

Modeling of cation diffusion in oxygen ion conductors using molecular dynamics

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Abstract

Cation diffusion in ionic conducting oxides is modelled using molecular dynamics (MD). As example systems LSGM (Sr- and Mg-doped LaGaO₃; perovskite structure) and YSZ (Y-doped ZrO₂; fluorite structure) were investigated. In both systems, cation diffusion is governed by diffusion via lattice vacancies and not via interstitials. In LSGM, the diffusion of all types of cations is correlated by the formation of a binary vacancy complex of two neighbouring vacancies on the A and B sites of the perovskite lattice, which are migrating together. This leads to very similar cation diffusion coefficients for all four cations. In YSZ, calculated diffusion coefficients of the two cations differ significantly (Y is five times faster than Zr), in good agreement with experiments. The calculated activation enthalpies were close to the experimental ones, indicating that cation diffusion is mainly governed by the migration enthalpy, while the formation enthalpy of a cation vacancy should be small.

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1. Introduction

Stabilised zirconium oxides, mainly obtained by adding yttrium oxide (yttria-stabilised zirconia, YSZ) and doped lanthanum gallate (doped with Sr on A site and Mg on B site; LSGM) show a very high oxygen diffusion making them very attractive for technological applications as sensor material or as electrolyte material in solid oxide fuel cells (SOFC).

The very fast oxygen diffusion is generally accompanied by very slow cation diffusion, which is less investigated

than the well-studied oxygen transport properties. Experimentally, the cation diffusion is found to be many orders of magnitude slower than oxygen diffusion [1,2].

Computer simulations of the cation diffusion in these systems are by now mainly done by performing Mott-Littleton-type calculations, where the migration energies for the migration of different cations in an almost perfect surrounding were calculated. For Zr and Y, in YSZ, migration energies in the range of 2–7 eV were calculated [3], while for La and Ga in LSGM values of nearly 10 eV (for the A site cations) and 2–3 eV (for the B site cations) were found [4]. In contrast, experimentally, the cation diffusion coefficients in LSGM seem to be very similar for all types of cations investigated so far [5], in particular for both A and B site cations.

One limitation of Mott-Littleton defect calculations is that the effect of temperature can only be handled with difficulty, which is especially crucial for cation diffusion,

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since most of the experimental data were only obtained at high temperatures (>1200 K). Another problem related to that is that the diffusion is generally calculated in a well-defined surrounding, free of much further disorder. Therefore, the properties of heavily disordered systems like LSGM and YSZ are still not easy to calculate.

Molecular dynamics has the advantage over other computer simulation methods in that absolute diffusion coefficients can be calculated at various temperatures. However, it has the disadvantage that only relatively fast processes can be modelled due to limited computer time. Therefore, up to now, molecular dynamics (MD) has only been used to describe the fast oxygen transport properties in ionic conducting oxides. In the present paper, MD is for the first time applied to model the normally slow cation diffusion processes. To do that, and to overcome the problems with the low cation diffusion, well-defined concentrations of cation vacancies were artificially introduced into the simulation boxes and their behaviour was modelled using long-time calculation runs. The influence of defect concentration was estimated using varying defect concentrations in the system YSZ.

2. Computer simulations set-up

For the molecular dynamics calculations, the program DL_POLY [6] was used. Simple Buckingham potentials (Eq. (1)) were used with the potential parameters adopted from the literature and being summarised in Table 1.

$$V(r) = A \exp\left(-\frac{r_{ij}}{\rho}\right) - \frac{C}{r_{ij}^6} + \frac{q_i q_j}{r_{ij}} \quad (1)$$

Using DL_POLY, different defect concentrations were simulated in YSZ by building up supercells with a size of $2 \times 2 \times 2$ to $4 \times 4 \times 4$ unit cells (each built-up by four ZrO_2 units) containing three different yttria concentrations (11, 19 and 31 mol% Y_2O_3 ; later referred to as YSZ-11, YSZ-19 and YSZ-31, respectively) and the corresponding amount of oxygen vacancies. Because the supercells were infinitely repeated throughout all space, a uniform and well-defined distribution of even high stabiliser concentrations can be

Table 1
Buckingham simulation parameters used for the MD simulations

Buckingham	A (eV)	ρ (Å)	C (eV Å ⁶)	Reference
<i>YSZ calculations</i>				
$\text{Y}^{3+}-\text{O}^{2-}$	1325.6	0.3461	0.0	[7],[8]
$\text{Zr}^{4+}-\text{O}^{2-}$	1024.6	0.376	0.0	[7],[8]
$\text{O}^{2-}-\text{O}^{2-}$	22764.3	0.149	27.89	[8]
<i>LSGM calculations</i>				
$\text{La}^{3+}-\text{O}^{2-}$	2088.79	0.3460	23.25	[10]
$\text{Sr}^{2+}-\text{O}^{2-}$	1956.702	0.3252	0.0	[9]
$\text{Ga}^{3+}-\text{O}^{2-}$	1605.720	0.2959	0.0	[10], mod.
$\text{Mg}^{2+}-\text{O}^{2-}$	2457.243	0.2610	0.0	[9]
$\text{O}^{2-}-\text{O}^{2-}$	25.41	0.6937	32.32	[9]

simulated [11,12]. From each supercell, one zirconium ion and two more oxygen ions were removed to create a Schottky defect as a starting point for the cation migration calculations. Similarly, $5 \times 5 \times 5$ LSGM supercells (each built-up by one LaGaO_3 unit) containing 20 mol% Sr and 20 mol% Mg were set-up by randomly distributing the appropriate amount of Sr and Mg cations on the perovskite A and B sublattices and randomly removing the respective amount of oxygen ions. Then, two cation vacancies were created in the A and B sublattices by removing one La and one Ga cation and three oxygen ions, in two different ways: First, the cation vacancies were chosen to be close together and, secondly, the cations vacancies were placed well-separated in the lattice. The cation migration of these two setups was followed up as a function of time and temperature.

The simulations were carried out for times of up to 1 μs , with a step time of 0.0005 ps. For low temperatures, even after such long calculation times the cation diffusion was too slow to calculate mean square displacements: which normally can then be transformed into diffusion coefficients [13]. Therefore, counting the number of jumps for the different cation types and converting them into diffusion coefficients using Eq. (2) gives estimated cation diffusion coefficients.

$$D(t) = 0.653 \times v_0^2 \times n/t \quad (2)$$

Here, v_0 is the jump length, n is the jump probability and t is the calculation time. The factor 0.653 is the correlation factor for cubic lattices. Since the number of jumps is slow, there might be preferential jumps, which could lead to a correlation factor not identical to the perfect one. All calculations were carried out using an NPT ensemble (NPT: constant number of particles, constant pressure, constant temperature).

3. Results and discussion

3.1. Yttria-stabilised zirconia

An Arrhenius-type plot of calculated yttrium and zirconium diffusion coefficients obtained according to Eq. (2) is shown in Fig. 1, where the cation diffusion coefficients for a cation vacancy concentration of $x(\text{V}_{\text{Zr}}^{4+})=0.004$ on the cation sublattice are compared to the experimental ones. It can be seen that the calculated diffusion coefficients are relatively close to the extrapolated measured ones. When measuring the cation self-diffusion, Y was found to be three times faster than Zr [14], but with a lower activation enthalpy of diffusion (which leads to extrapolated values being only slightly different). Here, yttrium diffusion is calculated to be roughly five times faster than Zr, which corresponds well with the experimental results assuming the same activation enthalpies for Zr and Y self diffusion. For higher cation vacancy concentrations, the

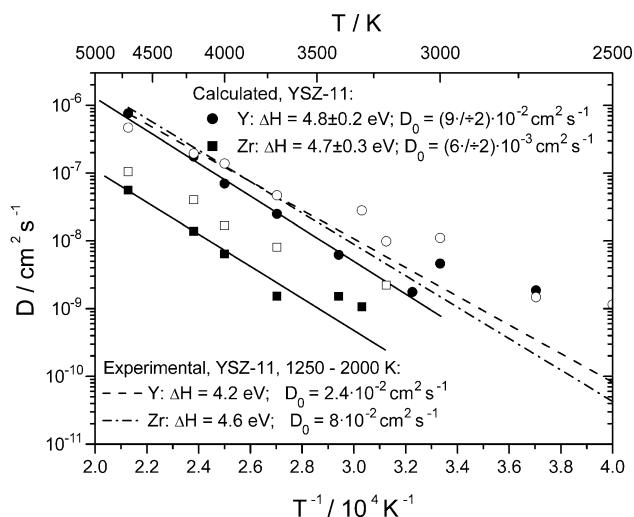


Fig. 1. Extrapolated experimental (taken from Ref. [2]) and calculated cation diffusion coefficients in YSZ containing 11 and 31 mol% Y_2O_3 . The concentration of intrinsically Schottky defects was chosen to be 0.004 (on the cation sublattice) for the MD calculations. Straight line: result of a fit of the calculated diffusion coefficient for YSZ-11. Dotted line: extrapolation of the experimental values [2], [14]. Open symbols: YSZ-31, closed symbols: YSZ-11.

cation diffusion coefficients are much higher than experimentally observed. When varying the yttrium content, the calculated cation diffusion coefficients are nearly independent of the yttrium content or even increasing, while experimentally they were observed to decrease with increasing the yttrium content [2], the difference is not yet fully understood.

Furthermore, the calculated activation enthalpies of migration are with 4.4 eV relatively close to the experimental values, where values between 4.3 and 5.3 eV were observed for different types and concentrations of stabilised zirconias [2]. Using defect chemistry, it was previously assumed that the experimentally obtained cation diffusion enthalpies are composed of formation, migration and association enthalpies [14]. According to the present results, the major part to the measured activation enthalpy of cation diffusion is the migration enthalpy, while the formation and association enthalpies should be relatively small, not exceeding 1 eV altogether. Nevertheless, there is still some uncertainty in the calculated (as well as the experimental) diffusion coefficients.

Using different concentrations of cation vacancies, it is possible to show that the cation diffusion coefficient is increasing with increasing the dopant concentration, but currently it is too difficult to use the calculated values of diffusion coefficients to obtain the concentration of cation vacancies in the YSZ lattice. In order to do that, one would need to perform calculations at lower temperatures close to the temperature of the experimental results, which are currently taking too much computing time.

Taking together experimental data and results of Mott-Littleton calculations, Chien and Heuer [15] estimated in the temperature range of 1100–1300 °C the concentrations of different types of cation vacancies ($V_{\text{Zr}}^{4'}$, $V_{\text{Zr}}^{4'} - V_{\text{O}}^{2-}$, $V_{\text{Zr}}^{4'} - 2V_{\text{O}}^{2-}$), and found values of up to 10^{-8} . Extrapolated to the temperatures of the calculations applied here, mole fractions of cation vacancies of up to 10^{-3} would be obtained, which are close to the values used here. However,

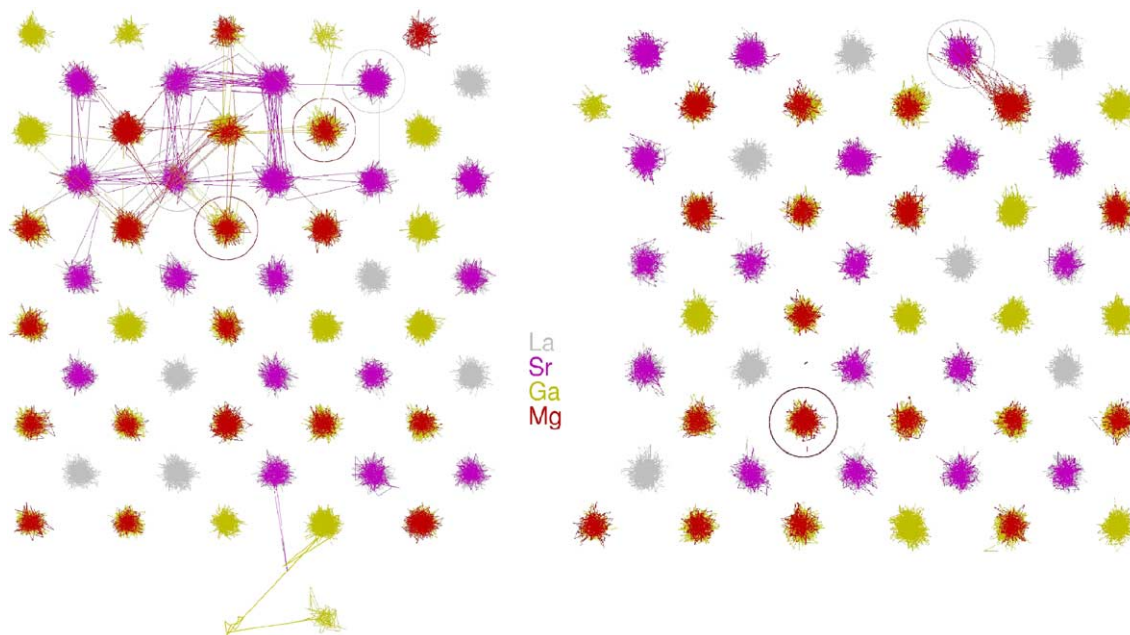


Fig. 2. Plot of migration pathways for cation migration in LSGM at 3400 K. View of the simulation cell along the z -axis. Calculation time: 25 ns. For clarity, only the positions of the cations after each 100 ps is shown, oxygen ions are suppressed. Left: cation vacancies initially placed close to each other in the above left part. Right: cation vacancies initially placed at the bottom left and above right. Circles indicate the initial and final positions of the vacancies.

in the work of Chien and Heuer, high formation enthalpies of at least 2.8 eV for the different types of complex cation vacancies were used in order to calculate the defect concentrations. According to the present computer simulation results, we think that these formation enthalpies might be significantly smaller than the values used by Chien and Heuer.

3.2. Strontium- and magnesium-doped lanthanum gallate

In Fig. 2, a sketch of the migration pathway in LSGM with two different starting configurations of the A and B cation vacancies are shown, with them being initially close together and separated. It can be seen that for the first configuration, the number of cation jumps is very high, and consists of both jumps along the A and the B sublattice of LSGM. For the latter configuration, there are only forward–backward jumps from the A lattice into the B sublattice, but no long-distance cation migration is induced. A closer inspection of the migration pathways confirms a transport mechanism for the B cations, which includes A antisite, and a cation diffusion mechanism as is shown in Fig. 3 can be proposed. For the diffusion of the A cations, the transport occurs via direct jumps from an A cation into a neighboring A cation vacancy. As a consequence, the diffusion of the A and B cations is coupled due to the formation of cation vacancy clusters. This results in cation diffusion coefficients, which are very similar for all four cations. The A cations can jump relatively quickly when they are close to a B cation vacancy, while they are nearly immobile when being isolated. There are more Sr stabiliser than La jumps (on A sublattice), and more Mg stabiliser than Ga jumps (on B sublattice), which might be due to the fact that the stabiliser ions having different ionic radius do not fit perfectly into the LaGaO_3 lattice.

It was calculated previously that the A and B site cations in perovskites have significantly different migration energies [4,16]. This effect can be also confirmed here since the jump numbers of A and B cation jumps

are different (see Fig. 2). Cation tracer diffusion experiments can only tell about the long-range diffusion, while other methods, e.g. mechanical spectroscopy [17], could monitor the elementary steps of the migration and one would in principle be able to distinguish between the jumps of the different types of cations. It will be interesting to perform such type of experiments in the future on LSGM which should result in (at least) two different activation enthalpies attributable to the two types of bulk cation jumps.

4. Summary

Molecular dynamics has been applied to investigate the cation diffusion in ionic conductors LSGM and YSZ. The following results were obtained for the two systems investigated:

- In both systems, the cation diffusion is mainly governed by diffusion via intrinsic lattice vacancies (Schottky defects) and not via interstitials [18].
- In LSGM, the diffusion of all cations is correlated and occurs via two neighbouring vacancies on the A and B sites of the perovskite lattice, which are only migrating together (forming a binary vacancy complex). The A cations are hopping directly to the next neighbour A site vacancy, while B cations are also hopping to a neighboured A site vacancy as an intermediate state. This leads to similar cation diffusion coefficients for all four types of cations.
- In YSZ, the activation enthalpy of cation migration is calculated to 4.4 eV for both Y^{3+} and Zr^{4+} , with the latter having smaller diffusion coefficients by a factor of 5. The calculated activation enthalpy is close to the experimental one, indicating that the cation diffusion in the material is mainly governed by the enthalpy of migration, while the enthalpy of formation of a cation vacancy should be relatively small.

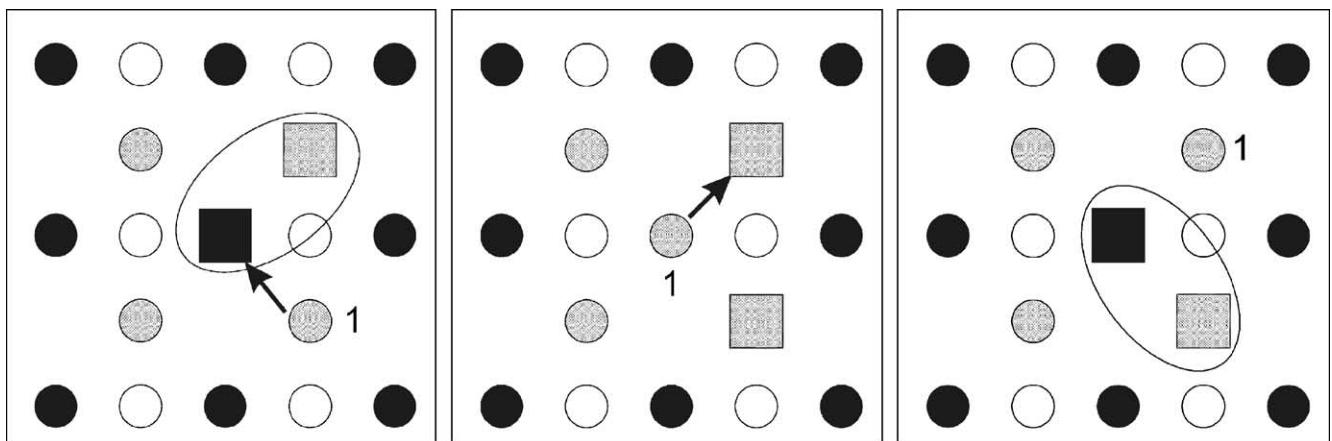


Fig. 3. Schematic view of proposed cation diffusion mechanism for a B site cation “1” in LSGM via A antisites. View perpendicular to (110). White: oxygen ion, black: A cation, grey: B cation. Squares: vacancies, circles: atoms. Left: starting configuration. Middle: B on A antisite. Right: end configuration.

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References

- [1] H. Solmon, C. Monty, M. Filal, G. Petot-Ervas, C. Petot, *Solid State Phenom.* 41 (1995) 103.
- [2] M. Kilo, G. Borchardt, B. Lesage, O. Kaitasov, S. Weber, S. Scherrer, *J. Eur. Ceram. Soc.* 20 (2000) 2069.
- [3] W.C. Mackrodt, P.M. Woodrow, *J. Am. Ceram. Soc.* 69 (1986) 277.
- [4] R.A. De Souza, J. Meier, *J. Chem. Soc., Faraday Trans. 5* (2003) 740.
- [5] O. Schulz, M. Martin, *Advances in Science and Technology* (Faenza Italy), Mass and Charge Transport in Inorganic Materials, Part A, vol. 29, 2000, p. 83.
- [6] DL-POLY is a package of molecular simulation routines written by W. Smith and T.R. Forester, copyright The Council for the Central Laboratory of the Research Councils, Daresbury Laboratory at Daresbury, Nr. Warrington (1996).
- [7] M. Kilo, C. Argiris, G. Borchardt, R.A. Jackson, *Phys. Chem. Chem. Phys.* 5 (2003) 2219.
- [8] A. Dwivedi, A.N. Cormack, *Philos. Mag.*, A 61 (1990) 1.
- [9] M.S. Khan, M.S. Islam, D.R. Bates, *J. Phys. Chem., B* 102 (1998) 3099.
- [10] L. Minervini, R.W. Grimes, K.E. Sickafus, *J. Am. Ceram. Soc.* 83 (2000) 1873.
- [11] A.N. Cormack, *Solid State Ionics* 8 (1983) 187.
- [12] R.A. Jackson, J.E. Huntington, R.G.J. Ball, *J. Mater. Chem.* 1 (1991) 1079.
- [13] M.P. Allen, D.J. Tildesley, *Computer simulation of liquids*, Clarendon, Oxford, 1987.
- [14] M. Kilo, G. Borchardt, B. Lesage, S. Weber, S. Scherrer, M. Martin, M. Schroeder, *Key Eng. Mater.* 206–213 (2002) 601.
- [15] F.R. Chien, A.H. Heuer, *Philos. Mag.*, A 73 (1996) 681.
- [16] R.A. De Souza, M.S. Islam, E. Ivers-Tiffée, *J. Mater. Chem.* 9 (1999) 1621.
- [17] M. Weller, *J. Mater. Educ.* 17 (1995) 1.
- [18] M. Kilo, G. Borchardt, R.A. Jackson, *Philos. Mag.* 83 (2003) 3309.