Growth of NaBr in the 5-5 Structure Type on $LiNbO_3$: A Feasibility Study

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Dedicated to Professor Wolfgang Jeitschko on the occasion of his 70th birthday

The feasibility of growing alkali halides in the hypothetical 5-5 structure type on a specially prepared substrate of $LiNbO_3$ has been investigated. The highest degree of steering towards this structure is achieved by growing NaBr on a $LiNbO_3$ (001)-surface, where the outermost layer of oxygen atoms is followed by a layer of niobium atoms. The kinetic stability, against transition into the rock salt structure, of the 5-5 structure grown on the substrate is enhanced compared to the bulk 5-5 phase, but the 5-5 structure will nevertheless still be metastable compared to the rock salt structure type that constitutes the thermodynamically stable bulk phase of NaBr under standard conditions.

Key words: Halides, Lithium Niobate, Surface Energies, Wulff Construction, Metastable Phases

Introduction

In recent years, the importance of metastable compounds has been increasingly recognized [1 – 7], but these compounds are often difficult to obtain when the synthesis conditions also allow the growth of thermodynamically more stable competitors. This is especially true for modifications with low kinetic stability. For these, we cannot use high temperatures during the synthesis, since the kinetic stability of the target modification would not suffice to keep the compound from transforming to a more stable phase. Thus it is necessary to apply soft chemistry methods or other low-temperature syntheses [2, 6, 8, 9]. An instance of such a synthesis route is realized by the growth of crystalline compounds in an amorphous matrix of the same atomic composition, which had been deposited at very low temperatures (liquid nitrogen or liquid helium temperature) using atom beams [10, 11]. In many cases [10 – 12], the modification formed when employing this method has proved to be a low density phase that is actually metastable at the low temperatures of the experiment.

However, this procedure by itself is not necessarily sufficient, and alternative or supplementary approaches need to be considered. An important question is, whether one can influence the formation of the metastable phase by finding a way to favor the formation of nuclei of the desired phase. For instance, one can employ a substrate, the surface of which matches well with a preferred growth face of the nucleus of the phase of interest, while inhibiting the formation of nuclei belonging to the thermodynamically stable phase [13, 14]. Theoretical studies can assist in this task in two ways. For one, the preferred surfaces of the nuclei of the metastable and the stable phases involved can be determined. Secondly, the effect of the substrate on the various nuclei can be investigated.

In this work, we have studied the possibility of enhancing the formation of the nuclei belonging to the so-called 5-5 structure type of the alkali halides. This structure type, an ionic analogue to the hexagonal boron nitride structure, was first predicted a decade ago during global investigations of the energy landscapes of the alkali halides [15], and was later found to be the aristotype of the ternary compound Li_4SeO_5 [16]. It is present as a hypothetical metastable modification in all alkali halides [17] and alkaline earth oxides [18], and *ab initio* calculations have shown that it is usually the third most stable modification in these systems after the rock salt (or the CsCl) and the nickel arsenide (or the wurtzite/sphalerite) structure types. However, the energy barriers surrounding this modification are relatively low [5, 18, 19], and thus already at or below room temperature the 5-5 phase would probably transform into the thermodynamically stable one, exhibiting the rock salt or CsCl structure type.

Thus, the synthesis of the 5-5 modification in the alkali halides requires both low temperatures and some

way to enhance the formation and growth of its nuclei. Here, we focus on the synthesis *via* deposition of atomically disperse monolayers from the gas phase on a suitable substrate. The results of the investigations suggest that the combination of $LiNbO_3$ as substrate and NaBr as the alkali halide appears to possess the best chance for synthesizing an alkali halide in the 5-5 modification.

Methods

Starting points of our investigations were earlier results of global energy landscape explorations of the alkali halides [15] that had been followed by local optimizations on the *ab initio* level of the structure candidates found [17]. Our general approach to the determination of these structure candidates has been given in detail elsewhere [5]. Here we just summarize the procedure: Quite generally, the structure candidates which should be capable of existence, at least at low temperatures, correspond to local minima of the enthalpy hypersurface ($H = E_{\mathrm{pot}} + pV$) of the chemical system under investigation. Finding these candidates required the use of a global optimization method, where we permitted free variation of atom positions, cell parameters, ionic charges and composition, during the global exploration of the empirical potential energy landscape. Next, we performed a local optimization on *ab initio* level of the cell parameters and atom positions, employing the quantum mechanical program CRYSTAL2003 [20].

Study of alkali halide nuclei

The first goal of this study is to identify growth planes of the nuclei of the 5-5 structure type (Fig. 1) and the competing rock salt structure type for the alkali halides. This task consists of two parts: Evaluation of the surface energies of the most important crystallographic planes, and the Wulff construction [21] of the shape of the nucleus.

In order to compute the surface energies of a given crystallographic plane, one needs to cut slabs out of the bulk crystal, the surfaces of which are parallel to the plane under consideration. This can be achieved by employing the SLAB-option of the *ab initio* solid state program CRYSTAL2003 [20]. If one provides the crystallographic plane (*hkl*) along which the cut is supposed to take place, and the desired number (n) of atom layers parallel to this plane, CRYSTAL then generates an appropriate slab from the original bulk solid, and

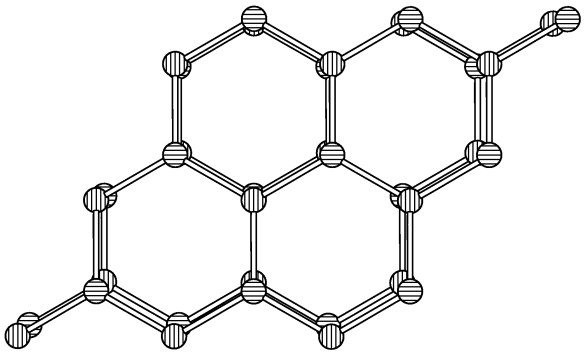

Fig. 1. Predicted 5-5 structure type for NaBr (Na = hatched vertically, Br = hatched horizontally) viewed along the [001] direction.

calculates the energy ($E^{\mathrm{hkl}}(n)$) of this slab. An estimate of the surface energy of the cut-plane based on a n-layer slab is then given by the formula

$$E^{\mathrm{hkl}}_{\mathrm{surf}} = [E^{\mathrm{hkl}}(n) - ((E_{\mathrm{bulk}}/N_{\mathrm{bulk}}) \cdot N^{\mathrm{hkl}}_{\mathrm{slab}}(n))]/(2 \cdot A^{\mathrm{hkl}}(n)) \quad (1)$$

where N_{bulk} and $N^{\mathrm{hkl}}_{\mathrm{slab}}(n)$ are the numbers of atoms of the primitive unit cell of the bulk and the n-layer slab, respectively. $A^{\mathrm{hkl}}(n)$ is the surface area of the n-layer slab, and we have to divide by 2 because each slab has two surfaces.

Computing this quantity for several values of n and plotting the $E^{\mathrm{hkl}}_{\mathrm{surf}}(n)$-curves allows us to estimate the surface energy for an infinitely thick slab by extrapolating these curves to the limit $n \to \infty$.

In the second step, the actual shape of the nuclei is computed based on these surface energies. For this, we employ the standard Wulff-construction [21], which is implemented in the program WULFFMAN [22].

Study of alkali halide layer deposited on substrate surface

The results of the Wulff-construction (see section Results below) showed that the (001) plane was the preferred growth plane for the 5-5 structure type in the akali halides. Since this plane consists of periodically repeated hexagons with alternating cations and anions, $LiNbO_3$ was chosen as a promising substrate material. For this compound, cuts perpendicular to the [001] direction exhibit a trigonal arrangement of oxygen atoms from which a periodically repeated set of oxygen hexagons can be selected, and furthermore periodically repeated hexagons can be made up of alternating Li- and Nb-ions. Both sets of hexagons might be

useful for inducing the formation of the cation-anion hexagons describing the (001)-plane in the 5-5 structure. On the other hand, trying to achieve an optimal placement of the preferred rock salt plane (001) onto the (001) plane of $LiNbO_3$ requires covering several unit cells of $LiNbO_3$ along the surface, and even then only a strongly distorted square lattice of anions and cations of the alkali halide results.

Evaluating the effect the substrate has on the formation of either a 5-5 structure or a rock salt structure, involves several steps: Construction of the surface of the chosen substrate as a slab, placement of the two alkali halide layers on top of this surface, and optimization of these placements.

Construction of $LiNbO_3$ layers

As a preliminary step, the structure of the $LiNbO_3$ bulk crystal needs to be optimized on *ab initio* level, in order to guarantee that both the surface of the substrate and the surface layer of the 5-5 structure correspond to relaxed states at the same level of quantum mechanical accuracy. This was achieved using the scriptprogram HARTREE [23, 24], which performs local optimizations of the structure of a crystalline compound using the *ab initio* program CRYSTAL2003 for the energy calculations.

The computation of the surface energy of a $LiNbO_3$ crystal cut along the desired (001) plane proceeds in the same fashion as described above for the alkali halides. However, since the unit cell of $LiNbO_3$ is considerably larger than the one of the alkali halide modifications, only part of it can be used in the computationally very expensive calculation of the final slab consisting of the $LiNbO_3$-plus-halide slab. Thus, we have employed the structure analysis and construction program KPLOT [25], in order to generate the desired surface slabs. Two different surfaces were considered, where in both cases the top layer facing the alkali halide layer was a layer of oxygen atoms: In one case (type A), the oxygen layer was followed by a layer containing lithium atoms and afterwards a layer with niobium atoms, while in the second case (type B), the order of lithium- and niobium-containing layers was reversed. These two cases correspond to two different cuts through the bulk $LiNbO_3$ crystal. We note that these distinct Li and Nb layers can be considered to be the result of systematic upward/downward vertical displacements of the Nb/Li or Li/Nb atoms within a single layer containing both Li and Nb atoms, which is located between two densely packed oxygen layers.

Optimization of a single alkali halide layer placed at different positions on the slab

The second step consisted of placing one alkali halide layer corresponding to the most stable face of the nuclei of the 5-5 modification onto the two different $LiNbO_3$ slabs. Again the program KPLOT [25] was used to perform this task. Three different arrangements of the (001) layer of the 5-5 structure with respect to the two surfaces of the substrate were investigated, resulting in six different substrate-plus-alkali halide slabs to be investigated for each alkali halide modification: 1) both cations and anions on top of the hexagonal arrangement formed by the oxygen atoms, 2) cations on top of the Li-positions and anions on top of the Nb-positions, and 3) cations on top of the Nb-positions and anions on top of the Li-positions.

In a third step, similar arrangements were tested for a rectangularly distorted (001) plane of the rock salt modification placed onto the one of the two substrate surfaces which resulted in the most stable 5-5 layer. However, in this case, we first transformed the hexagonal unit cell of $LiNbO_3$ to an orthorhombic one, in order to be able to place the alkali halide ions in a distorted but nevertheless periodic fashion onto the substrate. One should recall that the slab is still of infinite extent in the directions parallel to the surface, and thus two-dimensional periodicity is required, in order to allow the computation of the energies involved.

In all cases, the distance between the substrate and the alkali halide layer was optimized such that the total energy of the substrate-plus-halide slab was a minimum.

Basis sets

The choice of a basis set is a crucial step of the calculations, since we have to balance two conflicting issues: accuracy and computational cost, while taking into account the minimum basis set requirements. When computing the bulk alkali halides and $LiNbO_3$ we have employed both basis sets drawn from the literature and basis sets which we had optimized previously (see Table 1).

Results

Nuclei of alkali halides

For all twenty alkali halides *MX* (*M* = Li, Na, K, Rb, Cs; *X* = F, Cl, Br, I), we have calculated the ener-

Table 1. Basis sets employed. *MX* refers to the halogenides (M = Li,Na,K,Rb,Cs; X = F,Cl,Br,I). Basis sets are optimized versions [17, 24] of sets available in the literature [33, 34].

Chemical system	Atom	Basis set name	Basis set source
$LiNbO_3$	Nb	986-31(631d)G	[33]
$LiNbO_3$	O	8-411G	[33]
$LiNbO_3$, Li*X*	Li	6-1G	[33]
Cs*X*	Cs	ECP46MWB	[34]
*M*F	F	7-311G	[33]
*M*Br	Br	[HAYWSC]-31G	[33]
*M*I	I	[HAYWLC]-31	[33]
Optimized valence shells			
Na*X*	Na	86-311G*	[33]
K*X*	K	86-511G*	[33]
Rb*X*	Rb	[HAYWSC]-31G	[33]
*M*Cl	Cl	86-311G	[33]

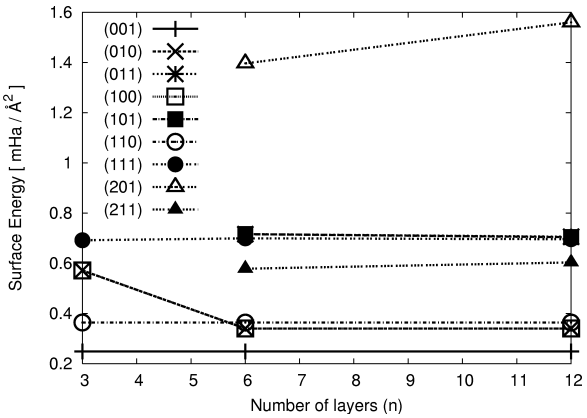

Fig. 2. Surface energy $E_{\mathrm{surf}}^{\mathrm{hkl}}(n)$ of NaBr slabs in the 5-5 modification as a function of the number of layers (n) obtained with Hartree-Fock calculations.

gies of slabs consisting of $n = 3 - 12$ layers cut out of the 5-5 modification for the following crystallographic planes: (001), (100), (010), (110), (101), (011), (111), (210), (201). For each of the halides, the bulk crystalline 5-5 structure had been optimized earlier on *ab initio* level using the program CRYSTAL2003 for the energy calculation [17]. For these optimizations and the slab calculations presented here, both the Hartree-Fock and the DFT (functional B3LYP) approximation were employed.

Fig. 2 shows the values of the energy of the slabs as a function of the number of layers n, for the various crystallographic directions, obtained for the example of NaBr. The trends found in these data are representative for all the alkali halides. In particular, the (001) plane always exhibited the lowest energy, followed by the (100) and (010) planes the energies of which were identical due to the symmetry of the structure. We note

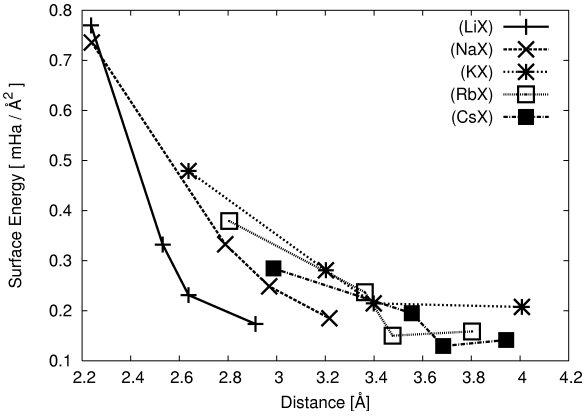

Fig. 3. Surface energies (on Hartree-Fock level) of the (001) surfaces of *MX* (M = Li, Na, K, Rb, Cs; X = F, Cl, Br, I), in the 5-5 modification, as a function of cation-anion distance, keeping the cation fixed.

that for the most important planes, the energy of the slabs had already converged for $n = 12$. In the figure, the energy values for the ($n = 3$) layer slabs of the (101), (201) and (211) planes are missing. In these cases, no neutral unit cell for a three-layer slab could be obtained, and thus the *ab initio* calculations did not converge. However, the results for $n = 6$ and $n = 12$ clearly show that these planes would be unfavorable.

Using these values, we computed the surface energies of the corresponding surfaces of the crystal. Fig. 3 shows these surface energies as a function of the cation-anion distances keeping the cation fixed in each case. We find that there is a degree of correlation with increasing cation-anion distance, in that the surface energy monotonically decreases with the cation-anion distance. This trend can be clearly seen for the families Li*X* and Na*X* (X = F, Cl, Br, I), while for K*X*, Rb*X* and Cs*X*, the decrease from F to Br is followed by a slight increase for the largest cation I. This trend is to be expected, since it is generally known that the lattice energies of the alkali halides are larger when the ions are small, due to stronger bonding of these ions [26].

Using the surface energies of the various crystallographic planes as input, we employed the program WULFFMAN [22] to generate the equilibrium shape of the crystal nuclei in the 5-5 modification for the alkali halides by performing a Wulff construction. In all cases, we found a dodecagonal prism, shown in Fig. 4 for NaBr. Clearly, the most distinctive of the surfaces of these prisms is the energetically preferred (001) plane. It is therefore to be expected that a layer corresponding to this surface consisting of hexagons of

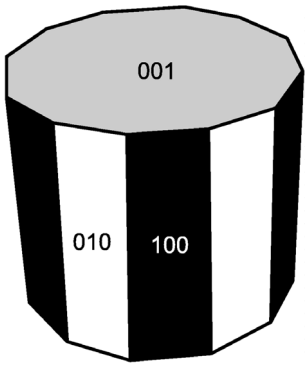

Fig. 4. Shape of a nucleus of the 5-5 modification of NaBr based on the Wulff construction.

alternating cations and anions would be the most likely candidate to grow on top of a substrate if a 5-5 modification is to be synthesized.

An analogous analysis was performed for the crystallographic planes of the rock salt modification of the alkali halides (or the CsCl modification for those halides where it constitutes the thermodynamically stable bulk phase). In each case, the (001) plane ((011) for CsCl) exhibited the lowest surface energy, and the crystal nuclei formed cubes according to the Wulff construction.

Substrate plus NaBr layer

A substrate that would enhance the growth of the 5-5 modification needs to possess a structure, where surfaces can be cut such that the top layer exhibits hexagons that match those of the cation-anion-hexagons of the (001) surface of the 5-5 modification. Of course, the size of the hexagons on the surface of the substrate need to match those of the alkali halide. But since twenty different alkali halides are available to choose from, this issue is not expected to be critical. One possible candidate for a substrate is $LiNbO_3$. This material is commercially available, and when cut perpendicular to the [001] direction, there exist two periodic hexagon arrangements that might serve as patterns for the growth of the 5-5 modification.

One pattern would be a subset of the hexagonal close packing of one layer of oxygen atoms, while the second pattern is given by the projection of two successive Li- and Nb-layers, which together form a periodic hexagon pattern with the same topology as the (001) layer of the 5-5 structure. Since a smooth surface onto which the alkali and halogen atoms can be deposited is only available if the top atom layer is made up of the

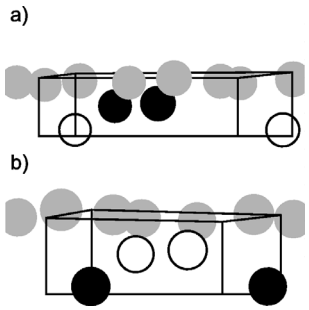

Fig. 5. Schematic representation of two possibilities, a) type A and b) type B, to cut a (001) three layer $LiNbO_3$ slab from the bulk (viewed parallel to the (001) surface). In type A and type B the second layer consists of Li and Nb atoms, respectively (grey = O, white = Nb, black = Li).

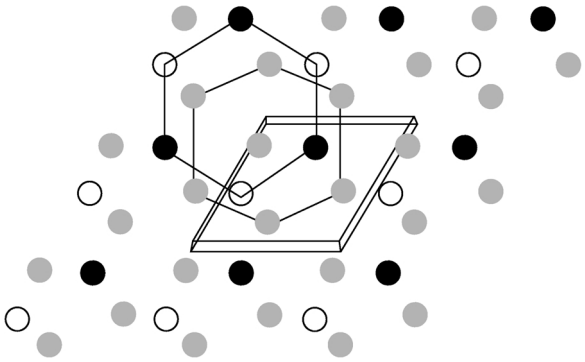

Fig. 6. Slightly tilted view of the first three layers of a $LiNbO_3$ slab (along [001]-direction), showing the hexagons that might be used to generate the 5-5 structure. Along this direction, no difference is visible between type A and type B surfaces. The shape of the (2d-periodic) unit cell of the $LiNbO_3$ slab is also shown (grey = O, white = Nb, black = Li).

closely packed oxygen atoms, there are only two different cuts possible: in one case (type A), the second atom layer consists of Li atoms and the third layer of Br atoms, and the reverse order in the second case (type B). Both of these cuts are shown in Fig. 5 (type A: view from the side of slab Nb-Li-O; type B: view from the side of slab Li-Nb-O). Fig. 6 shows for both cuts the atom arrangement of the top three atom layers of the $LiNbO_3$ substrate as viewed along the [001] direction. The hexagons formed by the cations and the hexagonal packing of the oxide anions are clearly visible.

In order to be able to select the alkali halide which fits best onto the substrate surface atoms, we have optimized the structure of bulk $LiNbO_3$ on the *ab initio* level. We find $a = 5.174$ Å, $c = 13.947$ Å, which

Table 2. Calculated atom-atom distances in the hexagons of the optimized 5-5 structures in the halides (a), and in the optimized (001) $LiNbO_3$ slab (b), respectively.

(a)				
	F	Cl	Br	I
Li	3.2824	4.3847	4.4774	5.0445
Na	3.8789	4.8294	5.1423	5.5705
K	4.5680	5.5467	5.8874	6.9413
Rb	4.8580	5.8240	6.0210	6.5865
Cs	5.0692	6.0337	6.2072	6.8290
(b)				
Li - Li (hex)	5.174	Nb - Nb (hex)	5.174	O - O (hex) 5.174

Table 3. Calculated interaction energies of a NaBr 5-5 monolayer on a three layer $LiNbO_3$ slab (type A and type B), for different configurations, at the equilibrium distance.

Combination	Energy [Ha]	Energy [kJ/mole]	Distance [Å]
$LiNbO_3$ (type A)			
Na and Br on O	−0.097446489	−255.8	1.9
Na on Li, Br on Nb	−0.000557578	−1.5	1.8
Na on Nb, Br on Li	−0.007948252	−20.9	2.6
$LiNbO_3$ (type B)			
Na and Br on O	0.002027098	5.3	3.6
Na on Li, Br on Nb	−0.003612486	−9.5	3.2
Na on Nb, Br on Li	0,000708942	1.9	4.8

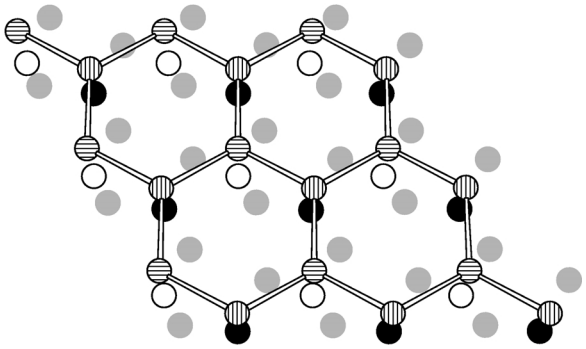

Fig. 7. Monolayer of NaBr in the 5-5 structure type, placed on top of the $LiNbO_3$ (001) surface. The Na atoms interact with Li atoms and the Br atoms interact with Nb atoms. In this slightly tilted view along the [001] direction, no difference is visible between type A and type B surfaces (grey = O, white = Nb, black = Li, hatched vertically = Na, hatched horizontally = Br).

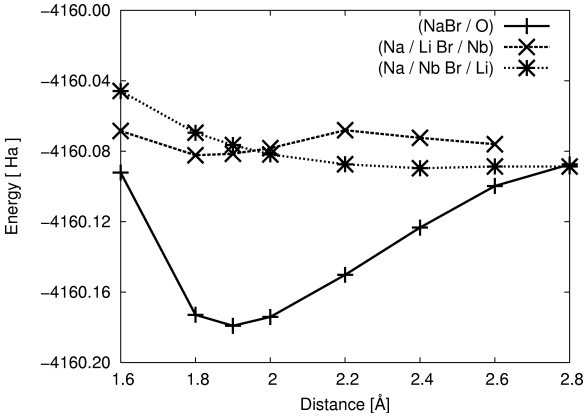

Fig. 8. Calculated energies using the Hartree-Fock approximation as a function of the distance between a NaBr monolayer (5-5 modification) and a $LiNbO_3$ slab (type A) for three different placements (Na and Br on O, Na on Li and Br on Nb, and Na on Nb and Br on Li).

compares well with the experimental data, *e.g.* $a_{\mathrm{exp}} = 5.138$ Å, $c_{\mathrm{exp}} = 13.848$ Å [27] or $a_{\mathrm{exp}} = 5.147$ Å, $c_{\mathrm{exp}} = 13.856$ Å [28]. From this, we find that the atom-atom distances within the hexagons are given by $d^{\mathrm{hex}}_{\mathrm{Nb-Nb}} = d^{\mathrm{hex}}_{\mathrm{Li-Li}} = d^{\mathrm{hex}}_{\mathrm{O-O}} = 5.174$ Å (*c.f.* Table 2).

Comparing these values with those found for the atom-atom distances in the hexagons of the optimized 5-5 structures of the alkali halides (*c.f.* Table 2), we find that the best fit exists for sodium bromide, $d^{5-5}_{\mathrm{Br-Br}} = d^{5-5}_{\mathrm{Na-Na}} = 5.1423$ Å *vs.* $d^{\mathrm{hex}}_{\mathrm{Nb-Nb}} = d^{\mathrm{hex}}_{\mathrm{Li-Li}} = 5.174$ Å. Thus, for the remainder of this investigations, we focus exclusively on the deposition of NaBr onto $LiNbO_3$.

As mentioned earlier, there exist for each of the two substrate surfaces three different ways to place the layer of NaBr-hexagons onto the substrate, resulting in six different combinations that need to be investigated: 1) on top of the oxygen atoms, 2) on top of the Li-Nb-hexagons, with Na over Li and Br over Nb (*c.f.* Fig. 7), and 3) on top of the Li-Nb-hexagons, with Na over Nb and Br over Li. As free optimization parameter, we have the distance between the layers of substrate atoms and the layer of alkali halide atoms in the [001] direction. We expect that there will be an optimal distance which minimizes the energy of the slab consisting of the top layers of the substrate and the single layer of the 5-5 modification.

Fig. 8 shows the energy as a function of the distance for the three different ways of placing a layer of NaBr-hexagons on the $LiNbO_3$ slab type A. We find that in the first and the second case there is a minimum in energy at a surprisingly short distance of 1.9 and 1.8 Å respectively, while in the third case, we find the equilibrium distance at 2 6 Å. Table 3 gives the total gain in energy compared to the sum of the energies of a free alkali halide 5-5 layer and of an empty substrate surface.

We note that for all those instances where the second layer of the substrate consists of Li atoms, there is a gain in energy. However, this surface does not appear

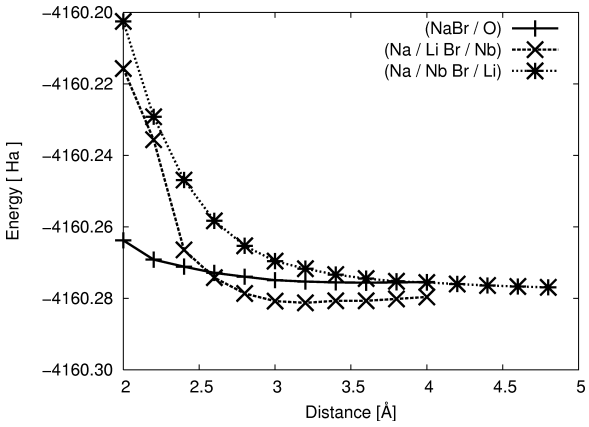

Fig. 9. Calculated energies using the Hartree-Fock approximation as a function of the distance between a NaBr monolayer (5-5 modification) and a $LiNbO_3$ slab (type B) for three different placements (Na and Br on O, Na on Li and Br on Nb, and Na on Nb and Br on Li).

to induce a clean 5-5 structure-like atom arrangement, since the most favorable arrangement corresponds to placing both Na and Br on top of the oxygen atoms. Since all oxygen sites are essentially equivalent, long range correlations induced by the substrate among the deposited atoms will be rather weak. Clearly, this lack of selectivity towards an alternating Na-Br arrangement would be a serious problem during the essentially random deposition of atoms from the gas phase.

In contrast, for the substrate surface type B where the second layer consists of Nb-atoms, the arrangement where the anion Br is located on top of the Nb-atom, and the cation Na resides over the Li-atom, is a clear winner (*c.f.* Fig. 9 and Table 3). Furthermore, in this second class of atom arrangements, the distance between the alkali halide atoms and the oxygen layer is much closer to the values one would expect for an ionic alkali halide layer, *i.e.* the atom-atom distances approximately equal the sum of the ionic radii. In contrast, in the first class, the optimal distances are much shorter and correspond much more to a covalent and/or van-der-Waals bond between the halogen atoms and the surface atoms of the substrate.

These observations are also supported by a simple Mulliken population analysis [29] in the two cases. For surface type B, the charges of Br and O are considerably more negative, and those of Nb more positive, than the ones of the same atoms for surface type A. The existence of such an ionic charge distribution within the alkali halide layer is of great importance, since this first NaBr-layer can serve as a substrate in its own right for the next layer of Na and Br atoms in the 5-5 modification.

We therefore conclude that the greatest enhancement in the formation of the 5-5 structure is to be expected for the second type of $LiNbO_3$ surface (type B) where the second atom layer contains Nb ions.

The second task the substrate should fulfill is to impede the growth of the thermodynamically stable rock salt type layer.[1] Inspecting Fig. 6 which depicts the substrate surface, one notes that it is not possible to place a periodic square lattice of NaBr-atoms corresponding to the energetically preferred (001) layer on top of either the oxygen atoms or the Li/Nb atoms. During an actual deposition, essentially one of two things can now happen: If the interaction within the layer is much stronger than between layer and substrate, one can to first order completely disregard the atomic structure of the substrate and have an essentially free layer of rock salt-like NaBr lie on top of the substrate, with only some van-der-Waals interactions between layer and substrate. Else, if the interaction between substrate and the alkali halide atoms dominates, the NaBr-layer will be distorted in such a way that some kind of match between layer and substrate occurs while keeping the periodicity of the substrate plus layer slab intact. We have treated both cases in our analysis. Here we only consider the deposition of the distorted rock salt layer onto the $LiNbO_3$ slab type B, because the type A surface is not expected to stabilize the 5-5 structure, and thus should be discarded.

Fig. 10 shows how a rectangularly distorted NaBr-layer could be placed on top of the $LiNbO_3$ surface.[2] Table 4 gives the energies of two possible arrangements, plus the energy associated with a free layer with no substantial interactions with the substrate: In case one, the Na- and Br- atoms are again both placed onto the atoms of the terminating oxygen layer, and in case two the Br atoms are placed onto the Nb atoms of $LiNbO_3$ and the Na atoms over a gap in order to complete the rectangular pattern. It is expected that the second arrangement would be the preferred one, because this arrangement has shown the lowest interaction energy for the 5-5 layer on the type B surface.

[1] Ideally, the deposition of a rock salt layer on the substrate would actually be less energetically favorable than the deposition of a layer of the 5-5 modification. However, this is unlikely to be the case.

[2] Clearly, there are strong elastic forces present within this layer, which will lead in practice to a cracking of the layer or a further distortion, possibly to the 5-5 modification.

Table 4. Calculated energies of a rectangularly distorted NaBr-layer, placed on a $LiNbO_3$ slab (type B) for two configurations; energy differences $\Delta E_{\text{distort}}$ between a free monolayer of NaBr and the distorted one.

System	Energy [Ha]	Energy [kJ/mole]
Na and Br on O	0.004504296	11.8
Br on Nb, Na at intersections	−0.002304689	−6.1
$\Delta E_{\text{distort}}$	−0.6251960	−1641.4

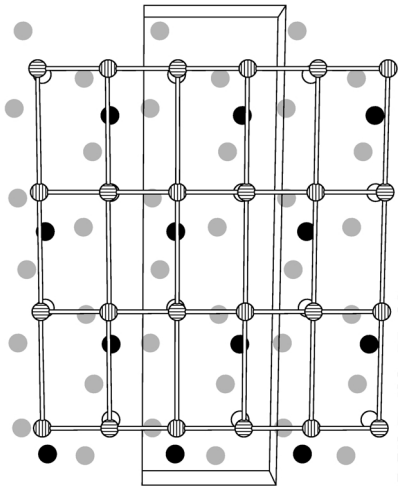

Fig. 10. Rectangulary distorted NaBr rock salt layer placed on top of the (001) $LiNbO_3$ surface, viewed along the [001] direction. The Br atoms are placed onto the Nb atoms of $LiNbO_3$, while the Li atoms are located at the intersections of the rectangular grid. Note how easily this NaBr-arrangement could be distorted to the hexagonal arrangement belonging to the 5-5 modification (grey = O, white = Nb, black = Li, hatched vertically = Na, hatched horizontally = Br).

We find that none of the distorted arrangements is energetically favorable compared to either the formation of a 5-5 type layer *via* a shift of the Na-atoms (the energy gained from this relaxation of the NaBr layer is 3.4 kJ/mole) or the second option, the "freely floating" rock salt layer. Regarding the latter case, the calculated energies for the distorted and undistorted rock salt layer show, that the loss in energy due to the distortion of the ideal rock salt structure to the rectangular pattern is about 1641.4 kJ/mole. Thus, the intralayer interactions override the layer-substrate interactions as far as the growth of the rock salt modification on $LiNbO_3$ is concerned.

As an alternative to the distorted arrangement of the (001) rock salt type layer, one might consider the growth of a (111) rock salt type layer on the substrate. However, we note that the Br-Br distance in this densely packed layer equals $d_{\text{Br-Br(rock salt)}} \approx 4.24$ Å. Thus, extreme mismatches are obtained, no matter whether one were to attempt to place the (111) layer consisting of Br-ions on top of a) the oxygen atoms ($d_{\text{O-O}} \approx 3.0$ Å), b) both Li and Nb atoms ($d_{\text{Li-Nb}} \approx 3.0$ Å), or c) only the Nb ions ($d_{\text{Nb-Nb}} = 5.174$ Å).

In the first two arrangements, a compression by *ca.* 25% compared to the relaxed (111) NaBr (rock salt) plane is to be faced. Judging by the very high distortion energies found for the rectangularly distorted (001) layer, such arrangements would be very unfavorable energetically. Furthermore, we note that the third arrangement would lead to such a large spacing among the Br-ions that it would clearly be favorable to fill the holes with Na-ions, leading to either the distorted (001) rock salt type NaBr layer discussed above or to a 5-5 type NaBr layer. Adding to this the fact that the (111) surface is energetically less favorable than the (001) surface to begin with[3], we have therefore decided not to perform *ab initio* calculations for the (111) arrangements.

Thus, we conclude that any growth process, where strong layer-substrate bonds of NaBr on the type B surface of $LiNbO_3$ are formed, should lead to a 5-5 modification and not to a distorted rock salt modification.

Discussion

The results of this study show that a careful choice of substrate (here: $LiNbO_3$), substrate surface (here: a cut along the (001) plane such that the first three atom layers contain only oxygen, niobium, and lithium atoms, respectively), and alkali halide (here: NaBr), will increase the likelihood that the 5-5 modification can be synthesized *via* deposition of NaBr on the substrate $LiNbO_3$ at low temperatures. The validity of this statement depends on the validity of the calculations and models that lie behind our considerations.

While both the DFT and the Hartree-Fock method only yield approximations to the true energies of the bulk compounds and slabs we have investigated, both the systematic and the statistical errors in the computed energies and the optimized cell parameters are relatively small. In particular, the sequence of surface energies is not expected to change due to systematic deficiencies, since these would apply in equal measure to all computed quantities. Together with the fact that both HF and DFT yield comparable results, we can conclude that the computed shapes of the nuclei of

[3] Straightforward electrostatic arguments [30] show that the (111) surface in the rock salt structure type is actually unstable for a bulk crystal.

the 5-5 modifications are reliable. One remaining question is whether the nuclei of a given phase, containing only relatively few atoms, might exhibit a shape different from that of the infinite crystal for which the surface energies are calculated. However, Fig. 2 shows that the sequence of surface energies is already established for quite thin slabs, and thus the dominant surface energies that control the shape of the nucleus are the same for small nuclei and infinitely large crystals.

Similarly, the numerical error in the atom-atom distances of NaBr (in the rock salt structure) and $LiNbO_3$ when compared to experiment ($a^{\mathrm{th}}_{\mathrm{NaBr(rock\ salt)}} = 6.0564$, $a^{\mathrm{exp}}_{\mathrm{NaBr(rock\ salt)}} = 5.9738$ [31]; $a^{\mathrm{th}}_{\mathrm{LiNbO3}} = 5.174$, $a^{\mathrm{exp}}_{\mathrm{LiNbO3}} = 5.138$ [27] or $a_{\mathrm{exp}} = 5.147$ Å [28], $c^{\mathrm{th}}_{\mathrm{LiNbO3}} = 13.947$, $c^{\mathrm{exp}}_{\mathrm{LiNbO3}} = 13.848$ [27] or, $c_{\mathrm{exp}} = 13.856$ Å [28]) is quite small. The difference between theoretical and experimental values should be similarly small for the hypothetical 5-5 modification of NaBr, and thus NaBr is the most likely candidate for a substrate-controlled synthesis, based on matching the hexagons on the substrate (001) surface and the 5-5 modification (001) surface.

The most problematic aspect of the calculations we have presented is the question of surface reconstruction. In the case of the two alkali halide modifications, all surfaces considered are relatively simple, and thus no major rearrangements within individual atom layers near the surface are to be expected. Only some, usually small, changes in the distances between neighboring layers as a whole might occur, which are not expected to result in a change of the order of surface energies of the various crystallographic planes. In particular, the surfaces with the lowest energies in the 5-5 modification, (001) and (100)/(010), are electrostatically balanced and thus less susceptible to large surface reconstructions.

This argument does not apply to the (111) planes in the rock salt structure, where some reconstruction is to be expected, and the reconstructed surface may compete energetically with the preferred (100)/(010)/(001) surfaces. But here the fact that our theoretical results regarding the shape of rock salt crystals agree with experimental observations shows that surface reconstruction of the (111)-plane is not a major factor that needs to be analyzed in greater detail, for the purpose of this study.

The situation is not quite as clear-cut in the case of $LiNbO_3$. As we had mentioned earlier, such a reconstruction is expected to be very extensive, if the outermost layer does not consist of a close packing of oxygen atoms that provide some shielding of the substrate crystal. Taken together with the concern that surface cations would easily interact with *e.g.* H_2O-molecules that might adsorb on the substrate, this has led us to only consider the two surfaces where the outermost layer is an oxygen layer.

Similarly, substantial gains in energy are to be expected by shifting the two cation layers closer to the surface, or conversely moving the oxygen layer further inward. However, the relative positions of the atoms in $LiNbO_3$ when projected onto the (x,y)-plane should not change by much, and thus the topology of the surface including the hexagons should be preserved. When estimating how strong the effect of this shift might be, we recall that our goal is to determine whether one of these two remaining possible substrate surfaces will further the growth and enhance the stability of the 5-5 modification on the substrate while impeding the growth of the competing rock salt modification. But this qualitative effect will not depend on to what extent the Li and Nb layers are moved closer to the final oxygen layer, and thus closer to the surface itself. It might actually well happen that moving the Nb layer closer to the surface would even increase the stabilization of the spatial arrangement of the Br anions on top of the Nb cations. This would thus enhance the selectivity of the surface favoring the 5-5 modification compared to the two competitors, the distorted rock salt arrangement and the essentially random placement of Na and Br on the substrate surface during the deposition phase.

Such a growth might not only take place directly during deposition from the gas phase, but should also occur when a thin amorphous NaBr-matrix resulting from an essentially random deposition of Na and Br, begins to crystallize upon slow heating. However, we note that it is still thermodynamically preferable to "separate" the NaBr-layer from the substrate surface and rearrange the atoms into a (001) layer of the rock salt-like structure. Nevertheless, the use of a substrate should increase the energy barrier against such a transformation. Clearly, one danger must be avoided at all cost: the formation of clusters of the rock salt modification in the gas phase, before deposition on the substrate takes place. These would just lie on top of the substrate at about one van der Waals distance, and serve as crystallization nuclei for the amorphous matrix, and would override any effect of the substrate as far as inducing

the growth and the stabilization of the 5-5 modification is concerned.

In practice, the deposition of Na and Br atoms on the substrate competes with the accretion of water vapor and other gases that exist in the imperfect vacuum of the experiment, of course. As a consequence, *e.g.* hydroxyl groups might 'poison' the substrate surface by occupying the Nb sites to be reserved for the Br atoms. While this danger appears to be real and unavoidable, we do not believe that the choice of *e.g.* a different substrate would alleviate this problem. Furthermore, it should be possible to employ a $Br:H_2O$ ratio of at least $10^4 : 1$ during the deposition [32], and thus it is to be expected that sufficiently large regions will exist on the substrate for an undisturbed deposition of Na and Br atoms to allow the synthesis of the 5-5 modification of NaBr.

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