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Experimental Substantiation of the "Energy Landscape Concept" for Solids: Synthesis of a New Modification of LiBr

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Our approach towards synthesis planning in solid-state chemistry is based on the so-called energy landscape concept.[1] Here, each chemical compound capable of existing for a given period of time in a given (equilibrium) geometry is associated with a locally ergodic minimum region on the energy landscape over the configuration space.[2] As a special feature of this approach, full reference is given to metastable configurations. Thus, for the alkali-metal halides, which at ambient conditions preferably adopt the rock salt or CsCl structure type, many further polymorphs exhibiting various different structures have been predicted to be kinetically stable. One of the most conspicuous structures among those predicted is the 5–5 structure type, in which cations and anions coordinate each other trigonal-bipyramidally, forming commutative partial structures.[2–4] In particular for the lithium compounds of the heavy halogens bromine and iodine, the wurtzite or sphalerite modifications are predicted to be rather low in energy (Figure 1).[4]

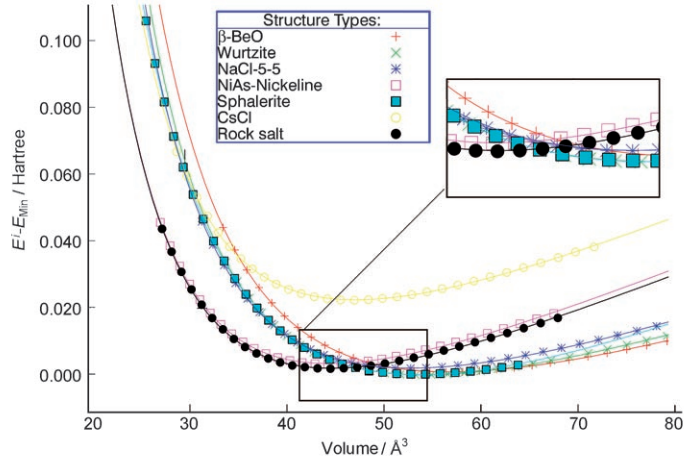

Figure 1. *E*/*V* curves for selected candidates for low-energy structures discovered by global searches of the LiBr energy landscape, followed by local optimization of each polymorph on the ab initio level ($E_{\mathrm{Min=Wurzite}} = -20.83888$ Hartree).[13,4]

It was shown previously that LiI can exist in a hexagonal modification, in addition to the conventional rock salt structure. However, no further details about the crystal structure were reported.[5] More recently Wassermann et al.[6] found that both hexagonal and cubic LiI structures were contained in films at room temperature that had been deposited from the gas phase. Conclusive evidence for LiI to also exist in the wurtzite type structure has been provided by the "low-temperature-deposition" technique[7] combined with the Rietveld analysis of the X-ray diffraction patterns as taken from thick-layer samples.[8] During that investigation it was shown that solid solutions $\mathrm{LiBr}_{1-x}\mathrm{I}_x$ ($0.25 \leq x \leq 0.8$) can also be obtained as hexagonal phases.[8] However, attempts to generate the respective modification for pure LiBr failed at that time.

Here, we report on a systematic study of LiBr, exploring the full parameter space of our deposition technique, which has revealed formation of the wurtzite polymorph under appropriate conditions.

In contrast to conventional molecular beam epitaxy (MBE)[9] and layer-by-layer deposition techniques,[10] where the substrates are heated to higher temperatures in order to allow the deposited matter to arrive at a structurally ordered state,[11] during the low-temperature-deposition approach the elemental starting materials are deposited atom by atom onto a cooled substrate. In this way amorphous starting mixtures are formed preferentially and the respective elements are homogeneously distributed and dispersed on the atomic level. This technique has been chosen to reduce as far as possible the diffusion paths during the solid-state reaction and in the crystallization of the desired compound, which would allow for running solid-state syntheses at extremely low thermal activation. This is a crucial prerequisite if one wants to realize the metastable solids predicted computationally. It has been demonstrated that solid-state reactions yielding crystalline products can indeed be performed below room temperature,[7] and highly metastable new compounds like $\mathrm{Na_3N}$[12] can be realized in this way.

In the experimental investigation of the energy landscape of lithium bromide we did not start from the elements but rather used the preformed binary compound in the deposition experiments. Systematically varying two of the most influential deposition parameters, the substrate temperature T_s and the vapor pressure of LiBr, yielded rather surprising results. According to the considerations given above, one would expect the metastable polymorph to be obtained, if at all, at a lower substrate temperature, and the stable modification to occur at a higher temperature.

In our experiments, at a deposition temperature below $T_s = -100\,^\circ\mathrm{C}$ and at low vapor pressures of LiBr (1×10^{-4} mbar) amorphous samples were obtained that transformed during heating into the stable rock salt polymorph. When a higher vapor pressure of LiBr was applied at very low

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temperature (−196 °C), broad reflections of the rock salt polymorph directly emerged. However, as displayed in Figure 2, at temperatures around −50 °C a new polymorph,

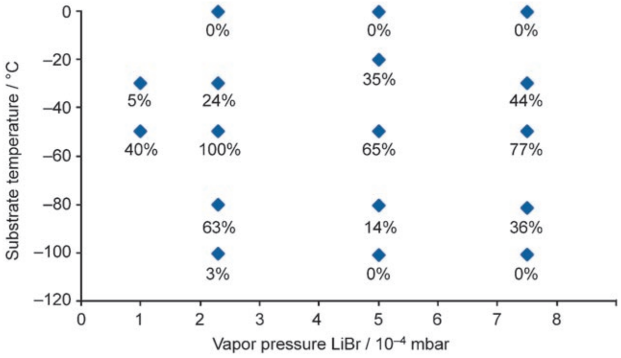

Figure 2. The crystalline fraction of β-LiBr as determined by Rietveld refinements of the β/α ratio of LiBr samples as a function of the substrate temperature and vapor pressure of LiBr (calculated from the crucible temperature) during deposition.

β-LiBr, formed preferentially. At −50 °C and a vapor pressure of LiBr of 2.3×10^{-4} mbar, single-phase samples were obtained. When warmed up to room temperature, such samples underwent a structural phase transition to the standard rock salt structure (see Figure 3). The ratio of the β polymorph in the α-LiBr/β-LiBr mixture decreased when the temperature or pressure deviated from $T_s = -50$ °C and a vapor pressure of 2.3×10^{-4} mbar, respectively. Finally, at $T_s = 0$ °C and $T_s = -100$ °C, only the rock salt structure type was found. The results, as displayed in Figure 2, appear to be independent of the substrate material (see the Experimental Section).

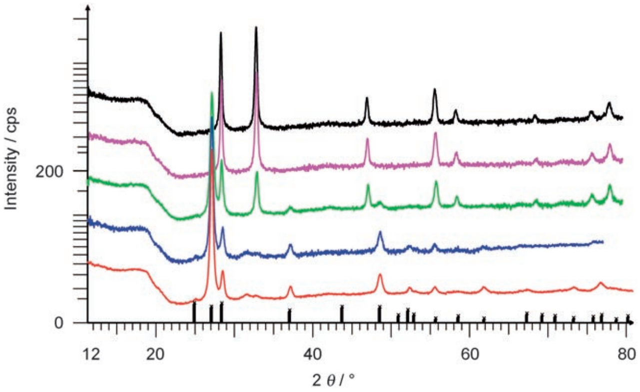

Figure 3. X-ray powder patterns for the LiBr system (deposited at −50 °C). Scans (from bottom to top) taken at −50 °C (wurtzite type), −30 °C(wurtzite type) , −10 °C (wurtzite and rock salt type), 10 °C and 25 °C (rock salt type); tick marks: β-LiBr.

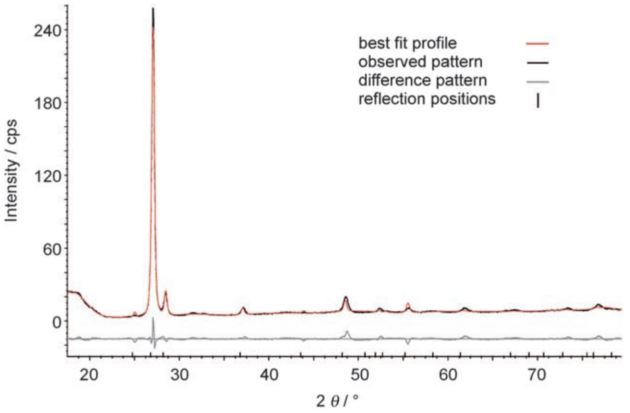

Figure 4. Rietveld refinement plot of β-LiBr.

Table 1: Crystallographic data for the Rietveld refinement of β-LiBr.

chemical formula	LiBr
space group	*P*6*mc* (no. 186)
cell parameters [Å]	$a = 4.1509(5)$ $c = 6.6502(2)$
cell volume V [Å^3]	99.23(5)
Z	2
T [°C]	−50
fw [g mol^{-1}]	86.8
ρ_{calc} [g cm^{-3}]	2.91
wavelength, λ [Å]	1.54059, 1.54449
measured range (2θ)	17.5°–79.5°
no. of reflections	19
Li site	(2b) 1/3, 2/3, 0
Br site	(2b) 1/3, 2/3, 0.379(1)
B_{eq}	8.1(2)
preferred orientation	(001): 0.405
R_p [%][a]	5.6
R_{wp} [%][a]	8.1
R_{Bragg} [%][a]	2.5

[a] R_P, R_{wp}, R_{Bragg}, and March-Dollase function for the preferred orientation as defined in Topas Version 3.0.[16]

The X-ray diffraction pattern of β-LiBr has been indexed and refined based on a hexagonal unit cell with the lattice constants $a = 4.1509(5)$ Å and $c = 6.6502(2)$ Å. The plot and structure data for the Rietveld refinement are shown in Figure 4 and Table 1, respectively. These results support the wurzite type (*P*6*mc*, No. 186) for the hexagonal modification of LiBr. During refinement, the effects of preferred orientation, which were strong, as would be expected based on the preparation method, were taken into consideration. Respective refinements assuming the NiAs structure type yielded unsatisfactory results. The size of the experimental hexagonal unit cell is in good agreement with the estimated lattice parameters $a = 4.13$ Å and $c = 6.67$ Å for LiBr (25 °C), which were obtained by extrapolating the lattice parameters of the solid solution $LiBr_{1-x}I_x$ towards $x = 0$.[8] Calculations on the ab initio level resulted in $a = 4.29$ and $c = 6.84$ Å for the lattice constants of LiBr in the wurtzite structure type.[4] The excessively high calculated values arise from the known systematic errors of such physical quantities, depending on the ab initio method employed.

The Li–Br distances for β-LiBr (2.52 and 2.53 Å) are 8 % less than those for α-LiBr (2.75 Å).[14] This compares well with the ratio between the interatomic distances in tetrahedrally and octahedrally coordinated Zn in, for example, the two polymorphs of ZnO (7%).[15] During the transition from β-LiBr to cubic α-LiBr the volume decreases by as much as 20%. Such a shrinkage in cell volume is typical for the transformation of metastable modifications into the stable ones, and amounts to 18% for LiI.[7]

The particular, yet strange, observations concerning the conditions needed to generate β-LiBr quite obviously have to be attributed to nonequilibrium phenomena connected to the otherwise rather selective steps of nucleation and growth. Typically, during the prestages of crystallization a dynamic population of subcritical nuclei develops, out of which those start to grow that first reach the critical size and thus stability. From our experiments we roughly deduct the following scenario. At intermediate temperatures, nucleation takes place locally; however, the seeds for the different structures do not equilibrate and do not undergo the common selection process. Instead, they start growing, with the growth feed from the gas phase. Two competing factors of influence determine the structure of the nuclei forming; these are temperature and internal strain, with the latter resulting from the volume shrinkage during the transition of the amorphous deposit to the crystalline states. Enhancing thermal activation favors the formation of the global minimum structure, that is, of the rock salt modification, while the negative pressure promotes crystallization of the lower density polymorph, that is, of the wurtzite structure. In accordance with such considerations, at temperatures above the intermediate range at about 0 °C exclusively α-LiBr is obtained.

By applying the low-temperature-deposition method a new metastable modification of LiBr has been synthesized as bulk (thick layer) samples. This is the first experimental proof that LiBr adopts the wurtzite structure type as a metastable polymorph; this was predicted previously by globally exploring the lithium bromide energy landscape computationally. We regard this result as further strong evidence for the feasibility of our energy landscape concept as an approach to rational solid-state synthesis.[1]

Experimental Section

Lithium bromide (99.999%, Aldrich), dried at 200 °C, was directly evaporated from a home-made resistance heater (stenan crucible, Hoechst CeramTec AG), which was held at a constant temperature between 420 and 470 °C, and deposited onto a cooled substrate inside an ultrahigh-vacuum chamber for a period of 3 to 5 h. The achieved thickness of the deposited films amounts to a few hundred nanometers. The chamber was evacuated to 3×10^{-8} mbar by a turbomolecular and cryopump system, which included a cold trap filled with liquid N_2 attached to the system. The residual gas of the chamber was monitored by a mass spectrometer (C-100M, Leybold-Inficon). During the experiments, the substrates—sapphire (0001) and (11$\bar{2}$0) orientated, lithium niobate (001) (all epitaxial polished, TBL-Kelpin), and polycrystalline copper (Mateck)—were kept at a constant temperature. The substrate temperature T_s was systematically varied from −100 °C up to room temperature and the vapor pressure of LiBr from 1.0×10^{-4} to 7.5×10^{-4} mbar (calculated from crucible temperature). Depositions of LiBr onto sapphire (0001) substrates down to −196 °C were also prepared. Figure 2 shows the results of the deposition onto sapphire (0001) substrates. Deposition of LiBr under similar experimental conditions onto substrates of lithium niobate, copper, and sapphire (11$\bar{2}$0) yielded results close to the values displayed in this diagram. The substrates bearing the deposited sample were transferred from the preparation chamber to a diffractometer, while maintaining vacuum and cooling, by means of a car-transfer system.

The powder diffraction patterns were recorded on a θ/θ X-ray powder diffractometer (D8-Advance, Bruker AXS) with parallel beam geometry (Goebel mirror, Cu$_{K\alpha}$), in an X-ray chamber under high vacuum (ca. 5×10^{-7} mbar) in reflection mode. The temperature of the samples was controlled using a temperature sensor (PT-100) placed in the sample holder. Each X-ray pattern was monitored at an angle of incidence of 10° using an area-sensitive detector (GADDS, Bruker AXS). The corresponding diffractogram was obtained by integration of the two-dimensional diffraction cones. X-ray measurements over the whole sample area revealed very low values of local fluctuations on the order of 8%. For indexing and structure refinements (Rietveld method), the software Topas (Version 3.0, 2006, Bruker AXS) was employed.[16] α-LiBr served as an internal standard. For this purpose, we redetermined the lattice constant of α-LiBr in an independent experiment[17] at room temperature to $a = 5.4972(1)$ Å (Lit. 5.50(8) Å[15]). The ratios of β- and α-LiBr content (wt%) were calculated from Rietveld structure refinements. An increase of the crystallite size with increasing substrate temperature was observed. Further details on the crystal structure (β-LiBr) investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-419071.

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