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PAPER

On the mechanisms of ionic conductivity in $BaLiF_3$: a molecular dynamics study

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The mechanisms of ionic conductivity in $BaLiF_3$ are investigated using molecular simulations. Direct molecular dynamics simulations of (quasi) single crystalline super cell models hint at the preferred mobility mechanism which is based on fluoride interstitial (and to a smaller extent F^- vacancy) migration. Analogous to previous modeling studies, the energy related to Frenkel defect formation in the ideal $BaLiF_3$ crystal was found as 4–5 eV which is in serious controversy to the experimentally observed activation barrier to ionic conductivity of only 1 eV. However, this controversy could be resolved by incorporating $Ba^{2+} \leftrightarrow Li^+$ exchange defects into the elsewise single crystalline model systems. Indeed, in the neighborhood of such cation exchange defects the F^- Frenkel defect formation energy was identified to reduce to 1.3 eV whilst the cation exchange defect itself is related to a formation energy of 1.0 eV. Thus, our simulations hint at the importance of multiple defect scenarios for the ionic conductivity in $BaLiF_3$.

Introduction

The investigation of the mechanisms that trigger ionic mobility in complex ion conductors reflects an ongoing challenge to both experiment and theory. Our need of high-performance ion conductors and the urge for a rational design of such materials form a strong motivation for in-depth characterization techniques offering an atomistic understanding. In parallel to NMR spectroscopy experiments, atomistic simulation approaches are becoming increasingly popular.[1] For the profound understanding of transport phenomena in ionic devices molecular dynamics simulations evolved to be an attractive method for *in situ* investigations at the atomistic level of detail.

In the present study, we employ molecular simulations to explore ionic conductivity in $BaLiF_3$ which, despite its apparent simplicity, has become an interesting model system to investigate ionic mobility in a ternary ceramic available as single-, nano- and microcrystalline samples.[2–4] In principle, two ionic species may account for the ionic conductivity in $BaLiF_3$—and both ^7Li and ^{19}F NMR investigations hint at strong differences of the conductivity mechanisms in nano- and microcrystalline samples.[4] These differences are accompanied by a drastic change in ionic conductivity, which is reflected by activation energies of about 0.7 eV and 1.0–1.2 eV observed for $BaLiF_3$ obtained from high-energy milling (nanocrystalline) and microcrystalline (annealed) samples, respectively.[4]

While the development of reliable interaction potentials paved the way to explore ionic conductivity mechanisms using molecular simulation, initial results were quite discouraging. Indeed, the energy of Frenkel defect formation was seriously overestimated to be 4–5 eV.[5] The aim of the present work is to extend the initial modeling studies related to structure optimization (zero Kelvin) approaches to larger super cell models subjected to constant temperature, constant pressure molecular dynamics simulations. Along this line, ionic conductivities are directly assessed from ionic trajectories whilst supportive defect constellations (as relevant to interstitialcy mechanisms) are explored from separate model systems.

Simulation details

The ionic interactions were modeled on the basis of the empirical potential developed by Jackson *et al.*[5] Despite its simple form (Coulomb, Buckingham and van-der-Waals type potential energy functions) this force field was demonstrated to reproduce the lattice constants, structure, elastic and dielectric constants of single crystalline $BaLiF_3$. As model systems, $10 \times 10 \times 10$ super cells were created using the experimental unit cell reported in ref. 6.

The molecular dynamics simulations were performed in the NpT ensemble at ambient pressure and at temperatures ranging from 0 to 1200 Kelvin (in steps of 100 K). Such an elevated temperature was found to be necessary for obtaining reasonable statistics of ionic diffusion coefficients within ns scale trajectories. The electrostatic interactions were treated by the Ewald summation using a real space cut-off of 1.2 nm.

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Using a time-step of 1 fs, Frenkel defect formation was analyzed from molecular dynamics simulation runs of 1 ns and 0.5 ns which were performed at 800–1000 K and 1100–1200 K, respectively. For the analysis of vacancy/interstitial migration mechanisms, separate model systems were used to incorporate Schottky *or* interstitial defects at 300 K. The latter exhibit a ± 1 net charge and were thus explored at constant volume (fixed to the average volume of the single crystal at 300 K).

Results

Mechanisms of charge carrier formation

An intuitive starting point to explore ionic mobility using molecular dynamics simulations is given by a series of runs in which the temperature is gradually increased.[1] This procedure was applied to 100 ps runs heated in steps of 100 K and using a $10 \times 10 \times 10$ super cell model mimicking a $BaLiF_3$ single crystal. Despite the drastic heating rate (if compared to the experiment), this allowed first insights into ionic mobility, namely the formation of F^- Frenkel defects and F^- mobility. To provide quantitative insights, extended simulation runs of 1/0.5 ns were performed and an Arrhenius plot was used to derive the activation energy related to F^- diffusion. While defect migration will be discussed later, here we shall focus on the formation energy required for F^- Frenkel defects which reflects the major part of the barrier to ionic mobility in $BaLiF_3$ (Table 1). The regular lattice sites of the fluoride ions represent the centers of (deformed) Ba_4Li_2 octahedra (Fig. 1). Fluoride interstitials are incorporated by sharing one of these octahedra and the formation of a $Ba_4Li_2F_2$ motif. Jackson *et al.* identified a formation energy of 5 eV (at zero Kelvin) which is in reasonable agreement with the barrier to F^- diffusion of 4.5 eV as calculated using our molecular dynamics simulations.

To reconcile the drastic difference to the experimentally found activation energy of about 1 eV, we considered more complex mechanisms of ionic mobility than accessible to the brute-force molecular dynamics simulation approach as described above. While the Li^+ ions were not found to move from their regular lattice sites in the $BaLiF_3$ single crystal model, this might be related to the short time-scales inherent to molecular dynamics runs. Real crystals, and simulation models based on much longer molecular dynamics runs, should be expected to comprise a finite density of defects. Apart from F^- Frenkel defects, Jackson *et al.* also explored Li^+ interstitial/vacancy arrangements.[5] While this could not resolve the overestimation of the activation energy for ionic conductivity, here we suggest $Ba^{2+} \leftrightarrow Li^+$ exchange defects as a key to F^- diffusion in $BaLiF_3$. To minimize Coulomb energy, we exchanged nearest neighbor sites of Ba and Li and quenched the system to a local energy minimum. From this the formation energy of a single $Ba^{2+} \leftrightarrow Li^+$ exchange defect was assessed as 1.0 eV. We then repeated the heating procedure and the evaluation of ionic diffusion coefficients in analogous to the previously described simulations related to the ideal crystal model. Strikingly, F^- Frenkel defect formation is drastically boosted in the proximity of the $Ba^{2+} \leftrightarrow Li^+$ exchange defect. The activation energy for fluoride diffusion was found to reduce to 1.3 eV. This value is in reasonable agreement with the experimentally observed activation barrier, hinting at the strong relevance of $Ba^{2+} \leftrightarrow Li^+$ exchange defects to ionic conductivity in $BaLiF_3$.

The interplay of $Ba^{2+} \leftrightarrow Li^+$ exchange defects and F^- Frenkel defect formation may be rationalized on the basis of the octahedra coordinating the fluoride lattice site. While regular F^- coordination is given by Ba_4Li_2 motifs with a formal charge of $+10$, exchange of two cations leads to the (local) formation of $Ba_3Li_3^{9+}$ and Ba_5Li^{11+} motifs. While Ba_5Li octahedra favor F^- interstitial incorporation, Ba_3Li_3 octahedra promote F^- vacancy formation.

Table 1 Activation energy to ionic mobility and defect formation energy (if applicable). For the ideal single crystal the theoretically derived activation energy of 4.4 eV is drastically larger than the experimental value of about 1 eV. However, by locally exchanging neighboring Ba and Li ions, a defect structure is derived which gives rise to a much lower activation energy for fluoride mobility of 1.3 eV. Such exchange defects are disfavored by 1 eV per pair

Description	E_{pot} (arrangement)	$E_{activation}$ (ion mobility)
Ideal single crystal	0.0 (reference)	4.4 eV
Ba $\leftrightarrow$ Li exchange defect	1.0 eV	1.3 eV

Mechanisms of charge carrier migration

While high-temperature molecular dynamics simulations are required to boost the formation of Frenkel defects, the subsequent migration of F^- interstitials and vacancies is known to be related to comparably small energy barriers of 0.5 eV.[7] To explore the mechanistic details of charge carrier diffusion, we performed additional molecular dynamics simulations dedicated to the migration of an isolated interstitial/vacancy. In separate model systems, a single fluoride ion was added/removed and, after relaxation, we studied the migration of the defect at temperatures of 100, 200, …, 500 K. From an Arrhenius fit the activation energy of interstitial and vacancy migration was derived as 0.13 and 0.17 eV, respectively.

The interstitial transport mechanism is illustrated in Fig. 1 (right). While the preferred interstitial arrangement is given by fluoride incorporation into a $Ba_4Li_2F_2$ motif (a, c, and e), F^- mobility requires the permeation of a Ba_2Li triangle (b and d). The mechanism for vacancy migration is completely analogous, however a larger migration barrier results from the less favorable displacement of a fluoride ion in the Ba_4Li_2F motif compared to the $Ba_4Li_2F_2$ motifs.

Role of grain boundaries/disordered structures

While molecular simulations dedicated to heterogeneous ion conductors of well-known structure may provide quantitative insights,[8] the realistic assessment of the grain boundaries in samples obtained from high energy milling constitutes a tough challenge to molecular modeling. Here, we instead explored a limiting case study, that is the glassy state as obtained by rapid (picoseconds scale) quenching of the melt. Unlike grain boundaries which are partially ordered and reflect two-dimensional structures, the glass state should be considered as the upper limit to disordering. Comparison of the single crystalline and the glassy models should hence provide qualitative insights and also indicate

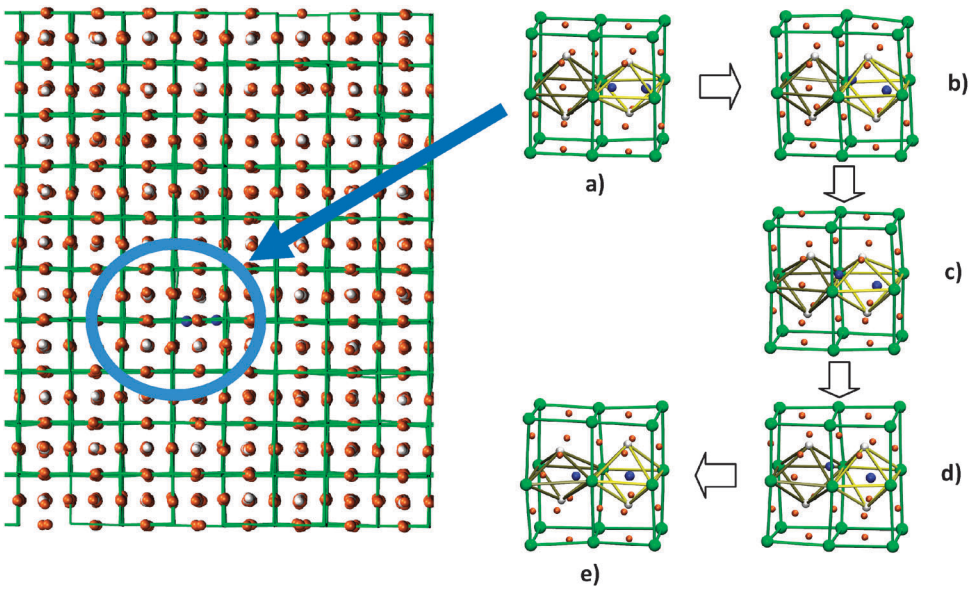

Fig. 1 Predominant mechanism of ionic conductivity in $BaLiF_3$. Left: $10 \times 10 \times 10$ supercell model. Colors: Ba (green), Li (white), F (red/blue). Right: the fluoride ions are preferentially located in the center of a Ba_4Li_2 octahedron. Similarly, interstitials are incorporated by sharing this octahedron and formation of a $Ba_4Li_2F_2$ motif (a, c, and e). By permeation of a Ba_2Li triangle (b and d), F^- ions may be displaced between octahedra that share a common face. While such interstitial migration is related to an activation energy of about 0.13 eV, vacancy migration was found to be slightly less favored (0.17 eV).

the range of conductivity which could be obtained from milling the real samples.

A snapshot of the model system is illustrated in Fig. 1, but the glassy state is shown in Fig. 2. After relaxation, 200 ps molecular dynamics simulations were performed at 300, 400, …, 700 K. From this, both Li^+ and F^- conductivity was identified. The Arrhenius plots indicate relatively low activation barriers of 0.4 eV for both ionic species.

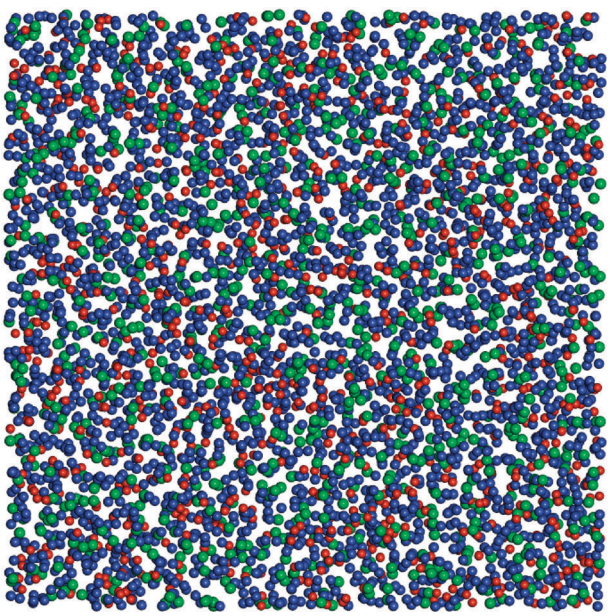

Fig. 2 Snapshot of the model system is a glassy state as obtained by quenching from the melt. Molecular dynamics simulations indicate both Li^+ and F^- conductivity at relatively low activation barriers of 0.4 eV for both ionic species. Colors: Ba (green), Li (red), F (blue).

On the basis of the glassy (0.4 eV) and the single crystalline models (1 eV) we can hence suggest a range of assessable activation energies through high-energy milling of $BaLiF_3$.

Conclusion

In conclusion we presented a conclusive picture of ionic conductivity in $BaLiF_3$. Single crystalline models of this ternary compound exhibit fluoride mobility only, however Li defects play a crucial role in the overall conductivity. $Ba^{2+} \leftrightarrow Li^+$ exchange defects locally boost the formation of F^- Frenkel defects and thus the formation of charge carriers in the ion conductor.

The picture of correlated Li and F defects is complemented by the differences in mobility of the two ionic species observed for nanocrystalline compounds.[4] Both, more detailed ^7Li and ^{19}F NMR investigations and molecular dynamics simulations on nanocrystalline samples, are necessary to shed light on grain boundary induced ionic mobility of $BaLiF_3$. Qualitatively, simulations dedicated to the glassy state indicate the lowering of the activation barriers to both F^- and Li^+ conductivity. This is particularly pronounced for Li^+ ions which were found to be immobilized in the single crystal model, but the disordered models exhibited the same activation barrier to mobility as observed for the fluoride ions.

The complexity of defects, grain boundaries and their effect on ionic mobility pose an ongoing challenge to the in-depth characterization of ion conductors. While we are still far from the rational design of such materials (and might never fully achieve this), the analyses of atomic scale conductivity mechanisms are crucial milestones *en route* to this ambitious goal. The example of $BaLiF_3$ demonstrates that even apparently simple compounds may exhibit unexpected phenomena that are

worthy of consideration when attempting new synthesis routes or interpreting experimental data.

References

1 D. Zahn, *J. Mol. Model.*, 2011, **17**, 1531.
2 A. Düvel, M. Wilkening and P. Heitjans, *Diffus. Fundam.*, 2009, **11**, 46.
3 A. Düvel, M. Wilkening, R. Uecker, S. Wegner, V. Sepelak and P. Heitjans, *Phys. Chem. Chem. Phys.*, 2010, **12**, 11251.
4 A. Düvel, M. Wilkening, S. Wegner, A. Feldhoff, V. Sepelak and P. Heitjans, *Solid State Ionics*, 2011, **18**, 65.
5 R. A. Jackson, M. E. G. Valerio and J. F. deLima, *J. Phys.: Condens. Matter*, 1996, **8**, 10931.
6 A. Boumriche, J. Y. Gesland, A. Bulou, M. Rousseau, J. L. Fourquet and B. Hennion, *Solid State Commun.*, 1994, **91**, 125.
7 G. E. Rush, A. V. Chadwick, R. A. Jackson, M. E. G. Valerio and J. F. de Lima, *Radiat. Eff. Defects Solids*, 2001, **155**, 393–396.
8 D. Zahn, O. Hochrein, X. Guo and J. Maier, *J. Phys. Chem. C*, 2009, **113**, 1315–1319.