

Synthesis of a New Modification of Lithium Chloride Confirming Theoretical Predictions

Andreas Bach,^[a] Dieter Fischer,^[a] and Martin Jansen*^[a]

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Abstract. In accordance with prior calculations, the new polymorph β -LiCl (wurtzite structure type) has been synthesised, by the low-temperature atomic-beam-deposition (LT-ABD) technique, in a mixture with α -LiCl (rock salt structure type) by depositing LiCl vapour (2 to 5.3×10^{-4} mbar) onto a cooled substrate (-30 to -60 °C). The maximum β -LiCl fraction of 53 % was obtained using a sapphire (0001) substrate at -50 °C and 3.7×10^{-4} mbar LiCl vapour pressure. The proportion of the new polymorph contained in the bulk sample decreases as temperature or vapour pressure deviate from these values, until finally the rock salt type LiCl is found exclusively. When the samples are warmed up to room temperature, β -LiCl irreversibly transforms to α -LiCl. The X-ray diffraction pattern of the two phase LiCl sample measured at -50 °C has been indexed and refined based on a

hexagonal unit cell for β -LiCl with the lattice constants $a = 3.852(1)$ Å and $c = 6.118(1)$ Å and a cubic unit cell for α -LiCl with the lattice constant $a = 5.0630(8)$ Å. By Rietveld refinement the wurtzite type of structure ($P6_3mc$, No. 186) was suggested for the new hexagonal modification of LiCl with the Li-Cl distances (2.32 and 2.34 Å) being 8 % smaller than those of α -LiCl. Moreover, the cell volume decreases as much as 16 % during the transition from β -LiCl to α -LiCl. Both the shifts in bond lengths and volume correspond well with the situation encountered for LiBr and LiI. Besides the variation of LiCl vapour pressure and substrate temperature, also different substrate materials were employed for testing their influence on formation of the β -LiCl polymorph.

Introduction

Projecting the world of chemical matter onto an energy landscape associated to the respective configuration space constitutes the foundation of our approach to rational chemical synthesis [1–3]. There is a “one to one” relationship between the ensemble of chemical compounds capable of existence and the structure of the energy landscape: each compound corresponds to a (local) minimum on the landscape and vice versa. In the first step of synthesis planning, the (meta)stable compounds of a given chemical subsystem are identified by globally exploring the related landscape, or more specifically, by identifying the minima. Realising the predicted compounds, in particular the metastable ones, by chemical synthesis often turns out to be an intriguing task. Our approach of rational synthesis planning, the prediction and realisation of new compounds, has proven to be rather efficient also with this respect [2], and among others, has enabled us to synthesise up to then elusive Na_3N [4].

Full exploration of the energy landscapes of the alkali metal halides has resulted in the prediction of many modifications to exist in addition to the known rock salt and CsCl types of structure [5]. For the lithium halides those modifications containing lithium in a tetrahedral coordination, i.e. zinc blende

and wurtzite types, have turned out to be energetically competitive with the stable rock salt structures. Indeed, using the LT-ABD technique [6], β -LiI and β -LiBr have been realised in the hexagonal wurtzite structures, recently [7, 8]. These findings are in a certain sense complying with the traditional structure field diagrams based on radii ratios of hard sphere ions. Here the stability range for an octahedral coordination, i.e. of the rock salt type, is $0.414 \leq r_K/r_A \leq 0.732$. LiI and LiBr with $r_K/r_A = 0.35$ and 0.39 , respectively, are border line cases or even beyond this range [9]. In contrast, LiCl exhibiting a ratio of $r_K/r_A = 0.42$ is clearly located within the stability range of the rock salt type. However, computational global searches and ab initio optimisation of the structure candidates [5] have shown that for LiCl as well, the energies for the wurtzite and zinc blende modifications are rather low, as one can deduce from the energy vs. volume curves displayed in Figure 1.

Here, we report on our experiments aiming at realising LiCl in one of the predicted metastable modifications.

Results and Discussion

The deposition of LiCl onto various substrates at low temperatures by the employment of our LT-ABD technique [6] resulted in transparent films, which changed into white opaque when warmed up to room temperature. With (0001)-oriented sapphire as substrate, the parameter field of deposition was explored. In the temperature range of -30 to -60 °C and vapour pressures from 2 to 5.3×10^{-4} mbar the new polymorph β -LiCl was found besides α -LiCl. The maximum β -LiCl fraction of 53 % was obtained at -50 °C sapphire substrate tem-

* Prof. Dr. M. Jansen
Fax: +49-711-6891502
E-Mail: M.Jansen@fkf.mpg.de

[a] Max-Planck-Institut für Festkörperforschung
Heisenbergstraße 1
70569 Stuttgart, Germany

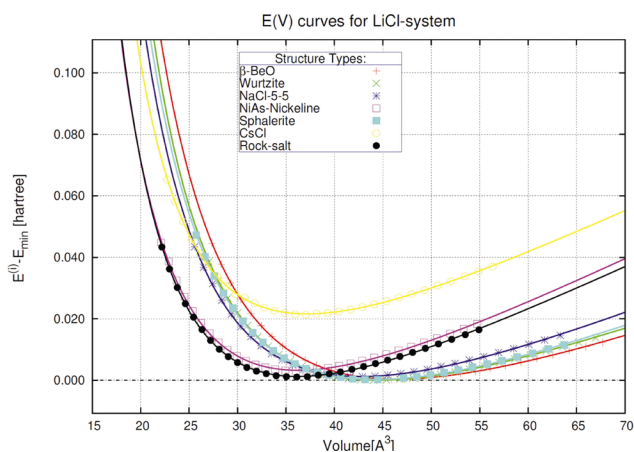


Figure 1. E/V curves for selected candidates for low-energy structures discovered by global searches of the LiCl energy landscape, followed by local optimisation of each polymorph on the ab initio level ($E_{\text{Min}} = E_{\text{Wurtzite}} = -467.86573$ Hartree) [5, 12].

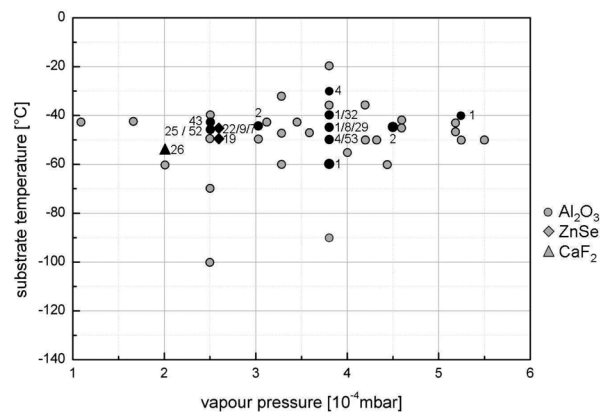


Figure 2. Percentaged crystalline fraction of β -LiCl [wt-%] as determined by Rietveld refinements of the two phase α - β -LiCl samples as a function of substrate temperature and vapour pressure of LiCl (calculated from crucible temperature) during deposition.

perature and 3.7×10^{-4} mbar vapour pressure. The proportion of the new polymorph in the sample decreases as temperature or vapour pressure deviate from these optimal values. Finally, outside the parameter window given above for the substrate temperature and the vapour pressure, only rock salt structure type α -LiCl is found. The fractions of β - and α -LiCl (wt-%) were calculated from Rietveld structure refinements and are displayed in Figure 2. Here, the percentaged crystalline fraction of β -LiCl is shown as a function of substrate temperature and LiCl vapour pressure during deposition for different substrate materials. When the sample is heated, β -LiCl starts to transform to α -LiCl around 0 °C with the phase transition completed at room temperature (Figure 3). The X-ray diffraction pattern of the two phase LiCl sample measured at -50 °C has been indexed and refined based on a hexagonal unit cell for β -LiCl [$a = 3.852(1)$ Å; $c = 6.118(1)$ Å] and the cubic unit cell for α -LiCl [$a = 5.0630(8)$ Å]. For the purpose of calibration, we used the lattice constant of α -LiCl at room temperature ($a = 5.131(1)$ Å; Lit.: 5.132 Å [11]). The two phase Rietveld refinement, also addressing the effect of preferred orientation, suggested the wurtzite structure type ($P6_3mc$, No. 186) for the new hexagonal modification of LiCl (Figure 4) with Li–Cl distances (2.32 and 2.34 Å) being 8 % smaller than those of α -LiCl (Table 1). Moreover the cell volume decreases as much as 16 % during the transition from β -LiCl to α -LiCl. Both observations correspond well with the situation encountered for LiI and LiBr [7, 8]. A comparison of the cell parameters and volumes for different lithium halides shows that the results for LiCl in principle follow the trends as encountered for (both α - and β -) lithium halides with heavier halogens (Figure 5). However, the decrease in volume for the cubic phases compared to the hexagonal ones is larger.

The ratio of α -/ β -LiCl appeared to be laterally constant within individual preparations, as monitored by X-ray diffraction. This is in accordance with the SEM pictures taken from the sample surface (Figure 6), which do not show any noticeable variations in lateral direction. We attribute the microstruc-

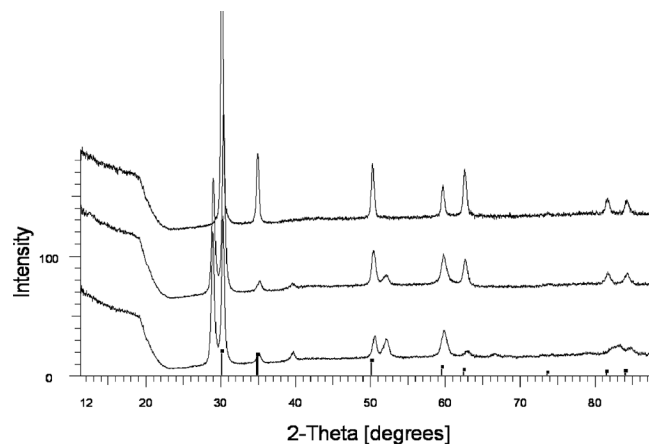


Figure 3. X-ray powder patterns of LiCl (deposited at -50 °C sapphire substrate temperature and 3.7×10^{-4} mbar LiCl vapour pressure), intensity deviation because of texture, scans from the bottom up: taken at -50 °C (wurtzite and rock salt type), 0 °C (wurtzite and rock salt type) and 25 °C (rock salt type), tick marks: α -LiCl.

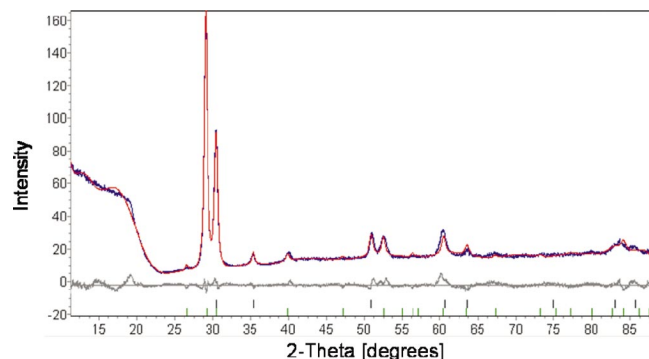


Figure 4. Rietveld refinement plot of LiCl (deposited at -50 °C sapphire substrate temperature and 3.7×10^{-4} mbar LiCl vapour pressure), two phase refinement, measured at -50 °C; observed pattern (blue), fitted profile (red), difference profile (grey), tick marks: α -LiCl (black), β -LiCl (green).

Table 1. Crystallographic data for the Rietveld refinement of LiCl.

chemical formula	LiCl
molar mass /g·mol ⁻¹	42.4
temperature	-50 °C
Cu-K _α wavelength, λ /Å	1.54059, 1.54449
measured range /2θ	11–88°
R _p /% ^{a)}	4.2
R _{wp} /% ^{a)}	5.6
β-LiCl	hexagonal
space group	<i>P</i> 6 ₃ <i>mc</i> (no. 186)
Z	2
cell parameters /Å	<i>a</i> = 3.852(1) <i>c</i> = 6.118(1)
cell volume /Å ³	78.65(4)
ρ _{calc} /g·cm ⁻³	1.8
crystal size /nm	26.0(2)
no. of reflections	20
Li site	(2b) 1/3, 2/3, 0
Cl site	(2b) 1/3, 2/3, 0.379 ^{b)}
preferred orientation	(002): 0.406(2)
B _{eq}	0.2(1)
R _{Bragg} /% ^{a)}	2.1
α-LiCl	cubic
space group	<i>Fm</i> 3 <i>m</i> (no. 225)
Z	4
cell parameter /Å	<i>a</i> = 5.0630(8)
cell volume /Å ³	129.78(6)
ρ _{calc} /g·cm ⁻³	2.2
crystal size /nm	24.3(4)
no. of reflections	8
Li site	(4a) 0, 0, 0
Cl site	(4b) 1/2, 1/2, 1/2
preferred orientation	(111): 0.3(1) (022): 0.3(2)
B _{eq}	3.5
R _{Bragg} /% ^{a)}	1.9

a) R_p, R_{wp}, R_{Bragg} and March-Dollase function for the preferred orientation as defined in Topas Version 3.0. [10]; b) Unrefined sites, taken from LiBr

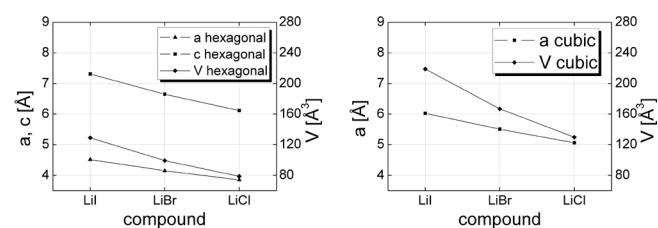


Figure 5. Cell parameters of wurtzite (left) and rock salt modifications (right) of different lithium halides as determined by Rietveld refinements, LiI (measured at 25 °C) [7], LiBr [8, 13] and LiCl (measured at 50 °C).

ture observed to volume shrinkage at the transition from α- to β-LiCl. An increase of the crystallite size with increasing substrate temperature was observed. In addition to sapphire (0001), different surfaces of various single crystal materials have been tested as substrates. When ZnO (0001), NaCl (111) and cleaved CaF₂ (111) were used, no β-LiCl was generated. The experiments on ZnSe (111) and CaF₂ (111) resulted in amounts of β-LiCl similar to those on sapphire (0001) sub-

strates. Because of these results, no direct relations seem to exist between the selected substrate exposing a certain surface and the formation of β-LiCl. Hence, if at all, the substrate surface only plays an inferior role for the emergence of hexagonal LiCl.

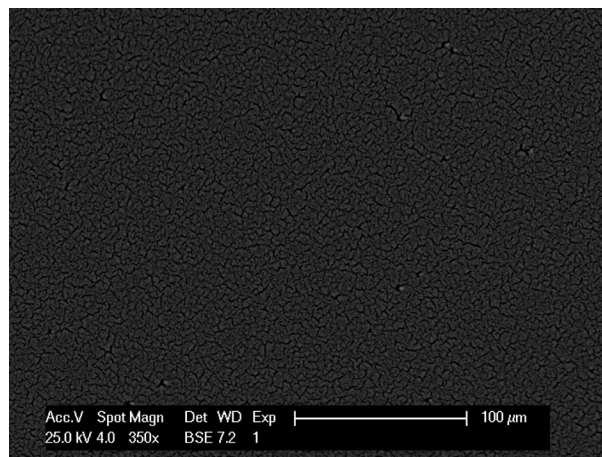


Figure 6. SEM picture showing homogeneity of LiCl surface, 350-fold magnification, deposited at -45 °C sapphire substrate temperature and 3.7×10^{-4} mbar LiCl vapour pressure, after warming up to 120 °C.

Furthermore, our results reveal a small window of synthesis parameter combinations (substrate temperature and vapour pressure), where β-LiCl can be obtained, with the substrate temperature being the more crucial influencing factor. Figure 2 shows that β-LiCl preferably forms at a substrate temperature of about -45 °C. At a first glance it is hard to rationalise that α- and β-LiCl crystallise simultaneously, and that the less stable polymorph survives together with the more stable one. The formation of β-LiCl, quite obviously, has thus to be attributed to non-equilibrium phenomena connected to the otherwise rather selective steps of nucleation and growth. Commonly, during the pre-stages of crystallisation a dynamical population of subcritical nuclei develops, out of which those start to grow that reach the critical size and stability first. In our experiments, in a small temperature window local nucleation takes place at which the seeds for the different structure types do not appear to equilibrate or to undergo the common selection process. Instead of that, in the case of LiCl, seeds start growing with the growth fed from the LiCl in the gas phase. If the substrate temperature is raised, thermal activation favours the transformation to the global minimum structure, i.e. the rock salt modification, and above -30 °C substrate temperature α-LiCl is obtained exclusively. The parameter window is significantly smaller as compared to the cases of β-LiBr and β-LiI [7, 8], and the temperature windows narrow from LiI (-196 to 0 °C) to LiBr (-100 to -20 °C) and LiCl (-60 to -30 °C).

These results confirm the high potential of the LT-ABD technique as to the formation of metastable compounds, though the parameter space needs to be explored very accurately to obtain the targeted possible polymorphs, and the parameter window for new polymorphs may be very small, like with LiCl.

Experimental Section

Lithium chloride (99,99 %, Aldrich) was dried at 200 °C in vacuum and directly evaporated from a home-made resistance heater (stenan crucible, Hoechst CeramTec AG), which was held at a constant temperature between 450 and 490 °C, and deposited onto a cooled substrate inside an ultra high vacuum chamber for a period of several hours. Ultra high vacuum of 1×10^{-8} to 5×10^{-9} mbar was maintained during preparation in the deposition chamber by using a turbo molecular and cryopump system including a liquid nitrogen filled cold trap. The residual gas was analysed and monitored by quadrupole mass spectrometers (QME 220, Pfeiffer Vacuum GmbH; C-100M, Leybold-Inficon). The substrate temperature (controlled using a temperature sensor PT-100 placed in the sample holder) was systematically varied from -196 °C to room temperature during deposition and X-ray diffraction measurement, and the vapour pressure of LiCl in a range between 1 and 8×10^{-4} mbar (calculated from crucible temperature). The deposition rates and the deposited layer thicknesses were controlled using a quartz crystal monitor (QCM, Inficon). Deposited LiCl was harvested quantitatively, and the amount of lithium in the sample was determined by ICP-OES in order to calibrate the QCM. Film thicknesses of up to a few hundreds of nanometers were achieved. The following materials were used as substrates (all CrysTec GmbH): sapphire (0001), ZnO (0001), ZnSe (111), CaF₂ (111), NaCl (111) (all epitaxial polished) and cleaved CaF₂ (111). The substrates with the deposited samples were transferred from the deposition chamber to an X-ray diffractometer, while maintaining vacuum and cooling, by means of a car transfer system.

The powder diffraction patterns were recorded with a θ/θ X-ray powder diffractometer (D8-Advance, Bruker AXS) with parallel beam geometry (Goebel mirror, Cu-K α) in an X-ray chamber under ultra high vacuum (ca. 5×10^{-8} mbar) in reflection mode. The chamber is supplied with a slit to absorb scattered radiation which considerably reduces the background under vacuum condition from 20° on in 2θ . Each X-ray pattern was monitored at an angle of incidence of 10° using an area sensitive detector (GADDS, Bruker AXS). The corresponding pattern 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. For indexing and structure refinements (Rietveld method), the software Topas (Version 3.0, 2006, Bruker AXS) was employed [10]. α -LiCl served as an internal standard. Further details on the crystal structure investigations can 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 numbers CSD-420954 and CSD-420955 for β - and α -LiCl, respectively.

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