JOURNAL OF SOLID STATE CHEMISTRY **128,** 137–141 (1997)
ARTICLE NO. SC967187

A Computer Simulation Investigation of Brownmillerite-Structured $Ba_2In_2O_5$

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Received July 15, 1996; in revised form October 7, 1996; accepted October 15, 1996

Atomistic simulation techniques have been used to investigate the crystal structure and defect energetics of $Ba_2In_2O_5$. An interatomic potential model was developed that reproduces the orthorhombic brownmillerite structure, with alternating layers of oxygen octahedra and tetrahedra. Defect calculations show that the most energetically favorable intrinsic defects are of the Frenkel type, with an oxygen vacancy on the O(1) site and an oxygen ion in an interstitial position in the tetrahedral layer. Calculated formation energies of electronic defects suggest that $Ba_2In_2O_5$ will oxidize with the formation of positive holes, contributing to the electronic conductivity that is observed experimentally. Finally, consideration of possible oxygen ion migration pathways in the structure found that energy barriers to migration are lowest between equatorial sites of oxygen octahedra in the [001] direction. © 1997 Academic Press

1. INTRODUCTION

The search for materials displaying fast oxygen ion conductivity for use in a range of high temperature electrochemical devices, including oxygen gas sensors, separation membranes, and solid oxide fuel cells, has recently been extended to oxides with the brownmillerite structure, $A_2B_2O_5$ (1). This structure can be considered to be a highly defective perovskite structure in which one-sixth of the oxygen ions are removed by completely replacing the small tetravalent cation with a trivalent cation. In the brownmillerite structure, the oxygen vacancies are ordered along the perovskite [101] direction, producing an orthorhombic unit cell with alternating layers of BO_6 octahedra and BO_4 tetrahedra along the long axis (shown in Fig. 1). In the brownmillerite structure, the “vacancies” are not normally occupied and must be treated as interstitial positions in the tetrahedral layers.

Heating of brownmillerite-structured oxides above a phase transition temperature, T_t, disorders the anion vacancies and results, in fast oxygen ion conduction in these materials (1). The compound $Ba_2In_2O_5$ has received considerable attention (2–5) because at 1000°C it has a conductivity comparable to that of yttria-doped zirconia, the most widely used solid state oxygen ion conductor (6). Below $T_t \approx 925°C$, however, the total conductivity is reduced by at least an order of magnitude, and electronic contributions to the total conductivity become significant (3).

It has recently been shown that the phase transition at T_t is not associated with complete disordering of the anion vacancies (4, 5). $Ba_2In_2O_5$ retains an orthorhombic structure until at least 1075°C, above which the structure reverts to that of a highly defective perovskite with cubic symmetry (5). The large discontinuity in the measured conductivity at $T_t \approx 925°C$, however, suggests that partial disordering of the structure is sufficient to allow fast oxygen ion conductivity through the material. Examination of the diffusion mechanisms in the ordered brownmillerite structure is therefore important in understanding fast oxygen transport in these materials, since fundamental mechanistic features are still uncertain. Results from experimental studies are rarely sufficient to identify fully the migration mechanism, despite recent models describing the defect energetics and dynamics in $Ba_2In_2O_5$ (3, 5). Computer simulation studies have therefore been used to clarify some of the factors controlling oxygen transport in $Ba_2In_2O_5$. These simulation techniques are particularly suited to probing ion migration on the atomic scale and have been successfully applied to other perovskite-based oxides (7), including the cuprate superconductors (8, 9). In this work, the energetics of intrinsic and electronic defects and of various pathways for oxygen migration have been explored.

2. METHODOLOGY AND POTENTIALS

Detailed reviews of the simulation techniques employed can be found elsewhere (10, 11), so only a brief account will be presented here. The cohesive properties of the perfect lattice structure were first calculated using energy minimization methods. Calculations of defect formation and

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0022-4596/97 $25.00

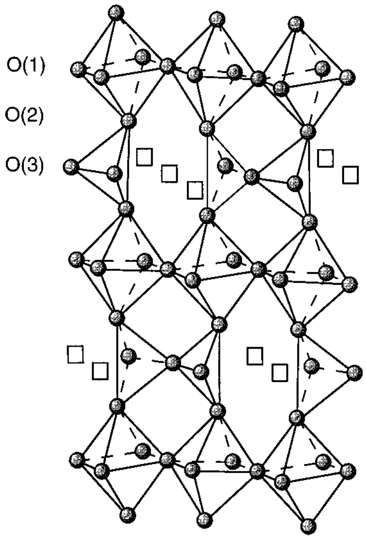

FIG. 1. Structural model of $Ba_2In_2O_5$ showing tilting of oxygen octahedra and distortion of tetrahedra, as well as oxygen vacancies (relative to the parent perovskite), and crystallographically distinct oxygen sites.

migration energies were then performed using the Mott–Littleton approach in which the ions in an inner region surrounding the defect are treated explicitly, while the remainder of the crystal, where the defect forces are relatively weak, is treated by quasi-continuum methods. In this way, local relaxation is effectively modeled and the crystal is not considered simply as a rigid lattice through which ion species diffuse.

Both perfect and defect lattice calculations are based on a Born model representation of polar solids, in which forces are assumed to be two-body and a function of the distance between particles, r, only. The interatomic interactions are divided into long-range Coulombic and short-range forces, with the short-range term described by an analytical function of the Buckingham form

$$\phi_{ij}(r) = A_{ij}\exp\left(\frac{-r}{\rho_{ij}}\right) - \frac{C_{ij}}{r^6}, \qquad [1]$$

where A_{ij}, ρ_{ij}, and C_{ij} are parameters particular to each ion–ion interaction.

Since charged defects will polarize other ions in the lattice, ionic polarizability must be incorporated into the potential model. The shell model (12) provides a simple description of such effects by treating each ion in terms of a core (representing the nucleus and core electrons) connected via a harmonic spring to a shell (representing the valence electrons). The non-Coulombic forces act only between shells, thus including the vital coupling between short-range forces and polarization by the remainder of the lattice. This coupling is of importance in the simulation of both elastic and dielectric properties of the crystal.

$Ba_2In_2O_5$ was assumed to be isostructural with $Ca_2Fe_2O_5$, which belongs to space group *Pcmn* (13), since a complete refinement of brownmillerite-structured $Ba_2In_2O_5$ has not yet been reported. Using the GULP program (14), the short-range potential parameters and shell model parameters were derived by empirical fitting to the orthorhombic lattice parameters observed by Kuramochi *et al.* (15) and are given in Table 1; the Ba–O potential was transferred directly from previous work of Lewis and Catlow (11). These parameters of $Ba_2In_2O_5$ successfully reproduce the alternating oxygen octahedra and tetrahedra backbone of the structure. The unit cell contains four formula units.

Before carrying out defect and migration calculations, the unit cell dimensions and ion positions were equilibrated under constant pressure conditions. The calculated bond distances and angles are given in Table 2. Table 3 lists calculated properties of the simulated structure. The lattice parameters vary by an average of 1.1% from the experimentally determined values. Unfortunately no additional experimental data on dielectric and elastic properties are available for further validation and refinement of the potential model.

3. RESULTS AND DISCUSSION

3.1. *Intrinsic Defects*

Calculations were performed on the energies of isolated point defects (vacancies and interstitials), with a cut-off distance of 7.5 Å for the inner defect region. These energies were combined to give the Frenkel and Schottky energies presented in Table 4. It is noted that indium interstitials were placed at several locations in the structure, but on

TABLE 1
Interatomic Potentials for $Ba_2In_2O_5$

(i) Short-range

Interaction	A (eV)	ρ (eV)	C (eV.Å^{-6})
Ba^{2+}–O^{2-}	931.7	0.3949	0
In^{3+}–O^{2-}	1495.6	0.3310	4.325
O^{2-}–O^{2-}	22764.3	0.1490	171.983

(ii) Shell model[a]

Species	Y(e)	k(eV.A^{-2})
Ba^{2+}	1.46	14.78
In^{3+}	− 6.1	1680.0
O^{2-}	− 2.24	42.0

[a] Y and k refer to the shell charge and harmonic force constant, respectively.

TABLE 2
Calculated Bond Distances and Bond Angles[a]

Separation	Distance (Å or Angle °)	Separation	Distance (Å or Angle °)
	Ba polyhedron		
Ba–O(1)	2.796 [1]	Ba–O(2)	3.102 [1]
Ba–O(1)	2.759 [1]	Ba–O(2)	2.762 [1]
Ba–O(1)	2.761 [1]	Ba–O(2)	2.931 [1]
Ba–O(1)	2.728 [1]	Ba–O(3)	2.749 [1]
		Mean Ba–O	2.824
	In(1) polyhedron		
In(1)–O(1)	2.1263 [2]	O(1)–O(1)	2.969 [2]
In(1)–O(1)	2.1293 [2]	O(1)–O(1)	3.049 [2]
In(1)–O(2)	2.2847 [2]	O(2)–O(1)	3.059 [2]
Mean In–O	2.1801	O(2)–O(1)	3.113 [2]
		O(2)-O(1)	3.133 [2]
O(1)–In(1)–O(1)	88.5	O(2)–O(1)	3.182 [2]
O(1)–In(1)–O(1)	91.5		
O(1)–In(1)–O(2)	87.7	O(1)–In(1)–O(2)	89.6
O(1)–In(1)–O(2)	92.3	O(1)–In(1)–O(2)	90.4
	In(2) polyhedron		
In(2)–O(2)	1.961 [2]	O(2)–O(2)	4.569 [1]
In(2)–O(3)	1.944 [1]	O(2)–O(3)	3.024 [2]
In(2)–O(3)	1.960 [2]	O(2)–O(3)	3.077 [1]
Mean In(2)–O	1.955	O(3)–O(3)	3.138 [1]
O(2)–In(2)–O(2)	137.4	O(2)–In(2)–O(3)	103.4
O(2)–In(2)–O(3)	101.5	O(3)–In(2)–O(3)	107

[a] Square parentheses indicate number of equivalent distances per polyhedron.

TABLE 3
Calculated Properties of the Perfect Crystal of $Ba_2In_2O_5$

Property	$Ba_2In_2O_5$
Lattice energy (eV.formula unit^{-1})	−207.96
Unit cell parameters (A)[a]	
a	6.08 (6.09)
b	16.40 (16.78)
c	5.94 (5.88)
Elastic constants (10^{11} dyn.cm^{-2})	
c_{11}	20.49
c_{12}	11.92
c_{13}	6.28
c_{33}	7.25
c_{44}	5.37
c_{66}	6.97
Dielectric constants	
$\langle \varepsilon_s \rangle$	7.28
$\langle \varepsilon_\infty \rangle$	1.98

[a] Experimental values in parentheses (15).

every occasion the structure became unstable, indicating that it is not possible for indium ions to form Frenkel defects according to this model.

Examination of the Frenkel and Schottky defect energies in Table 4 clearly reveals that the predominant mode of intrinsic disorder is of the oxygen Frenkel type, in accord with the model of Zhang *et al.* (3). Our calculated Frenkel energy of 0.91 eV agrees well with the experimental value of 0.84 eV (3), which provides additional support for the validity of the potential model. The low Frenkel energy suggests that the defect concentration will be significant in the ordered structure at intermediate temperatures. The oxygen vacancies were found to form slightly more preferentially on the O(1) site than the O(2) site (Fig. 1). Vacancies on the O(3) (tetrahedral layer) site could not be tolerated by the structure. Displaced oxygen ions were readily accommodated on interstitial sites in the tetrahedral layer. It should also be pointed out that anion Frenkel disorder is commonly observed in oxides with the fluorite structure, such as CeO_2 and ThO_2, and is responsible for ionic conductivity in the undoped phases (16).

3.2. *Redox Reactions*

Most applications of fast oxygen ion conductors require them to be used under a range of oxygen partial pressures, and hence it is important to determine the stability of these materials under variable redox conditions. Several redox reactions in $Ba_2In_2O_5$ were considered that may lead to deviations from ideal stoichiometry and consequently an electronic component to the total conductivity in the material.

TABLE 4
Calculated Energies of Atomic Defects in $Ba_2In_2O_5$

(a) Isolated point defects

Defect	Energy (eV)
Ba vacancy	18.94
In vacancy	50.52
O(1) vacancy	20.21
O(2) vacancy	20.66
Ba interstitial	−7.59
O interstitial	−18.39

(b) Frenkel and Schottky disorder

Type	Defect equilibrium[a]	Energy (eV/defect)
Ba Frenkel	$Ba_{Ba} = V''_{Ba} + Ba_i^{\bullet\bullet}$	5.68
O Frenkel	$O_O = V_O^{\bullet\bullet} + O''_i$	0.91
Schottky	$2Ba_{Ba} + 2In_{In} + 5O_O$ $= 2V''_{Ba} + 2V'''_{In} + 5V_O^{\bullet\bullet} + Ba_2In_2O_5$	3.56

[a] Kroger–Vink notation used.

For oxidation three possible situations can occur:

$$\tfrac{1}{2}\mathrm{O}_{2(g)} \rightarrow \mathrm{O}_i'' + 2h^{\bullet}, \qquad [2]$$

to give an oxygen excess material, or alternatively

$$\tfrac{1}{2}\mathrm{O}_{2(g)} + \mathrm{Ba}_{\mathrm{Ba}}^{\times} \rightarrow V_{\mathrm{Ba}}'' + 2h^{\bullet} + \mathrm{BaO} \qquad [3]$$

or

$$\tfrac{1}{2}\mathrm{O}_{2(g)} + \tfrac{2}{3}\mathrm{In}_{\mathrm{In}}^{\times} \rightarrow \tfrac{2}{3}V_{\mathrm{In}}''' + 2h^{\bullet} + \tfrac{1}{3}\mathrm{In}_2\mathrm{O}_3, \qquad [4]$$

to give a metal deficient material. For reduction, we considered only

$$\mathrm{O}_{\mathrm{O}}^{\times} \rightarrow V_{\mathrm{O}}^{\bullet\bullet} + \tfrac{1}{2}\mathrm{O}_{2(g)} + 2e' \qquad [5]$$

to give an oxygen deficient material, since introduction of indium interstitials was shown to be a highly unfavorable process; in this equation, $V_{\mathrm{O}}^{\bullet\bullet}$ relates to intrinsic vacancies in the structure due to reduction, rather than those due to Frenkel disorder. Our approach to electronic defects in $Ba_2In_2O_5$ follows that used for $LaMO_3$ perovskites (7) and the cuprate superconductors (8, 9), in which we model the hole centers as In^{4+} or O^- and the electron centers as In^{2+} or In^+. The resulting energies, listed in Table 5, favor creation of O^- and In^+ on oxidation and reduction, respectively.

Using these electronic terms, the energies of the four redox reactions were calculated and are given in Table 6. Owing to the uncertainties in the free-ion terms employed, we must be cautious in giving detailed interpretations.

The results of Table 6 show that oxidation is most likely to occur via incorporation of oxygen at interstitial sites in the tetrahedral layer (Eq. [2]). This suggests that *p*-type conductivity will be exhibited with increasing oxygen partial pressures, as observed experimentally (2). However, oxidation leading to a metal deficient material seems unlikely.

The reduction energy in $Ba_2In_2O_5$ shows that this material is more resistant to reduction than oxidation, which concurs with the defect model presented by Zhang *et al.* (3). It should be noted that entropic effects need to be included in our calculations to derive a quantitative relationship between oxygen partial pressure and defect concentration, which is a topic for further study.

In general, these results are consistent with experimental findings, which show mixed electronic/ionic conductivity and that *p*-type conductivity increases with increasing oxygen activity.

TABLE 5
Calculated Energies of Electronic Defects

Defect	Energy (eV)
In^{4+} ($h^{\bullet}$)	13.30
O^- ($h^{\bullet}$)	6.49
In^{2+} (e')	−0.70
In^+ ($2e'$)	−1.76

Note. Ionization energies of In: II(18.81), III(28.03), IV(54.4); Second electron affinity of O: 8.75.

TABLE 6
Calculated Energies of Redox Reactions of $Ba_2In_2O_5$

Redox process	Energy (eV/electron)
Oxidation	
Eq. [2]	2.22
Eq. [3]	14.38
Eq. [4]	23.02
Reduction	
Eq. [5]	4.30

3.3 Oxygen Migration

Oxygen diffusion in the low temperature ordered form of $Ba_2In_2O_5$ is made possible by the presence of Frenkel defects. Since vacancies on the O(1) site were shown to be more energetically favorable, diffusion might be expected to occur either through O(1) sites in the octahedral layer, or interstitial oxygen sites in the tetrahedral layer. Activation energies for these different migration pathways were estimated by placing single oxygen ions in "transition" states, as if frozen in the act of jumping from one site to another. The transition state was assumed to be the saddle-point of the energy surface between the initial and final sites of the migrating ion.

Distortion of the oxygen octahedra in the brownmillerite structure causes the jump distance for oxygen ions migrating between O(1) sites to be different in the [100] and [001] directions. The calculated migration enthalpies for motion in these two directions, as well as diffusion through the tetrahedral layer, are shown in Table 7.

TABLE 7
Energies of Migrating Oxygen Vacancies in $Ba_2In_2O_5$

Jump path	Migration energy ΔH_m (eV)	Distance (Å)
Octahedral [100]	1.47	3.05
Octahedral [001]	1.21	2.97
Tetrahedral [001]	1.34	2.97

These results predict that oxygen diffusion occurs preferentially through the octahedral layer in the [001] direction via vacancies due to intrinsic Frenkel disorder. The activation energy of 1.2 eV is consistent with the energies of ≈ 1.0 eV determined experimentally from conductivity measurements below T_t (3). Direct comparison with this experimental value is not straightforward, due to the presence of an electronic component to the conductivity even at low oxygen partial pressures. It is also interesting to note that the simulation studies reveal that the migration saddle-point is not directly at the midpoint between the two vacancies in the oxygen tetrahedra, but slightly bowed away from the central trivalent ion, suggesting that oxygen ions follow a slightly curved path in moving from one site to another. A similar pathway has also been predicted from simulation studies of the $LaMO_3$ perovskites (7).

4. CONCLUSION

The present computer simulation study is the first of its kind to investigate the complex brownmillerite structure containing ordered oxygen vacancies. Energy minimization and Mott–Littleton methods were used to probe the structure and oxygen transport properties of $Ba_2In_2O_5$, a compound that displays fast oxygen ion conductivity comparable to that of yttria-stabilized zirconia between 900 and 1000°C. The following conclusions can be made:

(1) Anion Frenkel disorder is the dominant intrinsic defect in the ordered, low temperature form of $Ba_2In_2O_5$; a defect formation energy of 0.91 eV is calculated which agrees well with the experimental Frenkel energy.

(2) Oxidation occurs via introduction of oxygen into the large interstitial positions in the tetrahedral layer, with associated formation of holes that contribute to *p*-type conductivity.

(3) $Ba_2In_2O_5$ is more resistant to reduction than oxidation as is observed experimentally. Reduction involves oxygen being removed from the octahedral oxygen layers with In^+ formation, which leads to *n*-type conductivity.

(4) The computer modeling results agree with experimental studies showing that $Ba_2In_2O_5$ is a mixed electronic/ionic conductor in its ordered, low temperature form.

(5) Detailed mechanistic studies showed that oxygen ions migrate preferentially in the [001] direction with an activation energy of 1.2 eV. Ions were found to follow a slightly curved trajectory in moving from one site to another.

ACKNOWLEDGMENTS

The authors thank the Royal Society for supporting C.A.J.F. during the course of this work. All simulations were performed in the Materials Modelling Laboratory of the Dept. of Materials, Oxford. We are also grateful to J. D. Gale for useful discussions and to R. W. Grimes for providing some of the potentials.

REFERENCES

1. B. C. H. Steele, *Mater. Sci. Eng. B* **13,** 79 (1992).
2. J. B. Goodenough, J. E. Ruiz-Diaz, and Y. S. Zhen, *Solid State Ionics* **44,** 21 (1990).
3. G. B. Zhang and D. M. Smyth, *Solid State Ionics* **82,** 161 (1995).
4. T. R. S. Prasanna and A. Navrotsky, *J. Mater. Res.* **8,** 1484 (1993).
5. S. B. Adler, J. A. Reimer, J. Baltisberger, and U. Werner, *J. Am. Chem. Soc.* **116,** 675 (1994).
6. R. Stevens, "Introduction to Zirconia," 2nd ed. Magnesium Elektron, London, UK, 1986.
7. M. Cherry, M. S. Islam, and C. R. A. Catlow, *J. Solid State Chem.* **118,** 125 (1995).
8. M. S. Islam and R. C. Baetzold, *J. Mater. Chem.* **4,** 299 (1994).
9. M. S. Islam, and L. J. Winch, *Phys. Rev. B* **52,** 10,510 (1995).
10. C. R. A. Catlow, *in* "Computer Simulation of Solids" (C. R. A. Catlow and W. C. Mackrodt, Eds.), Vol. 166 of Lecture Notes in Physics. Springer-Verlag, Berlin, 1982.
11. G. V. Lewis and C. R. A. Catlow, *J. Phys. C* **18,** 1149 (1985).
12. B. J. Dick and A. W. Overhauser, *Phys. Rev.* **112,** 90 (1958).
13. A. A. Colville, *Acta Crystallogr. B* **26,** 1469 (1970).
14. J. D. Gale, "GULP (General Utility Lattice Programme)," Royal Institution, 1993; *Phil. Mag. B* **73,** 3 (1996).
15. H. Kuramochi, T. Mori, H. Yamamura, H. Kobayashi, and T. Mitamura, *J. Ceram. Soc. Jpn* **102,** 1159 (1994).
16. P. Kofstad, "Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides," Wiley, New York, 1972.