

Molecular Dynamics Simulation in CaTiO₃

J. A. Souza^{(1)*}, J. P. Rino⁽²⁾

(1,2) Departamento de Física, Universidade Federal de São Carlos, São Paulo, Brazil.
e-mail: ^{1*} james.fisica@gmail.com; ² djpr@ufscar.df.br

* Corresponding author.

Abstract – CaTiO₃ has been simulated using the effective interatomic interaction potential of Vashishta-Rahman. This potential consists of two-body interactions including steric repulsions, Coulomb interactions, charge-induced dipole-interactions, and induced dipole-dipole (van der Waals) interactions. Using the molecular dynamics method, the interaction potential is used to study structural and dynamical properties of crystalline state of CaTiO₃ for several densities and temperatures. The lattice energy for orthorhombic (Pbnm) structure has the lowest energy, followed by the tetragonal (I4/mcm) and cubic (Pm3m) structures. The behavior of system with temperature, showing two phase transitions (Fig.1), and pressure (Fig.2) agree well with the experiments.

The solid state physics of perovskite-type compounds, like CaTiO₃, is very interesting, because it has many physical properties like phase transitions with temperature and pressure, and an impressive range of electrical and magnetic properties: superconductivity, colossal magnetoresistance, ferroelectricity, metallic conductivity, and others. Considering these properties these materials have high technological potential for manufacture of electronic devices, like microwave resonators, advanced optical devices, multilayer ceramic capacitors and dynamic or ferroelectric random access memories for computers.

We have executed the molecular dynamics (MD) simulations in CaTiO₃ using the effective interatomic potential of Vashishta-Rahman form [1]. The two-body potential includes steric repulsions due to atomic sizes, Coulomb interactions resulting from charge transfer between atoms, charge-induced dipole-interactions due to the electronic polarizability of ions, and dipole-dipole (van der Waals) interactions.

Energies of the crystalline forms of CaTiO₃ were calculated with the proposed interaction potential with the structural energy for orthorhombic (Pbnm) structure having the lowest energy, followed by the tetragonal (I4/mcm) and cubic (Pm3m) structures, Fig.1a. The behavior of the phase transitions induced by temperature was obtained in good agreement with the experimental data. The lattice parameters discontinuously change at the orthorhombic-tetragonal transition point, while a continuous change is observed for the tetragonal-cubic transition, Fig. 1b. These results indicate that the first transition is of first order and that the later transformation is of second order. The phase transitions were also analyzed through the change at slope of bulk modulus as a function of temperature. The symmetry of the crystal increases by increasing the temperature. Fig.2 shows the variation of the relative volume with pressure obtained by MD simulation and experiment [2], displaying very good agreement. Other physical properties such as melting temperature, vibrational density-of-states, and specific heat were also calculated showing excellent results.

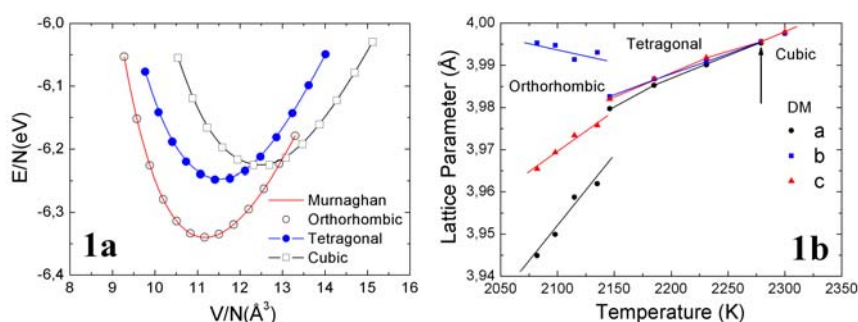


Figure 1: a) Total potential energy per particle for crystalline phases of CaTiO₃ as a function of volume per particle and b) Lattice parameters of phases of CaTiO₃ as a function of temperature.

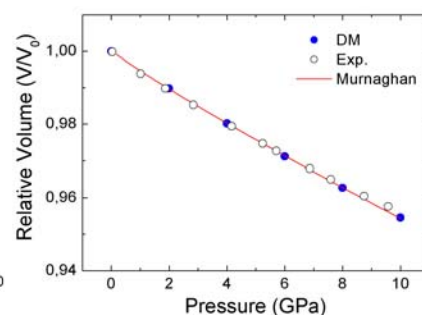


Figure 2: Variation of the relative volume with pressure of CaTiO₃ obtained by MD simulation and experiment [2].

[1] VASHISHTA, P. and RAHMAN, A.; Phys. Rev. Lett. **40** (20), 1337-1340 (1978).

[2] ROSS, N. L. and ANGEL, R. J.; American Mineralogist **84** (3), 277-281 (1999).