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Atomistic In Situ Investigation of the Morphogenesis of Grains during Pressure-Induced Phase Transitions: Molecular Dynamics Simulations of the B1–B2 Transformation of RbCl

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Dedicated to Professor Martin Jansen on the occasion of his 66th birthday

Abstract: The mechanistic details of the pressure-induced B1–B2 phase transition of rubidium chloride are investigated in a series of transition path sampling molecular dynamics simulations. The B2→B1 transformation proceeds by nucleation and growth involving several, initially separated, nucleation centers. We show how independent and partially correlated nucleation events can function within a global mechanism and explore the evolution of phase domains during the transition. From this, the mechanisms of grain boundary formation are elaborated. The atomic structure of the domain–domain interfaces fully support the concept of Bernal polyhedra. Indeed, the manifold of different grain morphologies obtained from our simulations may be rationalized on the basis of essentially only two different kinds of Bernal polyhedra. The latter also play a crucial role for the B1→B2 transformation and specific grain boundary motifs are identified as preferred nucleation centers for this transition.

Keywords: grain boundary structures · molecular dynamics · nucleation mechanisms · polymorphism · solid-state structures

Introduction

Most crystalline materials are composed of many small crystallites. The properties of such polycrystalline solids dramatically depend on the shape and size of the grains and the structure of its boundaries. Characteristics such as elasticity, fatigue, and fracture behavior to a large part account to the polycrystalline nature of the compound. Indeed, the most common approach to modifying the mechanical properties of a bulk material is to manipulate the size of its grains.

Despite its tremendous importance, the investigation or worse the rational design of grains is far from being a routine job. This particularly applies to dynamical processes taking place at the atomistic scale. While electron microscopy allows the assessment of the atomistic structure of the interfaces separating the grains from each other, issues like domain nucleation and growth, grain boundary formation, and morphogenesis call for in situ experiments that are not yet available. On the other hand, studies of high resolution in both time and length scale may be performed by means of molecular dynamics simulations.

Recently, we presented a molecular dynamics simulation strategy for exploring the atomistic mechanisms of pressure-induced phase transitions.[1,2] Along this line, nucleation events, the growth of phase domains, and the formation of domain–domain interfaces became accessible to in situ investigations based on atomistic simulation models.[3,4] This motivated the elaboration of a generally applicable simulation setup for the study of grain boundary formation, its atomistic structure, and the role of the interfaces during a pressure-induced phase transition as it shall be described in the following.

Simulation models and methods

While the simulation scheme presented in this work in principle is transferable to the study of the solid-state polymorphism of practically any (poly-)crystalline material, here we decided to focus on a simple alkali halide compound. The latter materials have been investigated in detail both

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experimentally and theoretically.[5] Along this line, we recently demonstrated that differences of the ionic species in terms of the polarizability of the electron shell account for specific nucleation characteristics during the pressure-induced structural transformation from the NaCl-type (B1) to the CsCl-type (B2) structure and vice versa.[4] Strong contrasts in the chemical hardness and softness of the ions cause the phase transition to occur via many nucleation centers and result in a particularly large density of domains. This phenomenon makes a compound like RbCl (composed of soft anions and hard cations) a very favorable candidate for the study of domain morphogenesis and grain boundary evolution.

From high-pressure experiments at room-temperature, RbCl is known to transform from the B1 to the CsCl-type B2 structure at a pressure of 0.52 GPa.[6] Unless differently specified, the same conditions were chosen as a model scenario for our studies. While straightforward molecular dynamics simulations are subject to prohibitively large hysteresis effects,[2] employing the transition path sampling protocol[7,8] allows bridging the time-scale problem and studying the phase transition exactly at the conditions used in the high-pressure experiments.[1]

Transition-path sampling reflects an iterative method for exploring the manifold of dynamical pathways of the B1–B2 transformation. Starting from artificially prepared transition routes as described in the next paragraph, the sampling iterations imply trajectory rectifications that converge to the favored mechanism. The latter issue represents a powerful feature of the simulation method, as it offers an unbiased investigation of the phase transition. For each iteration step, a snapshot of the preceding trajectory is taken and slight modifications are incorporated.[1,2] Propagation of the newly generated configuration in both directions of time leads to a trial trajectory, which is checked for the process of interest. In case the nearest-neighbor coordination number changes from 6 to 8 or vice versa, the new path is accepted as a B1→B2 or B2→B1 transition route, respectively.

For the preparation of the initial B1–B2 pathways, we followed traditional geometric modelling approaches.[9] Therein the transition is described by a continuous unit cell transformation via predefined intermediate structures. Preparing transition trajectories from such models allows starting transition path sampling in specific regions of trajectory space. The B1–B2 pathway rectification was investigated for two parallel sets of sampling iterations, each initiated from a different mechanistic route. Therein the evolution of both runs to the same type of transformation pathways was taken as a convergence criterion.

We have performed four sets of simulation runs with periodic boxes containing $5\times5\times5$, $6\times6\times6$, $12\times12\times12$, and $14\times14\times14$ supercells of rubidium and chloride ions, respectively. The atomic interactions were described by the empirical force field of Tosi and Fumi, which has been found to be very robust in many simulations dedicated to alkali halides.[10] For the molecular dynamics simulation a time step as small as 0.2 fs was chosen to provide time-reversibility. In accordance with the experiments, the simulations were performed at constant temperature and pressure (300 K and 0.52 GPa, respectively). Therein, anisotropic shape changes of the simulation box were allowed for, so as not to bias the mechanistic analysis.

Results and Discussion

The most striking observation from the variety of first-order phase transitions studied so far by transition-path-sampling molecular dynamics simulations is related to the quick evolution of pathways in favor of nucleation and growth. The preparation of the initial B1–B2 transition trajectories of RbCl involves collective transformations of the simulation box. However, after only a few trajectory rectification steps such concerted atomic displacements disappeared and the transition occurs via nucleation and growth. Apart from the evolution to local structure changes, during a few tens of iterations the parallel sets converged to a single mechanistic picture as described in the following.

The analysis of local events such as the nucleation of a new structure clearly is subjected to finite size effects of the simulation cell. As a consequence of the periodic boundary conditions, emerging phase nuclei are in close proximity (about 1 nm for our smallest model) to their periodic image. This coupling promotes collective transformations and spoils the mechanistic analysis if the simulation model chosen is too small. We therefore performed a systematic study of the finite size effect from a variety of setups of different size.

All of our simulation models were chosen sufficiently large to observe nucleation and growth events. In the smallest of our simulation models (counting $5\times5\times5$ unit cells) we typically identified that the transition occurs via a single nucleus. Therein the ionic displacements correspond to the mechanism suggested by Hyde and O'Keeffe, which is characterized by an antiparallel shuffling of adjacent (110) layers along the [001] direction.[11] While the overall transition mechanism was found to be the same for all of our simulation models, the pathways nevertheless exhibit a considerable variety. Indeed, the trajectories differ in terms of the position of the nucleation site and the orientation of the layers being shifted. Thus (110), (101), and (011) layer shuffling along [001], [010], and [100] occurs at the same likeliness.

The latter issue is of crucial importance for transition trajectories in which multiple nuclei are observed. For the B2→B1 transformation of our simulation systems of medium size ($6\times6\times6$ and $12\times12\times12$ supercells) we identified coexisting domains that originate from separate nucleation events (Figure 1). Therein the ion shuffling occurs at different orientations, for example as (110) and (−110) layers. Both phase domains follow the same mechanism and only differ in the way the transition route is implemented. In the course of phase growth the differently oriented domains get in contact and establish a well-defined interface. The latter reflects a mirror plane and causes a twinning of the final B1-type structure (Figure 1).

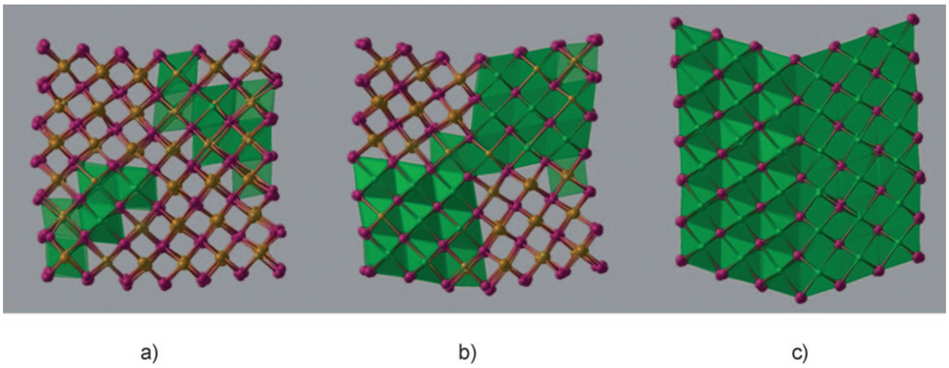

Figure 1. a, b) Formation of two nucleation centers and domains in the simulation box, viewed along the [001] direction of the B2 structure. The formation of B1 motifs (octahedral coordination) is highlighted in green. c) Stable contact of two B1 domains separated by a mirror plane as grain boundary.

To this point our observations are fully analogous to previous studies of KF and KBr in which similar simulation models were used.[3,4] However, for the largest RbCl model ($14 \times 14 \times 14$ supercell) we identified more complex transition trajectories leading to more sophisticated grain boundary structures. A typical B2→B1 trajectory is illustrated in Figure 2 and its final B1-type structure is shown in Figure 3. From these, one can clearly observe different types of grain boundary structures. The first type of domain interfaces corresponds to the mirror planes discussed previously. The second type, in the following termed as 'rough' interfaces, is attributed to a phenomenon that could not be assessed in the smaller models. While domain contacts with (110) and (−110) layer shuffling leads to planar (100) or (010) interfaces, the 'rough' grain boundaries can not be described by a single plane. The latter result from contacts of domains in which the sense of the layer shifting differs too strongly to allow a smooth interface. For example, this applies to domains formed by (110) and (101) layer shuffling. While a (110)/(−110) layer shifting combination implies a common [001] direction for ion dislocation, this is not the case for (110)/(101) shuffling.

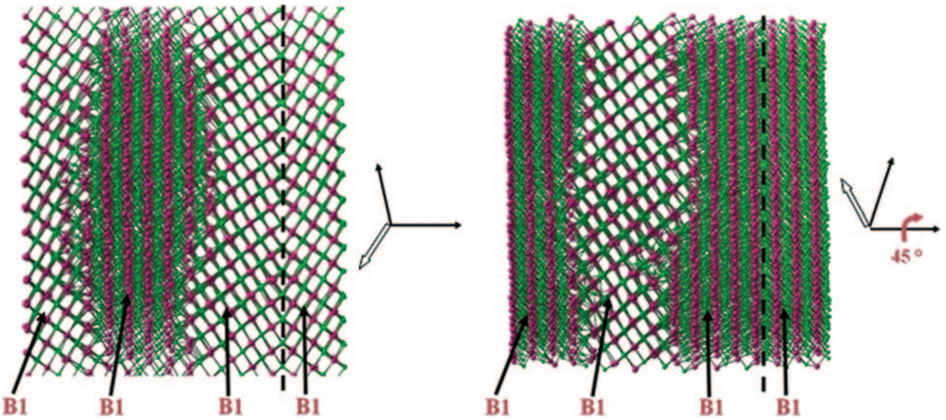

Figure 2. Grain boundary formation in the B1 structure illustrated from the final configuration of a representative trajectory obtained from our transition path sampling simulations. To elucidate the stability of the observed structures, all configurations were propagated for a further 250 ps. During this period no significant rearrangements occurred. From this we conclude the metastability of the grain boundaries found in the simulation model.

The different types of grain boundary structures resulting from the contact of two domains are denoted in Table 1. From a simple permutation of all possible shuffling combinations, one would expect rough domain interfaces to occur much more frequently than mirror planes. However this is not the case. Actually, mirror plane-type interfaces are more prevalent and for the medium-sized simulation cells the rough grain boundary structure could not be observed at all. From this observation we conclude a distance dependence of the shuffling sense applies to neighboring nucleation centers. A (110)/(101) layer shifting combination can only be realized for well-separated, that is, truly independent nuclei. Sharing a common dislocation direction, (110)/(−110) shuffling reflects far fewer mismatches of the ionic displacements and may hence also occur in nearby, partially correlated nucleation centers. From our simulations, the minimum distance of nucleation sites leading to mirror plane-type domain contacts was found to be about 1 nm, whereas the rough grain boundary type requires nuclei that are separated by 2 nm or more.

The two different types of domain interfaces can be rationalized on the basis of Bernal polyhedra. The characteristic nearest neighbor arrangement in the B1 structure is represented by octahedra. In polycrystalline B1 structures some of the octahedra must be deformed/replaced to accommodate interfaces between differently oriented B1 domains. The resulting Bernal polyhedra still correspond to sixfold nearest neighbour coordination, but of different style, as illustrated in Figure 3. From our simulations we could clearly relate specific Bernal polyhedra to each of the observed grain boundary structure types (Figure 3).

It is noteworthy that both types of grain boundary structures are preferentially constructed of $RbCl_6$ Bernal polyhedra, whereas the formation of $ClRb_6$ Bernal polyhedra is clearly disfavored. For the domain interfaces represented by mirror planes this phenomenon was recently explained by

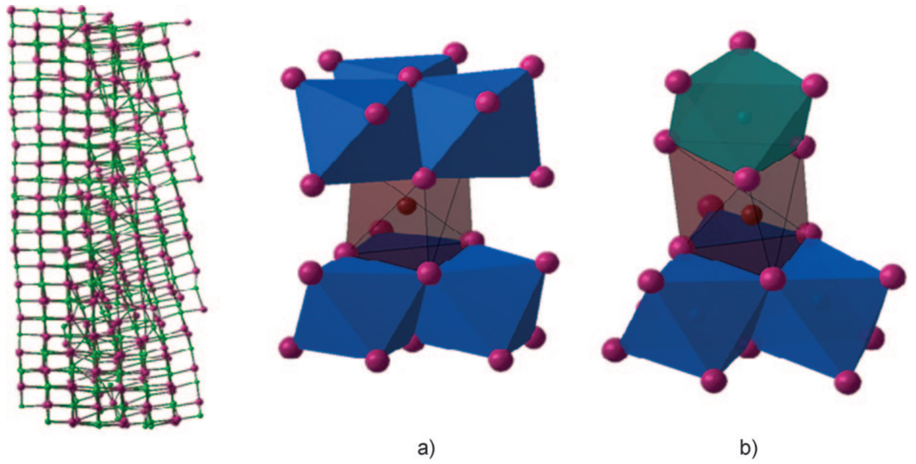

Figure 3. Close-up of the rough grain boundary and the two types of Bernal polyhedra (a, b) identified as dominant structural motifs at the domain–domain interface. While mirror planes are implemented by type a) polyhedra, both types are found in the rough grain boundaries.

Table 1. Comparison of the different possibilities of layer shuffling senses in two nuclei of the B2→ B2 transition and the resulting type of grain boundary structures.

Layer shuffling in nucleus 1	Layer shuffling in nucleus 2	Grain boundary structure formed
(110)	(110)	no interface
	(110)	(100) or (010) mirror planes
	(101)	'rough' domain interfaces
	(101)	
	(011)	
	(011)	

using the chemical concept of ionic hardness and softness.[3,4] Along this line, the softer ionic species was found to better accommodate the unfavorable nearest neighbor constellations at the interface of twin domains.[4] The present simulations fully support this concept. Indeed, for RbCl the ion selectivity is observed for both the mirror plane type and the 'rough' grain boundary structures. From the evidence collected so far, it appears reasonable to suggest a general rule for grain boundaries in multinary compounds: we expect the local reorganization of coordination polyhedra from bulk-like structure motifs (here: $RbCl_6$ octahedra) into less favored Bernal polyhedra to generally imply a preference of the softer atomic/ionic species at the domain–domain interfaces.

It is not surprising that the different coordination polyhedra (octahedra of the bulk B1 structure and the two Bernal polyhedra types found at the grain boundaries) undergo different transformations in the course of the B1→B2 transition. These differences have important implications on the nature of the B1→B2 transition. From our simulations we clearly identify the grain boundaries as preferred nucleation sites. This is best seen for our largest model (14×14×14 supercell). As illustrated in Figure 4, the rough domain interfaces are most preferred for initiating the transformation to the B2 structure, but also the mirror planes represent favorable nucleation sites. During nucleation at the grain boundaries the ionic displacements of the corresponding Bernal polyhedra cause the formation of equally oriented B2 structures in the differently oriented B1 domains (Figure 4b and c). The polycrystalline character hence diminishes in the course of the B1→B2 transition. Indeed, even our largest simulation cell (ca. 4 nm × 4 nm × 4 nm) is transferred to a single B2 domain.

Conclusions

Using RbCl as the example, we presented a molecular dynamics strategy for exploring reconstructive phase transitions at different length scales. Independent of the system

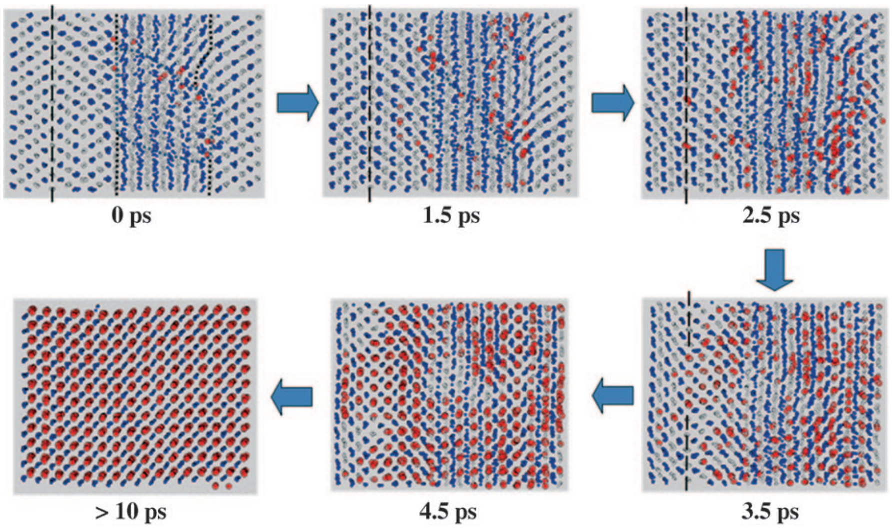

Figure 4. Representative trajectory highlighting the role of the grain boundaries as dedicated nucleation centers for the B1→ B2 transition. Color code: Cl^- ions: blue; Rb^+ at sixfold (B1): gray; and Rb^+ at eightfold (B2): red.

size, we identified a unique transformation mechanism that corresponds to the antiparallel shuffling of (110) layers suggested by Hyde and O'Keefe.[11] However, the central focus of our work is dedicated to the study of nucleation events. For the B2→B1 transformation of RbCl we observed B1 phase nuclei to emerge within a nanometer range. The respective orientation of the resulting domains depends on the distance between the nucleation centers. The interfaces of nearby (ca. 1 nm) B1 nuclei represent mirror planes and account for a polysynthetic twinning at the nanometer scale. Nucleation sites that are separated by about 2 nm or more may be considered as fully independent. Growth of the corresponding nuclei may lead to two types of domain interfaces. The mirror planes and a 'rough' grain boundary structure may be constructed on the basis of a specific Bernal polyhedron for each interface type. The latter play a crucial role during the reverse, that is, the B1→B2 transformation. This includes a clear preference as B2 nucleation centers. Along this line, both types of Bernal polyhedra promote the reorganization of differently oriented B1 grains into a single B2 domain, which results in a dramatic reduction of the polycrystalline nature of the material. Thus, we provided an extensive picture of a reconstructive phase transition, in which the global mechanism, nucleation events, formation of coexisting domains, polycrystallinity, and asymmetry between the forward and backward transformation are explored from an unbiased simulation setup.

Acknowledgements

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