + S_{55} + S_{66})}$$  \hspace{1cm} (10)

Hill’s approximation uses the average value of Voight and Reuss approach and gives the value of bulk modulus and shear modulus.

$$K = \frac{K_{\text{Voight}} + K_{\text{Reuss}}}{2}$$  \hspace{1cm} (11)

$$G = \frac{G_{\text{Voight}} + G_{\text{Reuss}}}{2}$$  \hspace{1cm} (12)

From values of $K$ and $G$, the Young’s modulus $E$ and Poisson’s ratio $\eta$ can be obtained as follows:

$$E = \frac{9KG}{3K+G}$$  \hspace{1cm} (13)

$$\eta = \frac{3K-2G}{2(3K+G)}$$  \hspace{1cm} (14)

In a cubic crystal, the elastic anisotropy is given by the Zener anisotropy ratio $(A)$ defined as

$$A = 2\frac{C_{44}}{C_{11} - C_{12}}$$  \hspace{1cm} (15)

For isotropic solids $A$ equals to 1, which gives $C_{44} = (C_{11} - C_{12})/2$.

The ion dynamics in the simulated model is analyzed using velocity autocorrelation function (VACF) which provides the information on dynamic motion of atoms with time. It is defined as

$$C(t) = \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle / \langle \mathbf{v}(0) \cdot \mathbf{v}(0) \rangle$$  \hspace{1cm} (16)

in which $\mathbf{v}(t)$ is the atom velocity at time $t$ and $\mathbf{v}(0)$ is the velocity at time 0. This function helps to understand how fast the initial velocity memory is lost.
2. Additional results and figures

Figure S1. Velocity autocorrelation function in the simulated FLiBe model.
Figure S2. Ball and stick representation of final equilibrated FLiBe model at simulated temperatures.
Figure S3. Calculated total density of states in the simulated FLiBe at different temperatures.
Figure S4. Distribution of partial charge for Li, Be and F atoms in the simulated model at different temperatures.
Figure S5. Averaged partial charge for each atom in FLiBe.
Figure S6. Calculated real and imaginary part of dielectric functions in FLiBe at different temperatures.
Figure S7. Calculated energy loss functions in the simulated FLiBe at different temperatures.
References:
1. Aryal, S.; Rulis, P.; Ching, W. Y., Mechanical Properties and Electronic Structure of Mullite Phases Using First-Principles Modeling. *J. Am. Ceram. Soc.* **2012**, *95* (7), 2075-2088.
2. Liang, L.; Rulis, P.; Ouyang, L.; Ching, W., Ab initio investigation of hydrogen bonding and network structure in a supercooled model of water. *Phys. Rev. B* **2011**, *83* (2), 024201.
3. Baral, K.; Adhikari, P.; Ching, W. Y., Ab initio Modeling of the Electronic Structures and Physical Properties of a-Si–xGeO2 Glass (x= 0 to 1). *J. Am. Ceram. Soc.* **2016**, *99* (11), 3677-3684.
4. Baral, K.; Ching, W.-Y., Electronic structures and physical properties of Na2O doped silicate glass. *J. App. Phys.* **2017**, *121* (24), 245103.
5. Ching, W.-Y.; Rulis, P., Electronic Structure Methods for Complex Materials: The orthogonalized linear combination of atomic orbitals. Oxford University Press:Great Clarendon Street, Oxford, United Kingdom, 2012.
6. Mulliken, R. S., Electronic population analysis on LCAO–MO molecular wave functions. I. *J. Chem. Phys.* **1955**, *23* (10), 1833-1840.
7. Mulliken, R., Electronic population analysis on LCAO–MO molecular wave functions. II. Overlap populations, bond orders, and covalent bond energies. *J. Chem. Phys.* **1955**, *23* (10), 1841-1846.
8. Dharmawardhana, C.; Misra, A.; Ching, W.-Y., Quantum mechanical metric for internal cohesion in cement crystals. *Sci. reports* **2014**, *4*, 7332.
9. Yao, H.; Ouyang, L.; Ching, W. Y., Ab initio calculation of elastic constants of ceramic crystals. *J. Am. Ceram. Soc.* **2007**, *90* (10), 3194-3204.
10. Baral, K.; Li, A.; Ching, W.-Y., Ab initio modeling of structure and properties of single and mixed alkali silicate glasses. *J. Phys. Chem. A* **2017**, *121* (40), 7697-7708.
11. Voigt, W., Lehrbuch der kristallphysik (mit ausschluss der kristalloptik), edited by bg teubner and jw edwards, leipzig berlin. *Ann Arbor, Mich 1928.*
12. Reuss, A., Berechnung der fließgrenze von mischkristallen auf grund der plastizitätsbedingung für einkristalle. *ZAMM-Journal of Applied Mathematics and Mechanics/Zeitschrift für Angewandte Mathematik und Mechanik* **1929**, *9* (1), 49-58.
13. Hill, R., The elastic behaviour of a crystalline aggregate. *Proceed. Phys. Soc. Sect. A* **1952**, *65* (5), 349.
14. Zener, C., *Elasticity and anelasticity of metals*. University of Chicago press:Chicago, Illinois, 1948.