A transferable interatomic potential model for crystals and melts in the system $CaO–MgO–Al_2O_3–SiO_2$.

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Introduction

An accurate knowledge of the structural and thermodynamic properties of both crystals and melts in the system $CaO–MgO–Al_2O_3–SiO_2$ (CMAS) is essential for understanding the static and dynamic characteristics, and the conditions of formation and evolution of the Earth's crust and mantle. In a recent publication (Matsui and Price, 1992) we showed that the MAM0K potential, developed primarily for the simulations of $MgSiO_3$ ilmenite and perovskite (Matsui, 1988), is also well applicable to other $MgSiO_3$ polymorphs, such as enstatite, clinoenstatite, protoenstatite, and garnets, in spite of different structural features found in these polymorphs.

The reliability and transferability of interatomic potentials have also been established by static and/or dynamic simulations for silica polymorphs (Tsuneyuki *et al.*, 1988), minerals in the $MgO–SiO_2$ system (Leinenweber and Navrotsky, 1988), and aluminosilicates (Winkler *et al.*, 1991).

With these successful investigations, it is the aim of the present investigation to develop a transferable potential model that is still simple and effective enough for atomistic computer simulations of the structural and physical properties of a wide variety of crystals and melts in the CMAS system.

Simulation methods

The cohesive energy was approximated to be the sum of pairwise interactions between atoms of the form:

$$V(r_{ij}) = q_i q_j r_{ij}^{-1} - C_i C j r_{ij}^{-6} + f(B_i + B_j) \times \exp[(A_i + A_{j-r_{ij}})/(B_i + B_{j)}],$$

where the terms represent Coulomb, van der Waals, and repulsion interactions, respectively. Here r_{ij} is the interatomic distance between atoms i and j, f is a standard force of 4.184 kJ $^{-1}$ mol^{-1}, and q_i, A_i, B_i, and C_i are energy parameters peculiar of the kind of atom i (Matsui, 1988). MD simulations were carried out in the isothermal-isobaric ensemble. Quantum corrections to MD results were made based on the Wigner-Kirkwood expansion of the free energy using the technique proposed by Matsui (1989).

Results and discussion

The net charges on the ions are constrained to be q(Ca) = q(Mg) = q(Al) = ½q(Si) = –q(O) in order to preserve the requirement of transferability between phases with different composition. The energy parameters necessary for MD simulation were derived by fitting the parameters to both the observed structures and bulk moduli of 26 crystals in the CMAS system. The optimum energy parameters and the 26 crystals used for fitting are listed in Table 1.

TABLE 1. Potential parameters[a] used for simulations of crystals[b] and melts in the CMAS system.

	q	A	B	C
Ca	0.9450	1.1720	0.040	45.00
Mg	0.9450	0.8940	0.040	29.05
Al	1.4175	0.7852	0.034	36.82
Si	1.8900	0.7204	0.023	49.30
O	–0.9450	1.8215	0.138	90.61

[a] Units: q in |e|, A and B Å in , and C in $Å^3 kJ^{1/2} mol^{-1/2}$.

[b] Crystals studied in this work. Oxides: periclase (MgO), lime (CaO), corundum(Al_2O_3), spinel ($MgAl_2O4$); SiO_2 system: quartz, cristobalite, coesite, stishovite; $MgSiO_3$ system: clinoenstatite, enstatite, garnet, ilmenite, perovskite; Mg_2SiO_4 system: forsterite, b-spinel, spinel; Ca-silicates: wollastonite($CaSiO_3$), Ca-perovskite (CaSiO3), Ca-olivine (Ca_2SiO_4), diopside ($CaMgSi_2O6$), monticellite ($CaMgSiO_4$); Al_2SiO_5 system: andalusite, sillimanite, kyanite; garnets: pyrope ($Mg_3Al_2Si_3O_{12}$), grossular ($Ca_3Al_2Si_3o_{12}$).

The crystals studied here (see Table 1) have a wide variety of structural topologies. They include oxides and various silicates such as neso-, soro-, chain-, and tecto-silicates. High pressure phases with Si coordinated by six O are also included. The coordination numbers of cations in the 26 crystals range from 6 to 12 for Ca, from 6 to 8 (or 12) for Mg, and from 4 to 6 for Al.

In view of the diversity of the structural types and the simplicity of the potential, the MD results are quite satisfactory in reproducing the observed structures. For all the 26 crystals studied, the errors in the MD simulated values relative to the observed values are within 7% for molar volume, within 3% for lattice parameters, and within 3% for nearest-neighbour Ca-O, Mg-O, Al-O, and Si-O distances. In addition, the MD simulated bulk moduli are found to agree favourably well with available experimental data for the 26 crystals (Saxena and Shen, 1992; and references therein).

Considering the success in calculating both the structures and bulk moduli of the crystals in the CMAS system, we further applied the potential model (Table 1) to $MgSiO_3$, $CaSiO_3$, and $CaMgSi_2O_6$ melts, with the results that the MD simulated values for molar volumes, bulk moduli, and volume thermal expansivities of these melts at 2000 K and 0 GPa again compare reasonably well with the measured (or estimated) values (Bottinga *et al.*, 1982; Lange and Carmichaer, 1987).

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