University of Nebraska - Lincoln

DigitalCommons@University of Nebraska - Lincoln

Faculty Publications, Department of Physics
and Astronomy

Research Papers in Physics and Astronomy

1997

Molecular dynamics simulation of superionicity in neighborite, NaMgF₃

L. X. Zhou
University of Nebraska - Lincoln

J. R. Hardy
University of Nebraska - Lincoln

H. Z. Cao
University of Nebraska - Lincoln

Follow this and additional works at: <https://digitalcommons.unl.edu/physicsfacpub>

Zhou, L. X.; Hardy, J. R.; and Cao, H. Z., "Molecular dynamics simulation of superionicity in neighborite, NaMgF₃" (1997). *Faculty Publications, Department of Physics and Astronomy*. 175.
<https://digitalcommons.unl.edu/physicsfacpub/175>

This Article is brought to you for free and open access by the Research Papers in Physics and Astronomy at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Faculty Publications, Department of Physics and Astronomy by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

Molecular dynamics simulation of superionicity in neighborite, NaMgF₃

L. X. Zhou,¹ J. R. Hardy and H. Z. Cao

Department of Physics and Center for Electro-Optics,
University of Nebraska-Lincoln, Lincoln, NE 68588-0111

Abstract. Superionicity in neighborite, NaMgF₃, has been studied by molecular dynamics using parameter-free Gordon-Kim potentials. These simulations show that this halide-based perovskite has a superionic phase. The onset temperature for superionicity is ~ 50 -100 K below the melting point. This is a novel type of superionicity in a halide, occurring as it does in a perovskite rather than a fluorite. Superionicity is demonstrated to occur whether one uses the full ionicity for Mg²⁺ and F⁻ or employs reduced charges derived from a Quantum Chemistry calculation. The relevance of these findings to predictions of superionicity in the oxide perovskite MgSiO₃ [Matsui and Price, 1991] is discussed.

1. Introduction

The phase diagram of the perovskite MgSiO₃ is of great geophysical importance since magnesium rich silicate perovskite is thought to be the dominant phase in the Earth's lower mantle. It is thus of great interest to study this compound and its phase diagram theoretically by the technique of computer molecular dynamics, and there has been extensive work in this which has recently been reviewed by Vocadlo, Patel and Price (1995). In particular, an investigation by Matsui and Price (1991) has revealed what appears to be the onset of superionicity in the pre-melting temperature range, and earlier studies, with substantially different interionic potentials, also show this behavior.

However, these results from semi-empirical potentials differ substantially from *a priori* calculations from density functional theory by Wentzcovitch et al. (1993), which indicate that it is unlikely that MgSiO₃ ever enters the cubic phase before melting. Since this may indicate that there are inherent problems in treating an oxide-based system (probably due to charge redistribution in the O²⁻ ion, which is only stabilized by the crystal electrostatic field), it could be illuminating to study a closely similar system in which this problem is absent. Fortunately, this exists in neighborite NaMgF₃, a material isoelectronic with MgSiO₃. Moreover, this material is of geological interest in its own right.

In the past, we have made extensive studies of halide-based perovskites [Flocken et al., 1990] which have largely been concerned with their phase diagrams well below their melting points, and have achieved a wide quantitative as well as qualitative success, using a combination of computer molecular dynamics (CMD) and parameter-free pair potentials derived by the Gordon-Kim [Gordon and Kim, 1971] modified electron gas technique.

Most recently we have extended these to studies on superionic conduction in the fluorite CaF₂ [Zhou et al., 1996-I] and the antiperovskite Li₂O [Zhou et al., 1996-II] and their isomorphs. Since this behavior is only manifest close to the melting temperature in these systems, it is not something we would have discovered previously should it also occur in halide-based perovskites, where it may have been observed experimentally [O'Keeffe and Bovin, 1979]. Since we have not previously studied a magnesium-based halide perovskite in detail, it seemed best to initiate any CMD based theoretical search for superionicity on NaMgF₃ as part of an overall examination of the phase diagram of that system.

2. Molecular Dynamics Investigation

We thus carried out molecular dynamics simulations using our parameter-free Gordon-Kim [Gordon and Kim, 1971] potentials for rigid ions, using a periodic supercell with 320 ions (64 Mg²⁺, 192 F⁻, 64 Na⁺), heating from 0 K to 3000 K in 100 K steps, and averaging for 6 ps after each heat pulse.

In order to establish the existence of superionicity, we monitored the $\bar{a}\bar{b}$ cross section of our supercell. At the onset of superionicity, we observe "linear disorder" in the F⁻ sublattice coexisting with still ordered Na⁺ and Mg²⁺ sublattices, as can be seen in Figure 1, for which the temperature is 2880 K. This behavior is seen for temperatures of 2880 - 2930 K. Above 2930 K the cations also disorder and the crystal "melts." This "melting point" is much higher than the observed value of 1303 K. Thus, these results are only qualitatively interesting in that they show clearly the onset of superionicity *before* melting. At higher temperatures, the F⁻ sublattice becomes essentially disordered with ions clearly jumping into neighboring supercells. However, the cation sublattices remain intact.

In addition, the structural transformations reported at 1032 K and 1173 K [Chao et al., 1961] of which only

¹Department of Physics, Xiamen University, China

Figure 1. (a) Projections of the $\vec{ab}$ cross sections of the four layers of Na^+ and Mg^{2+} ions in our 320 ion supercell on the basal plane. The temperature is 2880 K and the ellipsoids bound the region over which each ion moves to during the simulation. Clearly both sublattices are fully ordered. (b) Same projections for the F^- ions – the large elongated and often displaced ellipsoids indicate superionic mobility. Both this Figure and Figure 2 are projections of all the layers on the $(x, y, 0)$ plane; the lowest layer corresponds to the solid lines and the others to broken lines.

the former is reproduced in very recent work, [Zhao *et al.*, 1993-I; Zhao *et al.*, 1993-II] are not reproduced either in temperature or in the observed change in symmetry. Specifically, we obtain only a single transition at ~ 850 – 900 K to a near-trigonal phase, $a \simeq b \simeq c = 3.6\text{\AA}$ at 300 K, c.f. $\simeq 3.8\text{\AA}$ (expt.) [Chao *et al.*, 1961; Zhao *et al.*, 1993-I]. The most likely origin of these discrepancies is a defect in the simple Gordon-Kim model, most probably in the description of the Mg^{2+} - F^- interaction, since this bond may well be poorly described by a superposition of Mg^{2+} and F^- charge distributions, owing to significant covalency. In this context, it is worth noting that MgF_2 has the rutile rather than fluorite structure – something that is not favored by close packing of purely spherical ions [Megaw, 1973].

In order to obtain a clearer understanding, we ran a Quantum Chemistry GAUSSIAN 94 calculation [Frisch and Foresman, 1994] for the $[\text{MgF}_6]^{4-}$ molecule and examined the Mulliken [Mulliken, 1955] populations of the orbitals. This gave a fluorine charge of -0.79 , implying an Mg charge of 1.37 in NaMgF_3 . Thus, as the simplest first approximation, we replaced the Gordon-Kim charges by these new values without changing the Gordon-Kim short-range potentials. Since each outer closed shell contains eight electrons, the average change for the $\text{F}^{-0.79}$ ions is only ~ 2 – 3% and ~ 5 – 8% for the $\text{Mg}^{1.37}$ ions; furthermore, it is only the $\text{F}^{-0.79}$ ions that have significant short-range interactions with units external to their octahedra.

We then repeated our molecular dynamics simulation using the same periodic supercell containing 320 ions ($64 \text{ Mg}^{1.37}$, $192 \text{ F}^{-0.79}$, 64 Na^+), and heating from

0 K to 2000 K in 100 K step averaging for 10 ps after each heat pulse. This single change produces dramatically improved agreement with experiment. The onset temperature for superionicity is now 1330 K, it persists at 1395 K and the “melting point” of the whole lattice is ~ 1400 K. In this case, we show in Figure 2 cross sections similar to those in Figure 1, but for a temperature of 1330 K, demonstrating F^- “chain disorder” coexisting with still ordered cation sublattices. Similar behavior is seen at a higher temperature (1395 K) prior to the final heat pulse which produces full disorder or “melting.”

In Figure 3, we show the phase diagram below the superionic transition. Clearly the lowest temperature phase is orthorhombic in agreement with Mulliken (1955) and O’Keeffe and Bovin (1979). Also, the values of the axial lengths, a , b and c agree well with the experimental values [$a = 3.79\text{\AA}$, $b = 3.88\text{\AA}$, $c = 3.83\text{\AA}$ (expt.) [Chao *et al.*, 1961; Zhao *et al.*, 1993-I]: $a = 3.80\text{\AA}$, $b = 3.83\text{\AA}$, $c = 3.83\text{\AA}$ (theory), both for 300 K]. However, the onset of the transition away from the cubic phase, present above 1200 K, appears to occur at ~ 1175 K to what may be a transient near-tetragonal phase between ~ 1175 K and ~ 1030 K. This assertion is obviously very tentative, since the changes in axial lengths are clearly within the limits of the statistical fluctuations at these temperatures. Below 1020 K, the lattice is definitely orthorhombic, although the a and b axes switch below ~ 450 K. While these first two temperatures agree closely with the experimental values in Mulliken (1955) and O’Keeffe and Bovin (1979) have fairly definitively ruled out the existence of the tetragonal phase. As far

Figure 2. The same cross sections as those shown in Figure 1, but for $\text{Mg}^{+1.37}$ and $\text{F}^{-0.79}$: (a) $\text{Mg}^{+1.37}$ and Na^+ , (b) $\text{F}^{-0.79}$. This time the temperature is 1330 K. Again, we see clear superionicity in the $\text{F}^{-0.79}$ sublattice, while the cation sublattices are still ordered. The single large ellipsoid in Figure 2(a) represents a transient excursion of a single Na^+ ion which disappears at 1395 K.

as the lower temperature transition on which Mulliken (1955) and O'Keeffe and Bovin (1979) agree, there is good agreement with our calculated value of ~ 1030 K.

3. Discussion

That CMD may be showing a transient tetragonal phase suggests that such a phase might, depending on particular circumstances (e.g., growth conditions), be

transiently metastable and be seen experimentally. Possibly this occurred for the work in Mulliken (1955). Whether the CMD "melting" temperature corresponds to that at which real melting would occur is questionable. However, since the most likely discrepancy for CMD with periodic boundary conditions is marked superheating, the fact that the superionic transition temperature is closely reproduced while "melting" occurs only 50-60° K higher (at $T_c \sim 1400$ K, close to the ob-

Figure 3. Axial lengths plotted as a function of temperature from our simulation of $\text{Na}^+ \text{Mg}^{+1.37} \text{F}_3^{-0.79}$.

served melting temperature) suggests that superheating, at least, is not present to any significant degree in the present simulation.

While our simple assumption of reduced ionicity in the Mg - F bond can be questioned, we believe that the principal reason for its success is that it expands the MgF_6 octahedra and thus the lattice (hence, the improved lattice constants). Apparently this improvement also gives more realistic "double-well potentials" for the MgF_6 rotations so that they order in the manner described in Zhao et al. (1993-I) (equal antiphase rotations about two axes and an inphase rotation of different magnitude along the third).

Since any improvement over the fully ionic Gordon-Kim potential must also achieve these aims, it is not unreasonable to argue that it, too, must predict the onset superionicity ~ 50 -100 K below the melting point. In addition, the fact that even the fully ionic potentials, which show superheating by almost a factor of two, also predict the onset of superionicity 50-100 K below melting, further supports the reality of this effect.

Acknowledgments. This work was supported by the U.S. Army Research Office under Grant No. DAAL-03-92-G-0366.

References

- Chao, E. C. T., H. T. Evans, Jr., B. J. Skinner, and C. Milton, Neighborite, NaMgF_3 , a new mineral from the Green River formation, South Ouray, Utah, *The American Mineralogist*, **46**, 379-393, 1961.
- Flocken, J. W., W. M. Mei, R. A. Guenther, J. R. Hardy, P. J. Edwardson, and L. L. Boyer, Ferroelectric phase transitions in NaCa halide perovskites, *Phase Transitions*, **20**, 113-115, 1990.
- Frisch, M. J., and J. B. Foresman, GAUSSIAN 94, Carnegie-Pittsburgh, Gaussian Inc.: Pittsburgh, PA 1994.
- Gordon, R. G. and Y. S. Kim, Theory for the forces between closed-shell atoms and molecules, *J. Chem. Phys.*, **56**, 3122-3133, 1971.
- Matsui, M. and G. D. Price, Simulation of the pre-melting behavior of MgSiO_3 perovskite at high pressures and temperatures, *Letters to Nature*, **351**, 735-737, 1991.
- Megaw, H. D., *Crystal Structures: A Working Approach*, W. B. Saunders: Philadelphia 1973, p. 258.
- Mulliken, R. S., Electron population analysis on LCAO-MO molecular wavefunctions, I, *J. Chem. Phys.*, **23**, 1833-1840, 1955.
- O'Keeffe, M., and J. O. Bovin, Solid electrolyte behavior of NaMgF_3 geophysical implication, *Science*, **100**, 599-600, 1979.
- Vocadlo, L., A. Patel and G. D. Price, Molecular dynamics: some recent developments in classical and quantum mechanical simulations of minerals, *Mineralogical Magazine*, **59**, 597-605, 1995.
- Wentzcovitch, R. M., J. L. Martins, and G. D. Price, *Ab initio* molecular dynamics with variable cell shape: Application to MgSiO_3 , *Phys. Rev. Lett.*, **70**, 3947-50, 1993.
- Zhao, Y., D. J. Weidener, J. B. Parise, and D. E. Cox, Thermal expansion and structural distortion of perovskite-data for NaMgF_3 perovskite, Part I, *Phys. Earth Planet. Inter.*, **76**, 1-16, 1993.
- Zhao, Y., D. J. Weidener, J. B. Parise, and D. E. Cox, Critical phenomena and phase transition of perovskite, Part II, *Phys. Earth Planet. Inter.*, **76**, 17-34, 1993.
- Zhou, L. X., J. R. Hardy, and H. Z. Cao, Dynamical simulations of superionicity in alkaline-earth halides, *Solid State Commun.*, **98**, 341-345, 1996.
- Zhou, L. X., J. R. Hardy, and H. Z. Cao, Dynamical simulation of superionicity in antiperovskites and in mixed systems, *Solid State Commun.*, **99**, 637-640, 1996.
- L. Zhou, Department of Physics and Center for Electro-Optics, University of Nebraska-Lincoln, Lincoln, NE 68588-0111, USA Department of Physics, Xiamen University, China
- J. Hardy, Department of Physics and Center for Electro-Optics, University of Nebraska-Lincoln, Lincoln, NE 68588-0111, USA
- H. Cao, Department of Physics and Center for Electro-Optics, University of Nebraska-Lincoln, Lincoln, NE 68588-0111, USA

(Received June 25, 1996; revised December 2, 1996; accepted February 12, 1997.)