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Molecular Simulation

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To cite this Article MacDónaill, D. A. , Jacobs, P. W. M. and Rycerz, Z. A.(1989) 'Molecular Dynamics Simulation of the Fast Ion Conductor δ -Bi₂O₃', *Molecular Simulation*, 3: 1, 155 – 165

To link to this Article: DOI: 10.1080/08927028908034625

URL: <http://dx.doi.org/10.1080/08927028908034625>

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MOLECULAR DYNAMICS SIMULATION OF THE FAST ION CONDUCTOR δ -Bi₂O₃

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(Received April, 1988; in final form September, 1988)

Molecular Dynamics simulations of the superionic δ -phase of Bi₂O₃ are reported. Initial configurations were based on 100,000 time-step ($\Delta t = 5 \times 10^{-15}$ s) equilibrations. Making use of recently determined thermal expansivity data on δ -Bi₂O₃, a series of simulations were performed at increasing temperatures, with appropriate lattice constants, until oxygen sub-lattice melting was observed. Calculations were restricted to the rigid-ion approximation and accordingly short-range potentials, adjusted to reproduce the static dielectric constant were employed, in addition to modified electron-gas potentials. The dielectrically adjusted potentials proved superior in most respects although they sometimes prompted phase changes. In agreement with static-lattice calculation predictions the primary charge migration mechanism is a cube-edge or $\langle\langle 100 \rangle\rangle$ vacancy migration. Cube-edge interstitials, half way along a cube-edge, predicted in static-lattice simulations and observed in neutron studies on yttria stabilized fluorite Bi₂O₃, are also found.

KEY WORDS: Bismuth oxide, bismuth sesquioxide, fluorite, molecular dynamics, fast ion conduction.

1. INTRODUCTION

δ -Bi₂O₃ has an oxide ion conductivity of the order of $\sim 1 \text{ S.cm}^{-1}$ [1] which is about two orders of magnitude greater than that of stabilized zirconia [2]. Its high conductivity is related to its "liquid-like," oxygen sub-lattice which has a degree of disorder comparable to that of the liquid state [3,4].

Experimental studies show Bi₂O₃ to have the fluorite structure, but details of the oxygen sub-lattice are imprecisely known and there is some disagreement about the nature and extent of the oxygen ordering [5,6]. Details of how the high ionic conductivity is achieved are as yet uncertain, and any full explanation must explain the difference between the energy barriers to migration [1,4,7] and the heat of transport [8,9]. The δ -phase of bismuth-oxide is of both scientific and technological interest.

We have previously reported [10-12] the results of an extensive static lattice study of δ -Bi₂O₃ using the computer code HADES [13]. The study provided a useful insight into disorder and charge migration in Bi₂O₃. However, the resulting model must be regarded as semi-quantitative, partly because of approximations necessitated by various computational difficulties but particularly because of approximations inherent in the Mott-Littleton model [14] embodied in HADES. For example, defects may only be considered at infinite dilution, in a perfectly ordered environment. This is an unsatisfactory feature if a quantitatively accurate model is desired since high defect concentrations are expected in so disordered a substance, and because a perfectly ordered lattice model which represents the physically disordered environ-

ment must be chosen, a choice complicated by a background of contradictory experimental reports.

The Molecular Dynamics (MD) method is particularly suited for the simulation of fast ion conductors since motion is explicitly considered and no assumption about ordering in the oxygen sub-lattice is required. However, the periodic boundary associated with the simulation box may still impose some artificial order, especially in a small model. Taken together, combined static and dynamic simulations can provide a more complete picture of fast ion conductors than either is capable of individually. In this paper the preliminary results of a series of MD calculations on $\delta\text{-Bi}_2\text{O}_3$ are reported. Attention is focused particularly on a qualitative interpretation of results in the light of static lattice simulations and experimental data. Some approximations inherent in the MD procedure used, and associated problems, are also considered. The work is continuing and detailed results from a more extensive series of simulations will be reported later [15].

2. CALCULATIONS

Calculations were performed using a locally modified version of the program MDIONS [16]. The simulation box, itself cubic, consisted of a $3 \times 3 \times 3$ array of fluorite cells of Bi_2O_6 (equivalent to a $6 \times 6 \times 6$ array of the smaller oxygen cubes) containing a total of 270 ions. In the simulations reported here the time step used was $\Delta t = 5 \times 10^{-15}$ s. Initial configurations were based on equilibrations of 100000 time steps. Such long equilibrations proved necessary because of metastable oxygen configurations, some of which persisted for up to 30000 time steps [17]. Once equilibration was achieved, approximately 2000 time steps were used to calculate the required quantities, as this is sufficient to give adequate statistical accuracy.

The MDIONS code is restricted to the rigid-ion approximation which is not ideally suited to bismuth oxide where the cation has a polarizability comparable with the large oxide ion polarizability (our current estimates are $1.77 \pm 0.07 \text{ \AA}^3$ for Bi^{3+} and $3.78 \pm 0.15 \text{ \AA}^3$ for O^{2-} [18]). In an attempt to both examine and overcome problems associated with this restriction without the computational expense of the shell-model for ionic polarizability, two kinds of potentials were employed. In the first kind, designated R for rigid-ion, electron-gas potentials are fitted to the properties of $\delta\text{-Bi}_2\text{O}_3$ with polarizability being accounted for by means of the shell model. No adjustment is made to the short-range parameters to compensate for the rigid-ion approximation which was not considered in the fitting. In the second, designated D for dielectrically adjusted, the Bi-O short-range potential is adjusted so as to reproduce the static dielectric constant, while conforming to the rigid-ion approximation. One expects potential set "R" to perform less favourably than set "D" since the former takes no account of ionic polarizability which enhances ionic diffusion. However, in static lattice calculations the "R" potentials proved most useful, together with potentials incorporating the shell model, of intermediate polarizability [10-12]. Moreover, the short-range parameters in the Bi-O potential are physically more realistic in set "R" than in set "D." Although intuitively less reliable the use of potential set "R" facilitates comparison with static lattice simulation results and, by comparison with the results of simulations using set "D," permits direct observation

of the consequences of adjusting the potential. Details of the properties fitted in the potentials (R1 and D1) used in our first set of simulations (Set I) have been reported previously [10]. The parameters of the short-range potentials are summarized in Table 1.

The simulations reported here may be divided into two classes consisting of those performed under "experimental" conditions and those performed under "relaxed" conditions. Under "experimental" conditions the temperatures correspond to the temperatures at which fast ion conduction is experimentally observed to occur, and the lattice constants used are those experimentally observed. However, calculations are still performed under conditions of constant volume. Simulations performed under "relaxed" conditions differ in that expanded lattice constants and elevated temperatures are used.

3. RESULTS AND DISCUSSION

3.1 Simulations Under "Experimental" Conditions

This first set of simulations (Set I) consists of two different simulation runs. Simulation conditions are given in Table 2. Calculations reported earlier showed that with rigid-ion potentials thermal equilibration could take up to 60000 time steps (300 ps) [17]. The fully equilibrated and non-equilibrated systems would differ presumably in the structure of the oxygen sub-lattices. Simulations are based, therefore, on configurations equilibrated for 100000 time steps (500 ps) from an initial $\langle 111 \rangle$ arrangement of oxygen vacancies. The simulations are designated I-R1 (Set I, potential R1) and I-D1, depending on the short-range potentials used.

Projections of the oxygen sub-lattice immediately show that in neither case has sub-lattice melting occurred and that there is no fast ion conduction (Figure. 1). However, simulation I-D1 appears to be closer to melting as evidenced by the larger vibrations, particularly noticeable in the oxygen sub-lattice (Figure 1), suggesting that the dielectrically adjusted potentials are superior. One or more oxygen jumps occurring along cube-edges ($\langle\langle 100 \rangle\rangle$ directions) can be observed in each of the simulations, just as would be expected for a vacancy mechanism in a fluorite structure, and in agreement with static simulation results [11]. The diffusion constant, as determined from the time dependence of the mean square displacement (MSD) is small, being only

Table 1 (a) Potential set R1.

Parameters in the short-range potentials $\phi(r)$ for δ -Bi₂O₃, $\phi(r) = A \exp(-r/q) + B \exp(-r/\sigma) - C/r^6$.

	$A(\text{eV})$	$q(\text{\AA})$	$B(\text{eV})$	$\sigma(\text{\AA})$	$C(\text{eV}\text{\AA}^6)$
$\text{O}^{2-}-\text{O}^2$	1290.0	0.30110	47863.4	0.14438	71.3
$\text{Bi}^{3+}-\text{Bi}^{3+}$	15983.1	0.25643	308744.4	0.10406	40.36
$\text{Bi}^{3+}-\text{O}^{2-}$	323.0	0.41631	5745.0	0.27283	0.0

(b) Potential sets D1, R2 and D2.

Only parameters in the $\text{Bi}^{3+}-\text{O}^{2-}$ potential differ from potential set R1.

$\text{Bi}^{3+}-\text{O}^{2-}$	$A(\text{eV})$	$q(\text{\AA})$	$B(\text{eV})$	$\sigma(\text{\AA})$	$C(\text{eV}\text{\AA}^6)$
D1	323.0	0.41631	250.0	0.45700	0.00
R2	323.0	0.41631	5745.0	0.26546	0.00
D2	323.0	0.41631	250.0	0.44237	0.00

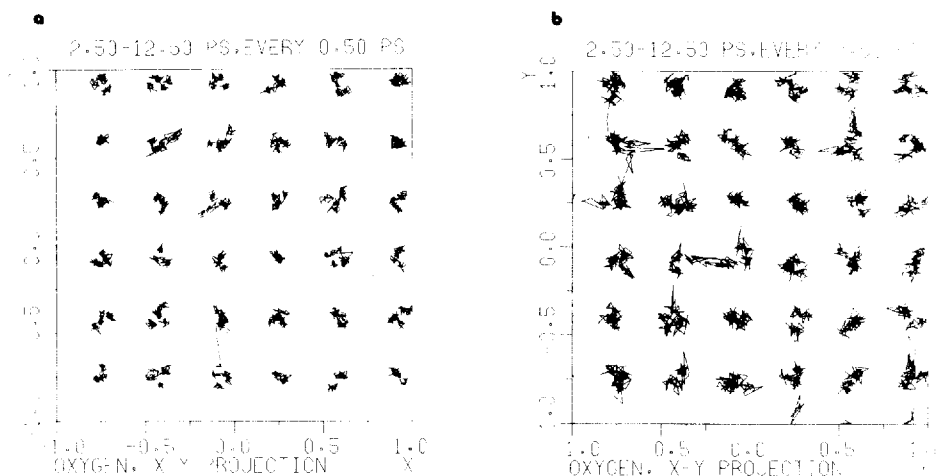


Figure 1 Projections in the X-Y plane of the anion sub-lattice, time elapsed = 10 ps (2048 time steps); (a) simulation I-R1 ($T = 1017$ K) and (b) I-D1 ($T = 1026$ K).

$0.008 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $0.023 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ in simulations I-R1 and I-D1 respectively.

Calculations under 'experimental' conditions failed to show fast ion conduction. Sub-lattice melting may have been prevented by the constant volume approximation to which calculations were restricted, by preventing local expansion. Constant pressure calculations ought, in principle, to remove any artificial inhibition of sub-lattice melting arising from constant volume approximation. However, our calculations show that the pressure is unstable, showing large fluctuations, presumably because of a tendency for short-range order in a relatively small simulation box (270 particles). Constant pressure calculations under such conditions would result in large perturbations to the system. Accordingly, the constant volume approximation is retained in the simulations reported below, and sub-lattice melting is facilitated by expansion of the lattice constant and by raising the temperature beyond the experimental melting point of 1097 K.

3.2 Simulations Under "Relaxed" Conditions

Performing simulations at higher temperatures and expanded lattice constants in a consistent fashion requires a knowledge of the thermal expansivity of $\delta\text{-Bi}_2\text{O}_3$. Unfortunately most diffraction studies lie within a narrow temperature range and no completely reliable values for the thermal expansivity may be determined. The thermal expansivity values reported in the literature disagree significantly [19,20]. Consequently, the short-range potentials used in simulations I-D1 and I-R1 were fitted to the high-temperature lattice constant reported by Harwig [3] of 5.644 Å and used here partly to facilitate comparison with static calculations using the same potentials. Recently however, a reliable room-temperature lattice constant for hypothetical

Table 2 Simulation conditions

Simulation	Lattice Constant (\AA)	Requested Temperature (K)	Equilibrated Temperature (K)
I-R1	5.644	1029	1017
I-D1	5.644	1029	1026
II-R2-1	5.696	1300	1294
II-R2-2	5.721	1500	1489
II-R2-3	5.734	1600	1591
II-D2-1	5.696	1300	1297
II-D2-2	5.721	1500	1489
II-D2-3	5.734	1600	1598

$\delta\text{-Bi}_2\text{O}_3$ ($a = 5.568 \text{ \AA}$) has been determined from the study of the stabilized fluorite phase in solid solutions obeying Vergard's rule [21]. Comparison with the high temperature lattice constants leads to a thermal expansivity of $2.26 \times 10^{-5} \text{ K}^{-1}$ [21], favouring the reported expansivity data of Levin and Roth [20] over those of Gattow and Schröder [19]. Assuming constant thermal expansivity a lattice constant of 5.531 \AA at 0 K is predicted. The σ parameters in the Bi-O short-range potentials R1 and D1 were adjusted to fit this new lattice constant yielding potentials R2 and D2 respectively (Table 1). No other parameters were adjusted and no other properties refitted.

A series of simulations (Set II) were performed at approximately 1300 K , 1500 K and 1600 K with potentials D2 and R2 (Table 2). Initial conditions were taken from the final configurations of earlier simulations equilibrated for 100000 time steps or more. In II-D2-2 ($T = 1489 \text{ K}$, $a = 5.721 \text{ \AA}$) fast ion conduction may be observed, and the oxygen diffusion constant calculated from the MSD is $0.29 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. Projections of the oxygen sub-lattice show significantly greater activity (Figure 2). By contrast simulation II-R2-2 ($T = 1489 \text{ K}$, $a = 5.721 \text{ \AA}$) shows no signs of fast ion conduction. Indeed, there is even less activity than in simulation I-D1, which was at

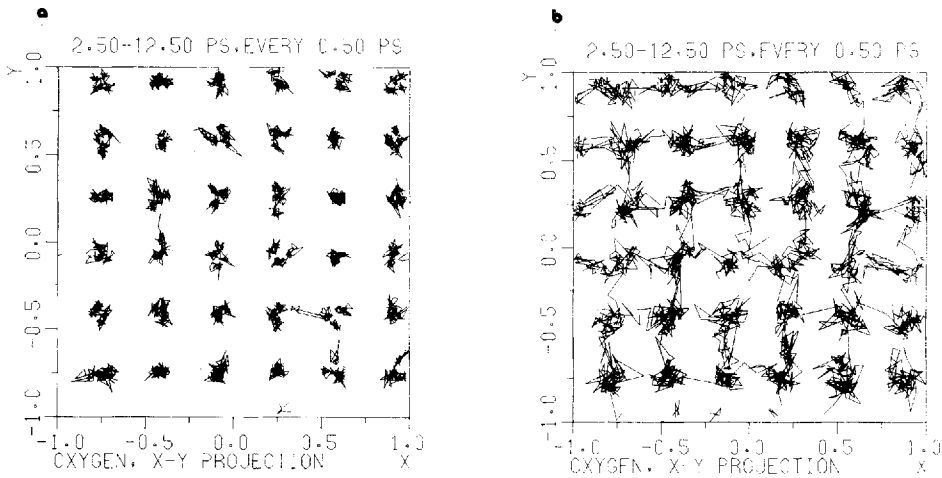


Figure 2 Projections in the X-Y plane of the anion sub-lattice, time elapsed = 10 ps (2048 time steps); (a) simulation II-R2-2 ($T = 1489 \text{ K}$) and (b) II-D2-2 ($T = 1489 \text{ K}$).

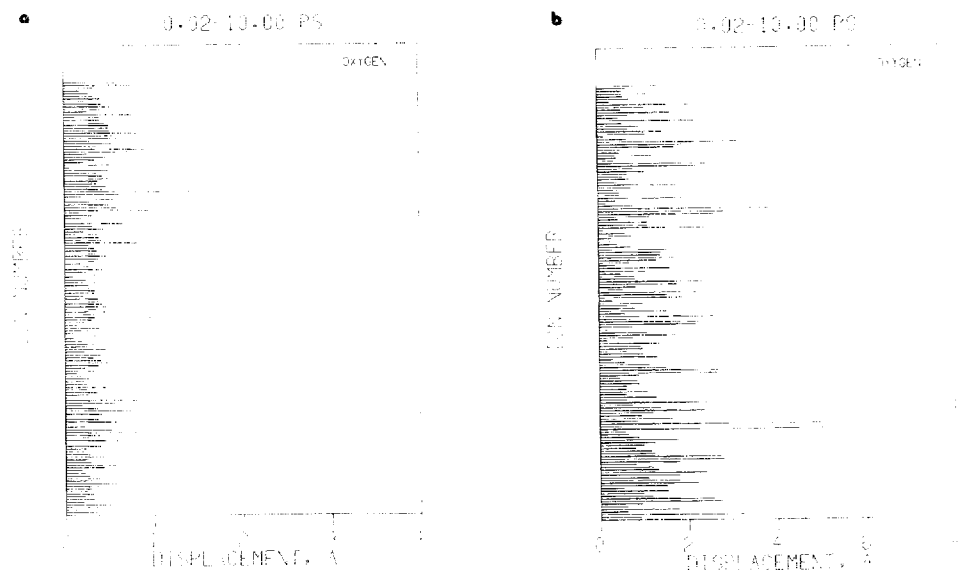


Figure 3 Ion displacement histograms for the oxygen sub-lattice; (a) II-R2-2 and (b) II-D2-2.

the much lower temperature of 1026 K with a smaller lattice constant of 5.644 Å. MSD calculations yield a value for the diffusion coefficient of zero within statistical uncertainty.

The ion-displacement histogram for II-D2-2 (Figure 3b) reflects the greatly increased activity, with numerous displacements of approximately 2.5–3.5 Å, corresponding to single oxygen jumps along cube edges over a period of 10 ps. Occasional greater displacements also occur. However, comparison with SrCl_2 at 1469 K (Figure 17 in [22]) where more than half the anions undergo jumps over a period of 5 ps shows that the activity is not quite as high as one might expect in a fast ion conductor.

The radial distribution functions in II-D2-2 are less structured than in II-R2-2, reflecting the disordered or "liquid-like" state of the oxygen sub-lattice (Figure 4). The mean square displacement (MSD) plot for II-D2-2 reflects oxygen diffusion whereas that for II-R2-2 does not (Figure 5).

Oxygen migration occurs by $\langle 100 \rangle$ jumps (Figure 6). Static lattice simulations support this, with calculated energy barriers to vacancy migration along $\langle \langle 100 \rangle \rangle$ directions in good agreement with experimentally determined values [11]. There is no evidence of $\langle 110 \rangle$ or $\langle 111 \rangle$ cube-centre migrations. Successive jumps are not necessarily collinear (Figure 6b). Oxygen ions also appear to occasionally spend some time half-way between two oxygen lattice sites (Figures 6a, 6c). These were observed in HADES static lattice simulations of defect complexes (Figure 6d) and were observed by Battle *et al.* [6] in a neutron diffraction study of yttria doped bismuth oxide, although they were not observed for pure $\delta\text{-Bi}_2\text{O}_3$.

In the above simulations oxygen sub-lattice melting was eventually achieved by increasing the temperature together with a corresponding increase in the lattice constant, and, most importantly, by adjusting the short-range potentials to reflect the static dielectric constant in the absence of a shell model. Significant adjustments were

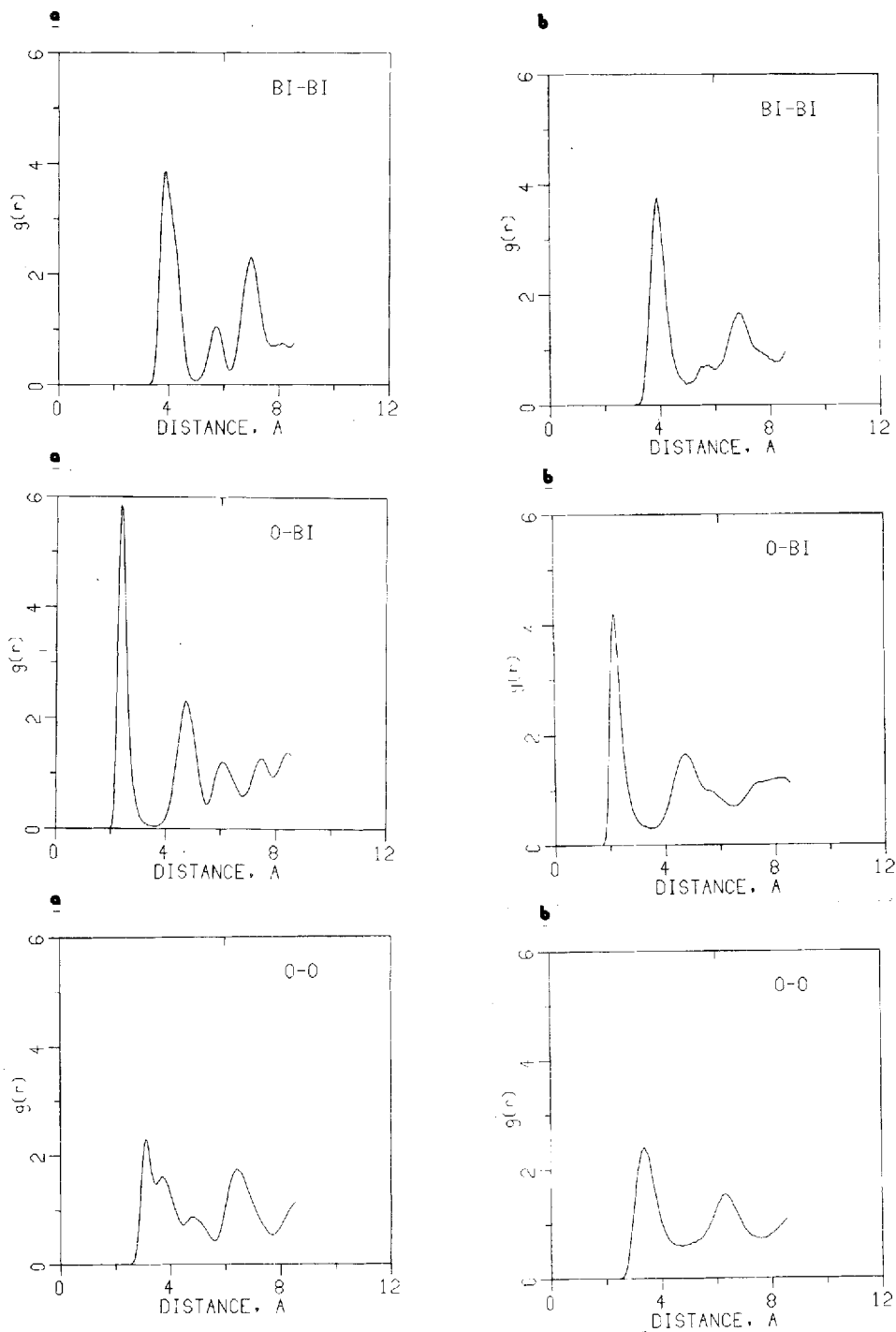


Figure 4 Radial distribution functions for simulated $\delta\text{-Bi}_2\text{O}_3$ at 1489 K; (a) II-R2-2 and (b) II-D2-2.

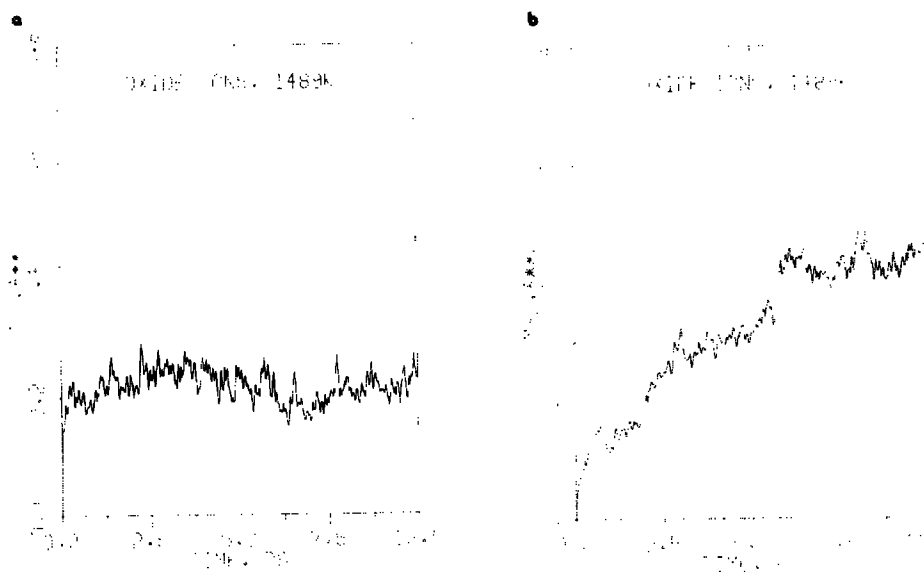


Figure 5 Mean square displacements for the oxygen sub-lattice at 1489 K; (a) II-R2-2 and (b) II-D2-2

necessary and, since the short-range potentials also determined the structure, there is always the possibility of destabilising the structure and prompting a phase-change. This sometimes occurred as in simulations II-D2-1 (1297 K) and II-D2-3 (1598 K. Figure 7).

It is possible, therefore, that the technique of adjusting a short-range potential to reflect the dielectric constant has reached its limit of applicability. Bismuth oxide has very high cationic and anionic polarizabilities so that the rigid-ion approximation is quite restrictive. Alternatively, a more complicated functional form for the potential might rectify this problem.

4. CONCLUSIONS

Oxygen migration is shown to occur by jumps along cube edges between lattice sites. Interstitials half-way along cube-edges are also observed, in agreement with neutron diffraction data and static lattice simulations.

In the rigid-ion approximation it is essential that short-range potentials be adjusted to reflect the static dielectric constant. Only in the cases where such adjustments were made was fast ion conduction observed. This in itself, however, is not sufficient and it also appears to be necessary to increase the temperature and expand the lattice constant, possibly because of the constant volume approximation.

It is proposed to perform further calculations on bigger systems. This might lessen the effects of having a finite simulation box by facilitating local expansion and reducing artificial ordering, in turn facilitating oxygen sub-lattice melting. There is, further, both experimental [24] and computational evidence [23] for the existence of

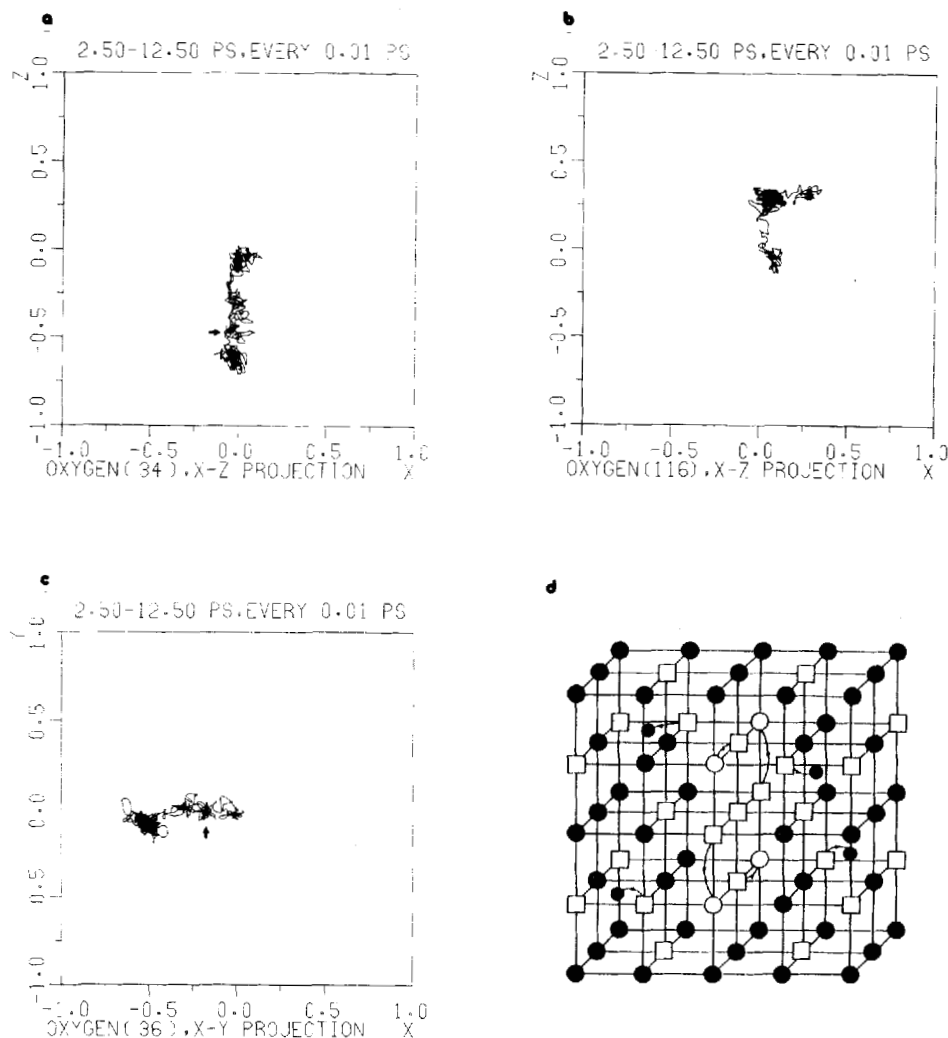


Figure 6 Trajectory projections of migrating oxygen ions. Particle coordinates at the beginning of the time-period are set to (0, 0, 0) for plotting; (a) $\langle 001 \rangle$ jump (0, 0, 0) \rightarrow (0, 0, -0.33) followed by a second $\langle 001 \rangle$ jump via a cube-edge interstitial (arrow) at (0, 0, -0.50); (b) Consecutive $\langle 001 \rangle$ and $\langle 100 \rangle$ jumps; (c) $\langle 100 \rangle$ jump via cube-edge interstitial (arrow) at (-0.17, 0.0, 0.0) followed by a second $\langle 100 \rangle$ jump. (d) Static-lattice simulation of Cyclo-⟨110⟩₄ with an associated vacancy shows the formation of four cube-edge interstitials [10]. Only the oxygen sublattice is shown.

structures with a periodicity in unit cells of $2 \times 2 \times 1$ and $2 \times 1 \times 1$ which are artificially precluded in a $3 \times 3 \times 3$ simulation box but permitted in a $4 \times 4 \times 4$ simulation box. Beyond this lie the substantially more expensive MD calculations incorporating the shell model of ionic polarizability.

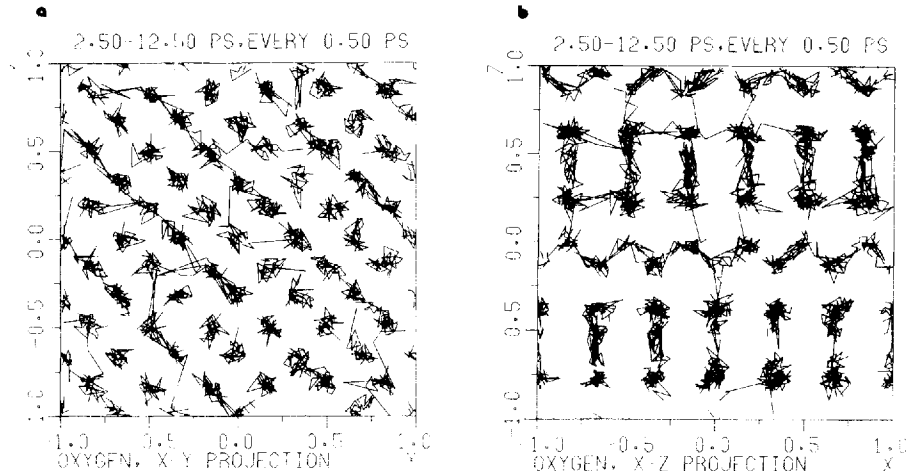


Figure 7 Projections of the anion sub-lattice after the phase change has occurred in simulation II-D2-3 at $T = 1598$ K.

Acknowledgements

This research was supported, in part, by the Natural Sciences and Engineering Research Council of Canada. We would like to express our gratitude to the referee for useful comments and observations.

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