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Pathways for ion transport in nanostructured BaF_2:CaF_2

S. Adams *, E.S. Tan

National University of Singapore, Department of Materials Science and Engineering, 117574, Singapore

Abstract

The experimentally observed drastic conductivity enhancement in epitactic BaF_2:CaF_2 heterolayers with respect to any of the two fluoride ion conducting phases is qualitatively reproduced by molecular dynamics simulations and analyzed in detail with particular emphasis on the variation of properties as a function of the distance to the two-phase boundary. Ion mobility varies with the distance to the interface but remains significantly enhanced throughout the modeled layers when compared to bulk materials. The bond valence method is utilized to study correlations between the conductivity enhancement and the microstructure. A time-averaged violation of local electroneutrality postulated in the mesoscopic multiphase model is verified by the bond valence analysis of the molecular dynamics simulation trajectories. Moreover the average coordination number of the fluoride ions is significantly reduced around the interface suggesting a redistribution of anions from regular sites to interstitial sites. The variation of the ion mobility can be related to the extension of clusters of unoccupied accessible pathway regions.

Keywords: Ion transport; BaF_2:CaF_2; Bond valence method

1. Introduction

Ion transport in nanostructured materials has attracted significant interest both for its practical applications, the enhancement of conductivity in solid electrolytes, and from a scientific point of view, because transport behavior changes qualitatively, when the spacing between adjacent interfaces becomes comparable to the order of magnitude of the space charge layer thickness. In our previous work we had found indications of such a "mesoscopic multiphase effect" [1] in periodic sequences of thin sub-Debye length thin β- and γ-AgI like layers. Soon thereafter Sata et al. [2] have been able to synthesize nanometer-scale planar BaF_2:CaF_2 heterostructures by molecular beam epitaxy and found an enhancement of the ionic conductivity with decreasing period length (i.e. with decreasing thickness of the individual layers) compatible with predictions based on the mesoscopic size effect. Here we investigate such BaF_2:CaF_2 heterostructures by molecular dynamics simulations using dedicated empirical force field parameters from [3,4] and various boundary conditions to contribute to a clarification of the conductivity enhancement at an atomistic level.

Details of the dynamic ion transport pathways in the local structure models can be extracted by applying our transport pathway analysis method (that utilizes the bond valence approach) [5–7] to series of instantaneous configurations extracted from the molecular dynamics trajectories.

2. Experimental details

BaF_2:CaF_2 heterostructures with a period length of ca. 6.3 nm are simulated by molecular dynamics simulations. It should be noted that the period length in our simulations is about 2–3 times smaller than for the experimental studies to keep the computational effort manageable. To closely mimic the heteroepitaxial layers investigated in the experimental study [2] the interface was always chosen to coincide with the low energy (111) surface of the fluorite structures. In the discussion the orientation of the parallel interfaces will be referred to as the *x–y* orientation, while the direction perpendicular to the (111) interface is referred to as the *z*-direction. All simulations use a dedicated set of force-field parameters taken from Sayle et al. [3], who have performed similar simulations using different boundary conditions and creation techniques for the heterolayers [4].

Our first set of simulations was performed for a 2-dimensionally periodic model that contains 5184 atoms. This model has been created simply by changing the nature of the cations in the central

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* Corresponding author.
E-mail address: mseasn@nus.edu.sg (S. Adams).

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section of a periodic BaF_2 superstructure, eliminating a slab perpendicular to the BaF_2:CaF_2 interfaces to allow for a relaxation of the layers. Unsurprisingly it is found that such a relaxation consistently leads to the formation of series of misfit dislocations at the interface (similar to the ones observed by electron microscopy in [8]). Despite a series of NVT and NPT simulations we could not achieve satisfactory relaxation of this 2D periodic system (which as demonstrated below can be monitored by analyzing the bond valence sums of the F^- ions in snapshots of the simulation).

Therefore a second series of simulations was based on a 3D periodic starting model where the central section of a BaF_2 superlattice has been replaced by a slab of the CaF_2 structure in the same orientation but with the relaxed lattice constants of the CaF_2 structure. Periodic boundary conditions are employed in the usual way by Ewald summation. A subsequent NPT relaxation leads to a structure that again is characterized by a regular sequence of stacking faults at the BaF_2:CaF_2 interface and a slight rotation of the two substructures around the *z*-axis. Unless otherwise indicated results discussed in this work will refer to this 3D periodic $(CaF_2)_{1103}(BaF_2)_{778}$ superlattice consisting of 5643 atoms.

Before each of the molecular dynamics production runs at $T=1000$ K, 750 K and 500 K these structures are relaxed by a 100 ps NPT simulation at the given temperature, and equilibrating the structure at the resulting relaxed lattice constant. For comparison MD simulations have been performed in an analogous way for crystalline BaF_2 and CaF_2. Bond valence analyses of the resulting MD simulation trajectories are based on our own BV parameter set softBV available from ref. [9].

3. Results and discussion

3.1. Ionic conductivity

Ionic conductivities calculated from series of MD simulations for both heterostructures, as well as for BaF_2 and CaF_2 are summarized in Fig. 1 and compared to previous experimental and simulation data from the literature [2,4]. Results for the two different models used in this MD study as well as for the heterostructure created in a slightly different way in [3,4] lead to only minor differences in the overall ion mobilities. For the experimentally accessible temperature range MD simulations predict an enhancement of the ionic conductivity by several orders of magnitude compared to the bulk materials.

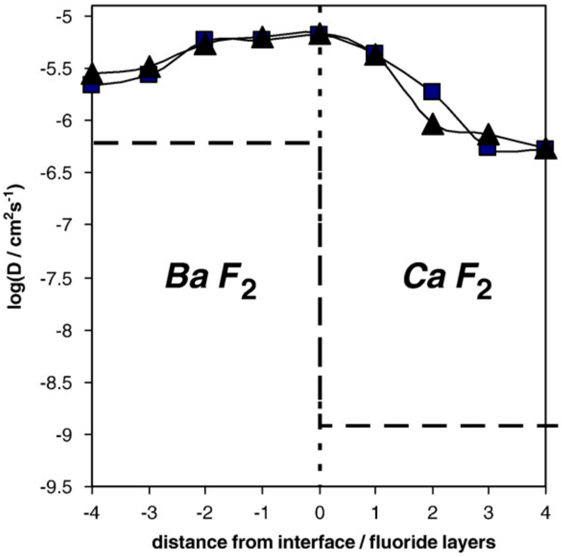

Fig. 2. Variation of the F^- diffusion coefficient as a function of the distance from the interface. The broken line indicates the diffusion coefficients for the corresponding bulk materials, while the vertical dotted line marks the interface.

To study more in detail the effect of the interface on the conductivity, Fig. 2 displays a layer by layer analysis of the diffusion coefficients. The conductivity reaches a maximum at the (BaF_2 side of the) interface. Even for F^- at the center of the thin BaF_2 or CaF_2 layers the diffusion coefficient does not drop to the values found in MD simulations for the pure bulk materials CaF_2 and BaF_2. Both interfaces in the simulated box behave in the same way. Despite the pronounced dependence of the local conductivity on the distance to the interface, there is no statistically significant anisotropy of the ion mobility for ions in the same layer: in all the F^- ion layers the ratio between the

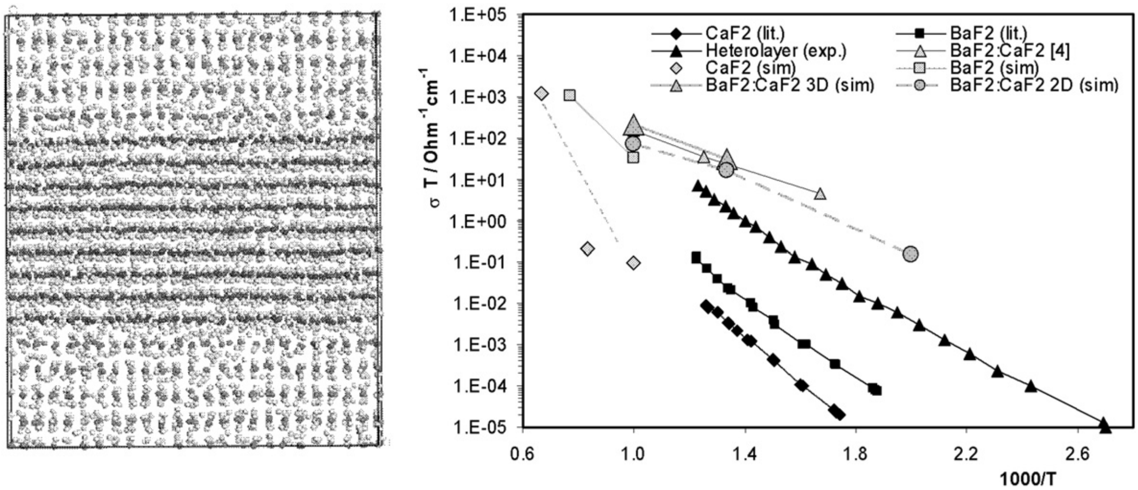

Fig. 1. (a) Projection of the periodic 5643 BaF_2 3D superlattice on the y, *z* plane. (b) Comparison between experimental conductivities (black symbols) and MD simulation results (grey symbols).

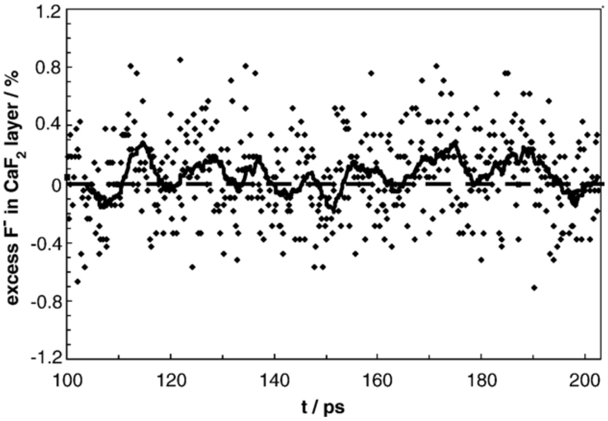

Fig. 3. Distribution of F^- ions between the CaF_2 and BaF2 layers displayed as percentage of excess F^- bonded to Ca^{2+} in 513 snapshots from the MD simulation. The solid line shows the moving block average (over 20 snapshots), while the broken line marks the ordered F^- distribution.

mobility parallel and perpendicular to the interface scatters around 1 (0.7–1.7).

3.2. Bond valence analysis

An analysis of MD simulation trajectories employing the simple bond valence approach can provide further insight into the ion transport mechanism in the interface region. The essential assumption in explaining the enhanced conductivity as a consequence of a mesoscopic multiphase effect is that F^- ions are enriched in the CaF_2 phase and F^- ion vacancies V_F are enriched in the BaF_2 layer. As the boundaries between the phases fluctuate during the simulation, a purely geometrical criterion cannot reliably determine the number of F^- ions in each layer, while the bond valence analysis of the MD simulation trajectory permits to verify this assumption: Whether a particular F^- in the simulated system is bonded predominantly to Ba^{2+} or to Ca^{2+} can be decided by comparing the contributions of Ba–F and Ca–F bonds to the BV sum of the F^- ion. The resulting F^- distribution for 513 snapshots from the second half of a 200 ps NVT simulation (T = 1000 K) is shown in Fig. 3. Of the 3762 F^- ions in the simulated heterolayer 2106 should belong to the CaF_2 layers and 1654 to the BaF_2 layer. On average the CaF_2 layer contains however the slightly higher value of 2107.2 F^-, i.e. 1.2 F^- or 0.056% more than in the fully ordered structure (with a standard error of the mean value 0.012%). Nearly the same average concentration of excess F^- is also found for the 750 K simulation. The pronounced fluctuation seen in Fig. 3 indicates that at 1000 K the mobility of the F^- is high enough to eliminate a bias of a particular initial configuration. Significantly longer trajectories and larger systems would be required to derive a statistically significant charge redistribution profile from such MD simulations.

Besides the slight excess vacancy concentration we noted a pronounced change of the F^- ion ordering in the interface region. In the ordered BaF_2 or CaF_2 structure F^- ions occupy 4-fold coordinated sites. The interstitial site in the center of the unit cell is too large so that a F^- cannot reach a matching bond valence sum at its center, but only at the corners of the central void (cf. Fig. 4). A simple way to determine the coordination number of an anion is to count the number of surrounding cations for which the bond distance corresponds to a bond valence exceeding a threshold value (I.D. Brown [10] suggested to use s = 0.04 valence units as the threshold). It should be noted that this definition of a coordination number does not necessarily lead to a complete coordination polyhedron. When applied to series of snapshots MD simulations it is expected that (especially for elevated temperatures) this method leads to average CN values slightly below 4 (since a small fraction of the F^- bonds will be elongated to an extent that the interaction is no longer counted as a bond). If the number of interstitials increases, the average coordination number will decrease (due to the asymmetric bonding of the F^- ions at the corners of the interstitial site). Such a pronounced decrease of the average coordination number is observed in a broad range around the interface of the BaF_2:CaF_2 heterolayer and the average coordination number remains reduced throughout the BaF_2

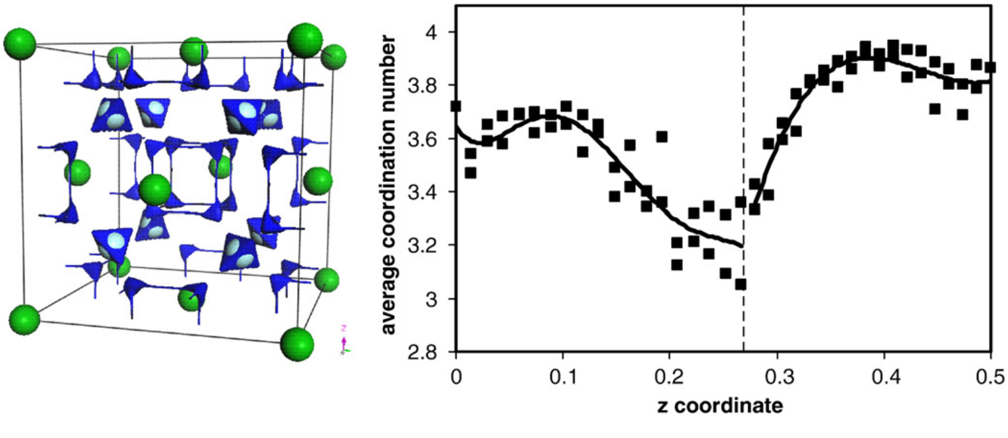

Fig. 4. (a) Isosurface of constant BV sum mismatch in the BaF_2 structure. Besides for the occupied tetrahedral sites local minima of the BV sum mismatch are also found at the corners of the interstitial site, but not at the central void (1/2,1/2,1/2). (b) Variation of the average coordination number of the F^- ions in snapshots of a MD simulation with the z coordinate averaged over the F^- ions in a z coordinate interval and 300 snapshots. Polynomial fits are shown as a guide to the eye for the separate phases (BaF_2 on the l.h.s., CaF_2 on the right hand side).

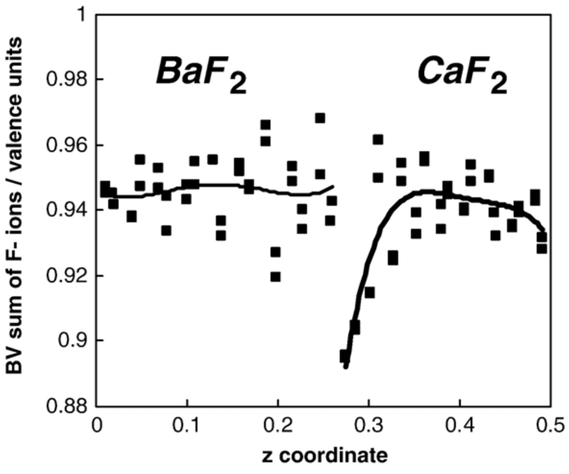

Fig. 5. Variation of BV sum of F$^-$ ions in snapshots of a MD simulation with the *z* coordinate averaged over the F$^-$ ions in *z* coordinate interval and 100 snapshots. Polynomial fits are shown as a guide to the eye for the separate phases.

layer when compared to the coordination number in a MD simulation of bulk BaF_2. Together with the observed slight charge carrier redistribution between the layers this reduced degree of F$^-$ ion ordering will contribute to the concentration of mobile charge carriers near the interface.

Fig. 5 exemplifies that the structural relaxation at the interface may be quantified by the BV approach. The variation of the average BV sums for F$^-$ ions in snapshots from the 3D periodic model clarifies that the structural relaxation occurs mostly on the expanded CaF_2 side of the interface, while BV sums within the BaF_2 do not exhibit a significant variation with the distance from the interface. (A slight underbonding of F$^-$ ions is characteristic of BV sums in snapshots from MD simulations due to the deviations of the instantaneous positions from the average positions in equilibrium crystal structures.). This observation is consistent with an experimental quantification of the structural relaxation in BaF_2:CaF_2 heterolayers [8].

3.3. Ion transport pathways

The bond valence approach may also be utilized to visualize characteristics of ion transport pathways in the interface region, by identifying regions in space that may host a F$^-$ ion (i.e. regions in space where a F$^-$ would have a matching bond valence sum). Details of this approach applied to ion conduction pathways in bulk materials have been discussed previously [5–7]. It is a particular feature of such bond valence maps that they identify occupied and vacant sites alike. In the present case of compressed BaF_2 layers and expanded CaF_2 layers it turns out that focusing on maps of only the unoccupied regions of the pathways provides a clearer image that is qualitatively consistent with the variation of ion mobilities as derived from the MD simulation trajectory (cf. Fig. 6). From the detail of the distribution of unoccupied F$^-$ ion transport pathways shown in the right-hand side graph of Fig. 6 it becomes obvious that accessible regions for a mobile F$^-$ inside the CaF_2 (top) and BaF_2 layer (bottom) are mostly isolated, while more extended unoccupied pathway regions near the interface permit longer distance motions. This tendency becomes even more prominent, when the time evolution of the pathways is taken into account by analyzing series of consecutive snapshots in the same way.

4. Concluding remarks

In molecular dynamics simulations of BaF_2:CaF_2 heterolayers the experimentally observed conductivity enhancement and reduced activation energy is qualitatively reproduced. The conductivity is found to be highest at the (BaF_2 side of the) interface, but remains significantly enhanced throughout the entire layers when compared to conductivity values determined from MD simulations of the pure bulk phases using the same

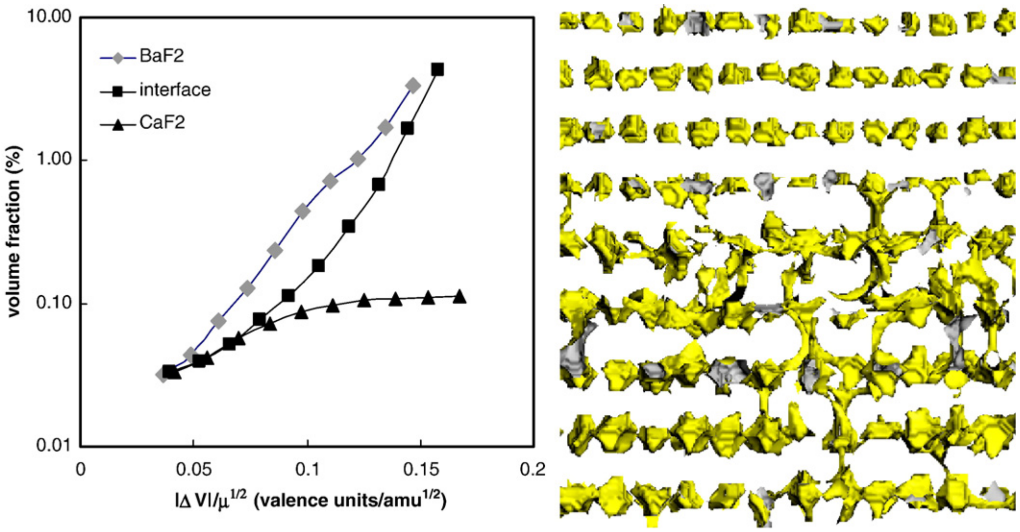

Fig. 6.

parameter set. Despite the strong variation of the local mobilities with the distance from the interface, the local displacements of the F^{-} ions do not show a comparably strong anisotropy.

The simple bond valence is shown to be a versatile and effective tool for analyzing the MD simulation trajectories in terms of structural relaxations, ion transport pathways and the ion transport mechanism. A bond valence analysis of the environment of F^{-} ions in snapshots of the MD simulation supports the slight deviation from local electroneutrality (postulated by the mesoscopic multiphase model) via a redistribution of fluoride ions between the layers. This leads to a slight enrichment of interstitial F^{-} within the CaF_2 phase and hence an increased fluoride ion vacancy concentration in the BaF_2 layer. Moreover a pronounced variation of the average F^{-} ion coordination number is observed suggesting a reduced degree of ordering of the anions on their regular sites. Further work is necessary to quantify the relevance of these two charge redistribution effects and to investigate their interrelation with micro-strain effects around the dense sequence of misfit dislocations at the interface that have also been reproduced in the simulations.

Acknowledgement

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References

[1] J.S. Lee, S. Adams, J. Maier, J. Electrochem. Soc. 147 (2000) 2407.
[2] N. Sata, K. Eberman, K. Eberl, J. Maier, Nature 408 (2000) 946.
[3] D.C. Sayle, J.A. Doig, S.C. Parker, G.W. Watson, Chem. Commun. (2003) 1804.
[4] D.C. Sayle, J.A. Doig, S.C. Parker, G.W. Watson, T.X.T. Sayle, Phys. Chem. Chem. Phys. 7 (2005) 16.
[5] S. Adams, Solid State Ionics 177 (2006) 1625.
[6] S. Adams, J. Swenson, Ionics 10 (2004) 396.
[7] S. Adams, Bull. Mater. Sci. 29 (2006) 587.
[8] N.Y. Jin-Philipp, N. Sata, J. Maier, C. Scheu, K. Hahn, M. Kelsch, M. Rühle, J. Chem. Phys. 120 (2004) 2375.
[9] S. Adams, NUS Singapore; http://www.softBV.net.
[10] I.D. Brown, The Chemical Bond in Inorganic Chemistry — The Bond Valence Model, Oxford University Press, New York, 2002.