

## Synthesis, structure and ionic conductivity in nanopolycrystalline BaF<sub>2</sub>/CaF<sub>2</sub> heterolayers†

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Atomistic simulations have shown that the calculated conductivity of nano-polycrystalline BaF<sub>2</sub>/CaF<sub>2</sub> heterolayers is considerably higher than the component bulk materials and we predict that grain-boundary diffusion is the key to fast ionic conductivity in these systems.

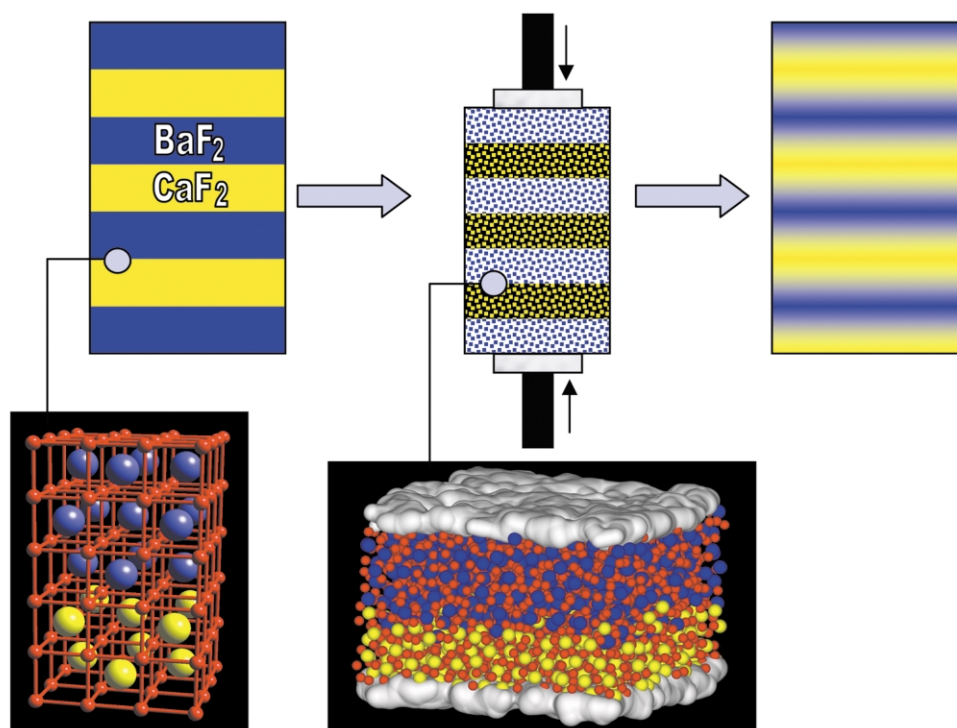
Ionic conduction remains central to many solid-state reactions, fuel cell technologies, high temperature batteries and sensors.<sup>1</sup> Crucially, the microstructure of such systems has a profound influence on the properties.<sup>2,3</sup> Experimental work by Sata *et al.* and Puin *et al.* on BaF<sub>2</sub>/CaF<sub>2</sub> heterostructures<sup>2</sup> and nanocrystalline CaF<sub>2</sub><sup>3</sup> demonstrates that control over the fabrication of a particular microstructure can lead to an increase in the ionic conductivity. Here, we present an analogous approach to experiment: that of computer aided design, which can be used to (1) synthesise, (2) structurally characterise and (3) calculate the conductivity of the resulting system. The strategy provides a

framework for the computational design of materials with tailored ionic conductivities.

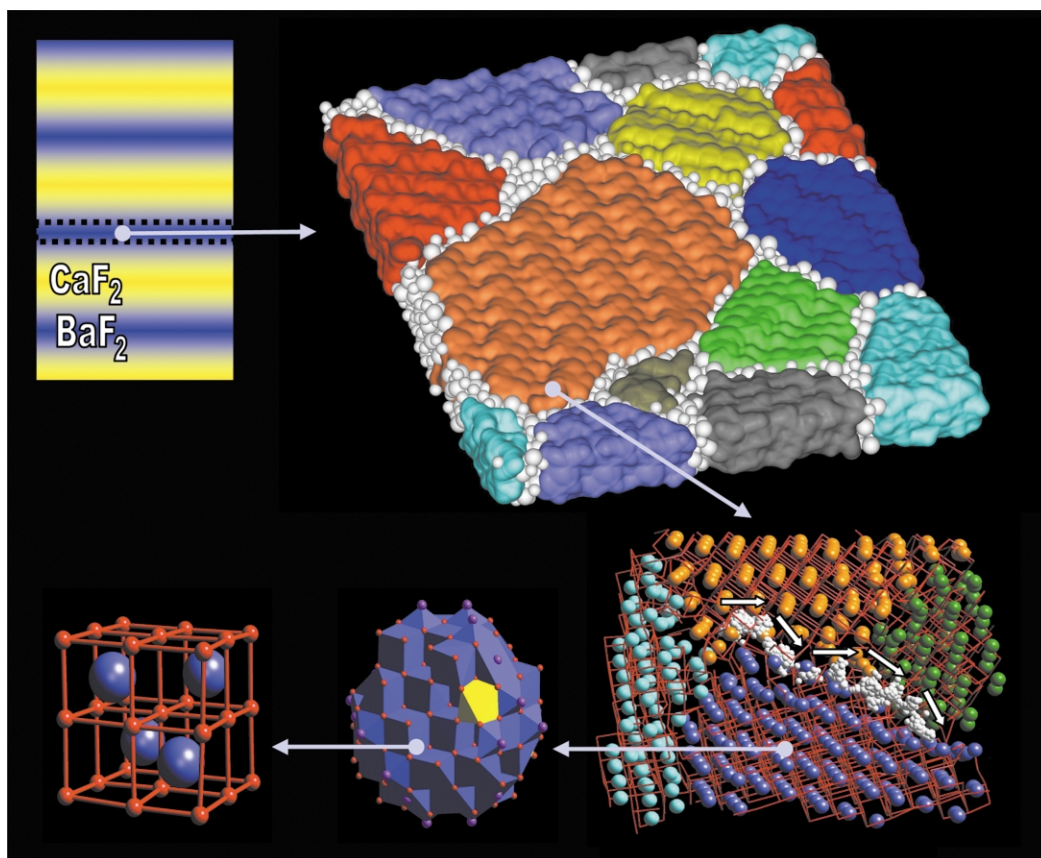
The computer aided design procedure is illustrated by synthesising models of nano-polycrystalline BaF<sub>2</sub>/CaF<sub>2</sub>, characterising the structure using graphical techniques, calculating the conductivity and observing the trajectories of the fast conducting fluoride ions within the lattice.

Nano-polycrystalline BaF<sub>2</sub>/CaF<sub>2</sub> heterointerfaces were synthesised using an amorphisation and recrystallisation strategy that we developed previously.<sup>4</sup> Specifically, a block of BaF<sub>2</sub> (15 552 ions) was placed on top of a CaF<sub>2</sub> substrate (10 800 ions) using periodic boundary conditions to generate a layered structure. To amorphise the system, the BaF<sub>2</sub> was then compressed by 27%. Under molecular dynamical (MD) simulation (performed at 1200 K for 2.5 ps) the considerable compressive strain results in the amorphisation of first the BaF<sub>2</sub> and then the underlying CaF<sub>2</sub>. The MD simulation was then continued at lower temperatures to recrystallise the system. Specifically, 75 ps at 1200 K; 1455 ps at 800 K; 795 ps at 400 K and finally 612 ps at 0 K, the latter acting as an energy minimisation. The strategy is illustrated in Fig. 1.

† Electronic supplementary information (ESI) available: potential parameters and pertinent calculated physical properties for the perfect BaF<sub>2</sub> and CaF<sub>2</sub>. See <http://www.rsc.org/suppdata/cc/b3/b305393h/>



**Fig. 1** Synthesis of nano-polycrystalline BaF<sub>2</sub>/CaF<sub>2</sub> planar heterostructure. Top: schematics illustrating the BaF<sub>2</sub> and CaF<sub>2</sub> layers; starting configuration (left), compression induced amorphisation (middle) and final structure (right). Bottom: ion positions in the preparatory configuration (left) and amorphous configuration (middle). Barium is coloured blue; calcium is yellow and fluorine, red.



**Fig. 2** Structural characterisation of the final configuration of the BaF<sub>2</sub>/CaF<sub>2</sub> system. Top left a schematic illustrating the BaF<sub>2</sub> and CaF<sub>2</sub> layers; top right, a slice is cut through a BaF<sub>2</sub> slice to depict the nano-polycrystalline BaF<sub>2</sub>. Bottom right, the positions of individual ions within four intersecting grains are shown; a calculated trajectory for a fast moving fluoride ion (white) is superimposed and its pathway highlighted by the white arrows. Bottom middle, a section of one particular grain with polyhedral rendering and bottom left, ion positions of a unit cell.

All simulations were performed using the DL\_POLY code<sup>5</sup> using an NPT ensemble. The interatomic potentials, describing the interactions between the ions, are based upon the Born model of the ionic solid in which the ions interact *via* long-range Coulombic terms and short-range repulsive terms. Potential parameters and pertinent calculated physical properties for the perfect BaF<sub>2</sub> and CaF<sub>2</sub> using this potential model are available as ESI<sup>†</sup>. The activation energy for diffusion of fluoride ions in bulk BaF<sub>2</sub> and CaF<sub>2</sub>, which is of prime importance in this study, is calculated to be 1.1 and 1.2 eV respectively and are within 10% of experimental values.

Graphical techniques were employed extensively to help understand and characterise the various microstructural features comprising the BaF<sub>2</sub>/CaF<sub>2</sub> system. Images for the final structure are presented in Fig. 2.

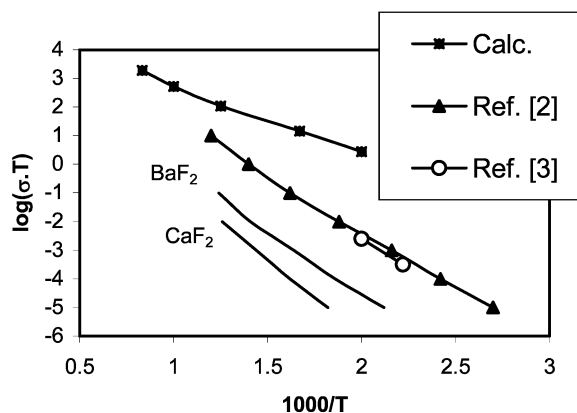
Inspection of Fig. 2 reveals that the BaF<sub>2</sub> thin film comprises numerous misoriented nanocrystallites, about 2–10 nm in size, which are separated by grain-boundaries and grain junctions. The BaF<sub>2</sub> thin film also comprises about 5% Ca ions, which have migrated from the CaF<sub>2</sub> layers: inspection of the interfacial boundaries between the BaF<sub>2</sub> and CaF<sub>2</sub> crystallites reveal that there is a smooth transition from Ba to Ca concentrations perpendicular to the layers. Inspection of the nanocrystallites confirms that the BaF<sub>2</sub> has crystallised back into the fluorite structure. The atomistic structures of the grain-boundaries are similar to those observed experimentally (for example see ref. 6), which shows that the procedure is capable of generating realistic models of complex microstructures; the CaF<sub>2</sub> films exhibit similar microstructures and nanocrystallite sizes to that of the BaF<sub>2</sub>. We now calculate the ionic conductivity for the final (recrystallised) system and compare directly with available experimental data.

Atomic transport properties including the diffusion coefficients, activation energies and conductivities, can be extracted from the simulations using time dependent Mean Square

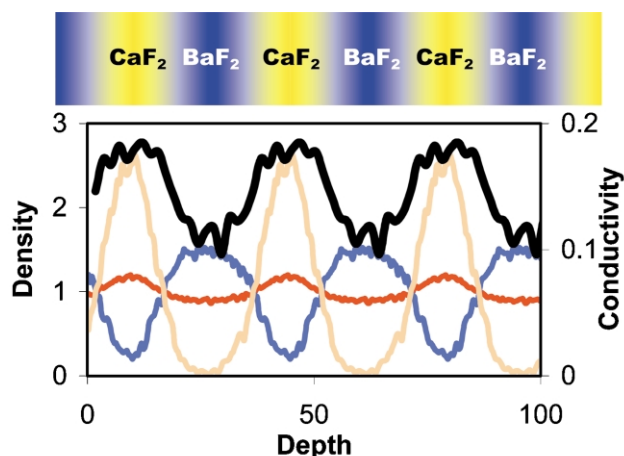
displacements (MSD) and following standard approaches.<sup>7</sup> To calculate the MSD's, MD simulations were run on the system for 300 ps at 500, 600, 800, 1000 and 1200 K. The calculated conductivities are presented in Fig. 3.

Inspection of Fig. 3 reveals that the calculated conductivity of the nano-polycrystalline BaF<sub>2</sub>/CaF<sub>2</sub> model system is significantly higher compared with the component BaF<sub>2</sub> and CaF<sub>2</sub> materials. In addition, the activation energy associated with fluoride ion mobility in this system is calculated to be about 0.5 eV, which is less than half the value for the pure component materials.

Experimentally, Sata *et al.*, who fabricated nanometer scale crystalline BaF<sub>2</sub>/CaF<sub>2</sub> planar heterostructures, using molecular beam epitaxy, observed that the conductivity was significantly



**Fig. 3** Calculated conductivities ( $\sigma$ ) for the nano-polycrystalline BaF<sub>2</sub>/CaF<sub>2</sub> system. Experimental values for planar BaF<sub>2</sub>/CaF<sub>2</sub> heterostructures,<sup>2</sup> nano-polycrystalline CaF<sub>2</sub><sup>3</sup> and bulk BaF<sub>2</sub> and CaF<sub>2</sub><sup>2</sup> are included as a comparison.



**Fig. 4** Ionic conductivity ( $S\text{ cm}^{-1}$ ) calculated as a function of depth ( $\text{\AA}$ ) through the  $\text{BaF}_2/\text{CaF}_2$  system. The relative densities of ions comprising the system as a function of depth are depicted also to show the location of the various  $\text{BaF}_2$  and  $\text{CaF}_2$  layers. F-red; Ba-blue; Ca-orange and conductivity-black.

higher than the bulk materials. Remarkably, they found that the conductivity increased proportionally with interfacial density; the measured conductivities for 16 nm films, taken from the study of Sata *et al.*,<sup>2</sup> are included in Fig. 3. Similarly, Puin *et al.* measured ionic conductivity in nanocrystalline  $\text{CaF}_2$  and concluded that the nanocrystalline  $\text{CaF}_2$  shows a significantly higher overall conductivity than microcrystalline  $\text{CaF}_2$ ; data, taken from the study of Puin *et al.*,<sup>3</sup> are also included in Fig. 3. Our model system, which comprises periodic nano-polycrystalline  $\text{BaF}_2/\text{CaF}_2$  layers, reflects microstructural attributes of both experimental systems.

One can also extract atomistic detail of the essential physics associated with ionic transport using our simulated models because the time-dependent atom positions are known explicitly. To illustrate this, Fig. 4 shows the conductivity (at 800 K) calculated as a function of depth through the  $\text{BaF}_2/\text{CaF}_2$  system. Surprisingly, our calculations suggest a higher conductivity within the  $\text{CaF}_2$  film compared with the  $\text{BaF}_2$ . In addition, a further calculation was performed to establish the trajectories taken by fast moving fluoride ions. A representative trajectory pathway is superimposed onto Fig. 2. Inspection of this figure reveals that the fluoride ion traverses through grain-boundary

regions within the  $\text{CaF}_2/\text{BaF}_2$  system. Similarly, detailed analyses of other fluoride ion pathways reveal that the trajectories follow complex pathways along various  $\text{CaF}_2/\text{CaF}_2$ ,  $\text{CaF}_2/\text{BaF}_2$  and  $\text{BaF}_2/\text{BaF}_2$  grain boundaries within the system with little impingement into bulk crystalline regions. As alluded to above, our calculations predict that the highest conductivity is within the  $\text{CaF}_2$  layers — specifically, fluoride ions traversing through  $\text{CaF}_2/\text{CaF}_2$  boundaries.

Our simulations help rationalise the experimental findings of Sata *et al.*<sup>2</sup> and Puin *et al.*<sup>3</sup> Specifically, we propose that grain-boundary diffusion facilitates the observed enhanced conductivity and epitomises the remarkable new structures and properties one can observe by traversing to the nanoscale.

The results presented here demonstrate that by modifying the computational synthetic procedure to fabricate a particular microstructure (this may also be modified to include, for example, different materials, layer thickness, nanocrystallite sizes, dislocations or other dopant species) and then calculating the conductivity, one can begin to identify the effect of microstructure on technologically important processes. Specifically, this study has illustrated that grain-boundary diffusion is the key to fast ionic conductivity in these nano-polycrystalline multilayered materials. Such insights assist in the design of new systems with promising applications where high conductivity is required at moderate temperatures such as fuel cells. Ultimately, the procedure can be exploited with an aim of predicting microstructures, which facilitate optimal conductivity. Accordingly, the strategy provides a framework for using the computational techniques to design systems with tailored ionic conductivities.

## Notes and references

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