American Mineralogist, Volume 83, pages 1220–1230, 1998

Molecular dynamics simulations of molten $CaAl_2Si_2O_8$: Dependence of structure and properties on pressure

DEAN NEVINS[1],* AND FRANK J. SPERA[1,2]

[1]Department of Geological Sciences, University of California, Santa Barbara, California 93106, U.S.A.
[2]Institute for Crustal Studies, University of California, Santa Barbara, California 93106, U.S.A.

ABSTRACT

Molecular dynamics (MD) simulations were carried out on molten $CaAl_2Si_2O_8$ at nine pressures from 0.2 to 76 GPa at 4000 K, well above the computed glass transition temperature. A simple effective pair-potential with both Coulombic interaction and Born-Mayer-Huggins short-range repulsion was used. Simulations of duration 30 ps long were performed in the microcanonical ensemble (NEV) utilizing 1300 particles (O+Ca+Si+Al). As pressure increases, profound changes occur in the relative abundance of $^{[4]}T$, $^{[5]}T$, $^{[6]}T$, $^{[7]}T$, and $^{[8]}T$ (T = Si,Al) as well as in the coordination of Ca by O. At low pressure, most T are in fourfold coordination with oxygen, oxygen is twofold coordinated to T, and Ca has six to seven nearest O atom neighbors. At 5 GPa, where $^{[5]}T$ maximizes, more than half of the T atoms are pentahedrally coordinated ($^{[5]}T$) in distorted trigonal bipyramids. Both $^{[4]}T$ (25%) and $^{[6]}T$ (18%) are present at 5 GPa and change rapidly as pressure increases ($^{[4]}T$ decreases and $^{[6]}T$ increases). At 5 GPa, the average coordination number (CN) of oxygen about Ca is 8. At 20 GPa, $^{[6]}T$ constitutes more than 50% of the TO_n subunit population and the CN of oxygen around Ca is 10. At medium range (3 to 10 Å), the most significant change in melt structure as pressure increases is replacement of corner-sharing ring-former TO_n polyhedra with edge-sharing polyhedra pairs such as TO_5-TO_6 and TO_6-TO_6. The destruction of the ring structure correlates with the maximization of Ar solubility as pressure increases. Ring structure collapse is geometrically captured by variation in the distribution of T-O-T angles with increasing pressure. The low-pressure maximum at 140° with large variance agrees with X-ray data and follows from the distribution of *N*-member rings with *N* ranging from 4 to 8 (or larger). At higher pressure, the T-O-T distribution narrows and shifts toward smaller angles around 105° consistent with the dominating presence of edge sharing between TO_6-TO_6 and TO_5-TO_6 pairs. Tracer diffusivities for O, Ca, Al, and Si increase at low pressure as pressure increases. The diffusivity of oxygen correlates with ring collapse and attains a maximum at 5 GPa ($D_{ox} = 6.6 \times 10^{-9}$ m²/s); the ratio of diffusivities for Ca, Al, and Si relative to oxygen are 0.67, 0.62, and 0.51, respectively. These data suggest that pentahedrally coordinated T acts as an ‘‘activated complex’’ for oxygen diffusion. Below 5 GPa, activation volumes (V^*) for all species are large in absolute value and lie in the range -25 to -35 cm³/mol; these are similar in absolute value to the partial molar volume of Ar in molten $CaAl_2Si_2O_8$ of 22 cm³/mol. The large absolute values for V_a at low pressure correlate with the contribution to the isothermal compressibility made by configurational effects inferred from Brillouin scattering experiments. At higher pressure, the anomalous diffusion disappears. V_a decreases for all species in absolute value and changes sign; at 20 GPa, V_a is about $+3$ cm³/mol, much smaller than the partial molar volume of Ar in molten anorthite.