

Reply to Comment on “Molecular dynamics simulation of phase transitions and melting in MgSiO_3 with the perovskite structure”

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In the preceding comment, Belonoshko contends that our (Chaplot et al. 1998) simulated melting temperatures in perovskite involved an incorrect method that yielded overestimates of 2000 K, and that our molecular dynamics (MD) simulations of the orthorhombic to cubic transition were an artifact. We disagree on both counts, and point out that:

(1) In Figure 1 of the preceding comment, Belonoshko selectively referred to only our results on perfect lattices, which were not appropriate for comparison with experiments since they involved overheating as explained in detail in our paper. In fact, our simulations on defective lattices involving an equilibrium level of defects yielded melting temperatures consistent with various experiments and their theoretical extrapolations over the entire range of mantle pressures (0–135 GPa). We had performed simulations on the defective lattices since those on perfect lattices, over the very short time scale of MD simulations, cannot be expected to correspond to thermodynamically equilibrated samples at high temperatures. In contrast, the two-phase simulations of perovskite by Belonoshko appear to lead to an unrealistic underestimate of the melting temperature when extrapolated to ambient pressure.

(2) The orthorhombic to cubic transition has been experimentally observed for $\text{Mg}_{0.864}\text{Fe}_{0.136}\text{SiO}_3$ perovskite (Meade et al. 1995) and should not be regarded as an artifact. (The effect of Fe impurities in MgSiO_3 perovskite are not found to be significant in (1) our MD simulations of phase transitions (Chaplot et al. 1998) and (2) the melting studies of Zerr and Boehler (1993). The ab initio LAPW studies of Stixrude and Cohen (1993) also indicate that substitution with Fe is unlikely to affect the phase stability of silicate perovskite). Our simulations indicated the observed transition to be associated with a sublattice melting. Structural phase transitions involving sublattice melting have long been well known, e.g., that in AgI has been experimentally observed and successfully simulated using the MD technique (Parrinello et al. 1983). In case of AgI, which has been much more thoroughly investigated than the perovskite, the sublattice melting transition was observed at a temperature of about 50% of the full melting temperature. In the case of our simulations of perovskite at 70 GPa, the corresponding ratio is about 80%, which appears to be reasonable considering the relative ionic sizes.

The overestimate of 2000 K (Belonoshko 2000) in the perfect lattice simulations appears to be exaggerated. Our calculated melting temperatures for perfect lattices and defective lattices at 70 GPa were 7000 K and 5800 K, respectively, as

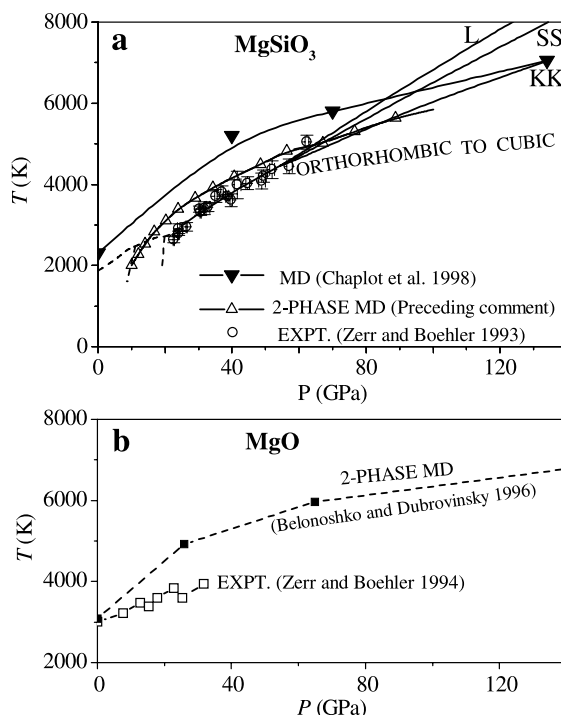


FIGURE 1. (a) The simulated melting temperature of MgSiO_3 perovskite as a function of pressure (Chaplot et al. 1998) with 1% vacancies (solid triangles) compared with the two-phase simulated results (open triangles) with an ideal lattice (preceding comment of Belonoshko). The calculated results are compared with the available experimental data on Fe-bearing perovskite (ZB = Zerr and Boehler 1993, open circles) up to 62.5 GPa and its extrapolations (L, S, and KK) to higher pressures using different melting relations as reported in ZB. The data below 25 GPa are from Ito and Katsura (1992) and Kato and Kumazawa (1985). (b) The two-phase simulated (MD) results of MgO with an ideal lattice (Belonoshko and Dubrovinsky 1996) compared with available experimental data (Zerr and Boehler 1994). Belonoshko et al. (2000) have argued that the actual melting temperature of MgO should be much higher than those reported from diamond anvil cell measurements of Zerr and Boehler (1994). The same arguments could also be extended to the measurements of melting temperature of MgSiO_3 perovskite by Zerr and Boehler (1993) shown in a.

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compared to the experimental value of 5200 K extrapolated from the data of Zerr and Boehler (1993). The corresponding simulated orthorhombic to cubic transition temperatures are 5400 K and 4600 K for the perfect and defective lattices, respectively. The values of simulated phase transition temperatures plotted by Belonoshko (2000) are much higher. Our simulated structural transition temperatures of the defective lattices are less than the experimental melting temperatures in contrast to the contention in the Comment by Belonoshko (2000). In fact, Belonoshko (2000) plotted the simulation results on only the perfect lattices, which are not physically appropriate.

The system size in MD simulations is an important parameter. Our simulation cell size was almost an order of magnitude larger than that previously employed (Matsui and Price 1991; Belonoshko 1996) in similar simulations. This was helpful in (1) distinguishing between the transformation to a tetragonal or a cubic phase, and (2) allowing for a much larger number of wave vectors of vibrational fluctuations to help initiate the phase transitions, sublattice melting, etc., and consequently reducing the likelihood of overheating, etc.

Belonoshko (2000) draws distinction between the phase transition temperatures, thermal instability and "thermal instability of an ideal lattice." Most of the molecular dynamics simulations of phase transitions to date were identified through the thermal instabilities though it is understood that overheating (or over pressurization) would be involved due to the small system size and small time scale, more so if one started with the ideal lattice. Phase transitions would be expected when the parent phase becomes less stable than the daughter phase, in general even in molecular dynamics simulations if long enough times were feasible with a sufficiently large system. This would also apply to the two-phase simulations although the overheating is reduced since the transition is encouraged at the interface. Two phase simulations (at high temperature) starting with defective lattices as we employed in our one phase simulation may be more appropriate than using ideal lattices. For a sufficiently large system observed over a sufficiently long time, phase transition may be related to the corresponding thermal instability keeping in view the likely hysteresis effects in the first order transition. Melting is also a first order transition in which the above considerations are relevant.

Melting is known to be a complex phenomena which has not been well understood yet. It is believed to initiate around defects which include various point defects and extended defects including the surface. In view of the complexity, various simplified methods have been used for its simulations. The two phase method as used by Belonoshko (1998), Belonoshko and Dubrovinsky (1996), and Belonoshko et al. (2000) allows for melting at the interface of an ideal lattice and melt. However, it does not allow for defects to be generated within the ideal lattice. As explained in our paper, in MD simulations starting with a perfect lattice, defects would not be created automatically due to the very short time scale involved in the simulations. We tried to improve the method by incorporating vacancy

defects into a perfect lattice at a level expected from the defect energies at the high temperatures. However, the various simulations of melting at high pressures, including those reported by Belonoshko and Dubrovinsky (1996) and Belonoshko et al. (2000) (see Fig.1b) appear to produce overestimates over the experimental melting temperatures.

Presumably the overestimates of transition temperatures at high pressures in the simulations, more so with perfect lattices, may be due to the inadequacy of mimicking the state of the experimental sample in terms of the defects, stress, etc. On the other hand, in experiments, large variations might occur, as discussed in our paper (Chaplot et al. 1998), due to the sample not being under thermodynamic equilibrium at a uniform temperature and hydrostatic pressure, due to the sample history, etc. It seems that while fully faithful simulations of the complex melting phenomena have not yet been feasible, our method involving equilibrium defects appears to be useful in understanding the experimental results. Moreover, while it would be hard to calculate the thermodynamic melting temperature for a given empirical potential, it would be of limited utility since the empirical potentials are often determined to reproduce only the quasiharmonic structures and dynamics, and might not fully faithfully represent the interatomic potential far away from the harmonic atomic displacements as needed in the very high pressure high temperature molten state.

REFERENCES CITED

- Belonoshko, A.B. (1998) Melting of corundum using conventional and two phase molecular dynamics simulation method. *Physics and Chemistry of Minerals*, 25, 138–141.
- (2000) Molecular dynamics simulation of phase transitions and melting in MgSiO_3 with the perovskite structure—comment. *American Mineralogist*, 86, 193–194.
- Belonoshko, A.B. and Dubrovinsky, L.S. (1996) Molecular dynamics of NaCl (B1 and B2) and MgO (B1) melting: Two phase simulation. *American Mineralogist*, 81, 303–316.
- Belonoshko, A.B., Ahuja, R., and Johansson, B. (2000) Molecular dynamics of LiF melting. *Physical Review B* 61, 11928–11935.
- Chaplot, S.L., Choudhury, N., and Rao, K.R. (1998) Molecular dynamics simulation of phase transition and melting in MgSiO_3 with the perovskite structure. *American Mineralogist*, 83, 937–941.
- Ito, E. and Katsura, T. (1992) Melting of ferromagnesian silicate perovskite under lower mantle conditions. In Y. Syono and M.H. Manghani, Eds., *High Pressure Research in Mineral Physics, Applications to Earth and Planetary Sciences*, p. 35–44, Terra Scientific, Tokyo.
- Kato, T. and Kumazawa, M. (1985) Garnet phase of MgSiO_3 filling pyroxene-ilmenite gap at very high temperature. *Nature*, 316, 803–805.
- Matsui, M. and Price, G. D. (1991) Simulation of the pre-melting behavior of MgSiO_3 perovskite at high pressures and temperatures. *Nature*, 351, 735–737
- Meade, C., Mao, H.K., and Hu, J. (1995) High temperature phase transition and dissociation of $(\text{Mg,Fe})\text{SiO}_3$ perovskite at lower mantle pressures. *Science*, 268, 1743–1745
- Parrinello, M., Rahman, A., and Vashishta, P. (1983) Structural transitions in superionic conductors. *Physical Review Letters*, 50, 1073–1076
- Stixrude, L. and Cohen, R.E. (1993) Stability of orthorhombic MgSiO_3 perovskite in the Earth's lower mantle. *Nature*, 364, 613–616.
- Zerr, A. and Boehler, R. (1993) Melting of $(\text{Mg,Fe})\text{SiO}_3$ perovskite to 625 kilobars: Indication of a high melting temperature in the lower mantle. *Science*, 262, 553–555
- (1994) Constraints on the melting temperature of the lower mantle from high pressure experiments on MgO and magnesio-wüstite. *Nature*, 371, 506–508.

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