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Lithium Aryloxide Thin Films with Guest-Induced Structural Transformation by ALD/MLD

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Experimental Details

The samples were deposited using an F-120 flow-type hot-wall ALD reactor (ASM Microchemistry Ltd.), from lithium bis(trimethylsilyl)amine (LiHMDS, 97 %, Sigma Aldrich), and hydroquinone (HQ, >99.5 %, Merck KGaA). Both precursors were kept inside the reactor at temperatures of 60 °C for LiHMDS and 95 °C for HQ. The Al₂O₃ capping layer was deposited using trimethylaluminum and H₂O. Nitrogen (99.999%, produced from air by Schmidlin UHPN 3000 nitrogen generator) was used both as purging and carrier gas. The films were deposited on Si(100) for general characterization and on borosilicate for the UV/VIS measurements. The reactor pressure was ~5 mbar. The sample thickness and crystallinity was determined with X-ray reflectivity (XRR) and grazing incidence X-ray diffraction (GIXRD), respectively using a PANanalytical X'Pert Pro diffractometer with a Cu K_α X-ray source. The thickness, density and roughness values were extracted from the XRR data by fitting with the PANanalytical X-ray Reflectivity software taking into account the Al₂O₃ capping layer. The LeBail profile fitting of the GIXRD data was conducted using the FullProf Software Suite¹. The IR data was collected with a Nicolet Magna 750 FTIR spectrometer in transmission mode on samples deposited on Si in range of 400-4000 cm⁻¹ using a resolution of 4cm⁻¹. The spectrum of bare Si was subtracted from the sample data. The atomic force microscopy (AFM) images were obtained with a Bruker Nanoscope V device operated in tapping mode. The UV/VIS measurements were conducted with a Hitachi U-2000 spectrophotometer in range of 200 - 1100 nm. The absorbance data was deduced from transmittance and reflectance measurements and the optical band gap was estimated from the square of the absorption coefficient plotted against the photon energy.

Computational Details

All density functional calculations, including full structural relaxation of both atomic positions and cell parameters, and vibrational properties at the Γ -point, were performed with the CRYSTAL14 program package.²⁻⁵ We applied the PBE0 hybrid functional method, which incorporates 25% of the Hartree-Fock exchange energy and 75% of the PBE exchange energy.^{6,7} A modified all-electron, Gaussian-type basis set based on the molecular Karlsruhe triple- ζ -valence + polarization (TZVP) basis set was used in the solid-state calculations (full basis set details are given below).⁸ A grid of 4×6×4 k -points in the Monkhorst-Pack scheme⁸ was used for the reciprocal space

sampling. The so-called TOLINTEG tolerance factors used for the Coulomb and exchange integrals were 8, 8, 8, 8 and 16. Default optimization convergence thresholds and integration grid for the exchange-correlation functional (XLGRID) were applied. In the harmonic frequency calculations, the SCF convergence threshold on total energy (TOLDEE) was set to 10^{-9} a.u.. IR intensities were obtained with the analytical coupled perturbed Kohn-Sham method.^{10,11} The final IR absorbance spectrum is a superposition of Lorentzian peak shapes with FWHM of 16 cm^{-1} .

Additional basis set details

In periodic calculations, the Gaussian-type localized atomic basis set must be chosen carefully. Basis sets originally developed for molecular calculations contain diffuse basis functions to model the tails of wavefunction, but in periodic calculations, where the whole space is filled with basis functions, such diffuse functions are usually unnecessary and lead into numerical difficulties and/or severe degradation of performance.¹² The following triple- ζ -valence + polarization (TZVP) basis sets were applied here:

H, C, O: The basis sets were taken from a previous study.¹³

Li: The Karlsruhe def2-TZVP basis set was used as a starting point.⁵ The most diffuse s- function was removed (exponent 0.029). The exponent of the most diffuse p-type function (0.06) was increased to 0.16 by dividing the second outermost p-exponent of 0.40 by a factor of 2.5. The exponent of the outermost s-type function (0.077) was then also increased to 0.16 by dividing the second outermost s-exponent of 0.51 by a factor of 3.2. Finally, the outermost s and p functions with an exponent of 0.16 were combined into a single sp-type function to increase the efficiency of the CRYSTAL code. The def2-TZVP basis set was thus changed from a (11s3p)/[5s3p] {62111/111} contraction pattern into (10s3p)/[4s3p] {6211/111}. The final basis set is listed below in CRYSTAL input format:

```

3 6
0 0 6 2.0 1.0
    6269.2628010      0.20540968826E-03
    940.31612431     0.15916554089E-02
    214.22107528     0.82869829707E-02
    60.759840184     0.33856374249E-01
    19.915152032     0.11103225876
    7.3171509797     0.27449383329
0 0 2 1.0 1.0
    2.9724674216     0.23792456411
    1.2639852314     0.30765411924
0 0 1 0.0 1.0
    0.51427489953    1.0000000000
0 1 1 0.0 1.0

```

```

0.16      1.0 1.0
0 2 1 0.0 1.0
3.327    1.0000000000
0 2 1 0.0 1.0
0.40     1.0000000000

```

Table S1. The calculated structural parameters for Li₂Q

<i>a</i>	11.49 Å				
<i>b</i>	10.38 Å				
<i>c</i>	4.74 Å				
Space group	<i>Pccn</i> (No. 56)				
Atom	Wyckoff position	x	y	z	Occ.
O1	8e	0.66277	0.15466	0.23304	1.000
C1	8e	0.61710	-0.02804	0.52177	1.000
C2	8e	0.53541	0.89482	0.65708	1.000
C3	8e	0.58426	0.07961	0.35994	1.000
Li1	8e	0.67373	0.16467	0.83392	1.000
H1	8e	0.70884	-0.05241	0.53699	1.000
H2	8e	0.56397	0.81236	0.77993	1.000

Interpretation of the IR spectrum

All IR active modes from the vibrational calculations are collected in the table below. Modes were assigned by inspection of the normal modes visualized using the Jmol program.¹⁴ Similar IR active modes are grouped together under one experimental peak.

Table S2. Interpretation of the experimental IR spectrum.

Corresponding experimental peak (cm ⁻¹)	Raw calculated frequencies (cm ⁻¹)	IR intensity (arb. units)	Irrep	Assignment
417	392	319	B _{1u}	Li breathing
	413	161	B _{2u}	
	422	653	B _{1u}	
453	435	7	B _{1u}	Li-O bend
	439	294	B _{3u}	
	448	1020	B _{3u}	

	458	504	B _{1u}	Li–O bend
	464	219	B _{2u}	
	489	1139	B _{2u}	
	495	301	B _{3u}	
	499	381	B _{1u}	
543	554	14	B _{1u}	Benzene ring out-of-plane bend
	563	1	B _{3u}	
	564	20	B _{2u}	
792	818	511	B _{3u}	C=C in-plane bending
	819	764	B _{2u}	
	831	428	B _{1u}	
839	855	356	B _{1u}	C–H out-of-plane symmetric bending
	856	186	B _{3u}	
	867	34	B _{2u}	
941	957	10	B _{1u}	C–H out-of-plane asymmetric bending
	968	20	B _{2u}	
	972	27	B _{3u}	
999	1018	3	B _{3u}	C–H symmetric bending
	1019	2	B _{1u}	
	1024	15	B _{2u}	
1094	1119	16	B _{3u}	C–H asymmetric bending
	1122	22	B _{2u}	
	1125	9	B _{1u}	
1245	1284	631	B _{3u}	C=C stretch
	1285	6	B _{2u}	
	1286	44	B _{1u}	
	1292	593	B _{3u}	
	1302	1510	B _{2u}	
1282	1334	218	B _{1u}	C=C stretch
1411	1458	93	B _{3u}	C=C stretch
	1462	19	B _{1u}	
	1463	49	B _{2u}	
1489	1536	1705	B _{2u}	C=O stretch
	1540	1254	B _{3u}	
1511	1572	616	B _{1u}	C=O stretch
3014	3173	81	B _{2u}	C–H stretch
	3178	5	B _{1u}	
	3179	9	B _{3u}	
3056	3191	23	B _{2u}	C–H stretch
	3194	1	B _{3u}	

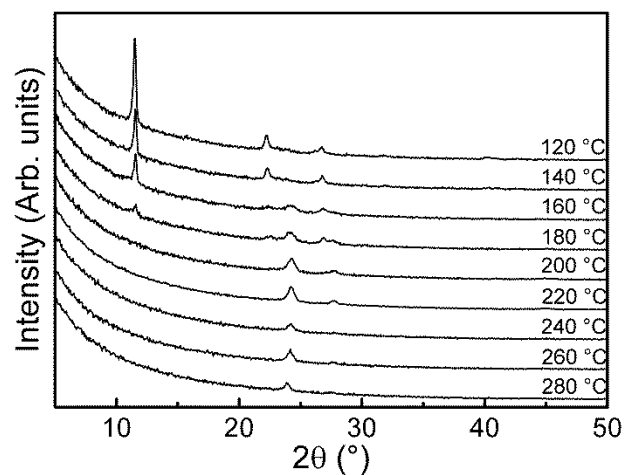


Figure S1. GIXRD patterns of Li_2Q samples deposited at different temperatures using 400 ALD/MLD cycles with pulse/purge lengths of 2.0s/2.0s and 10s/20s for LiHMDS and HQ, respectively.

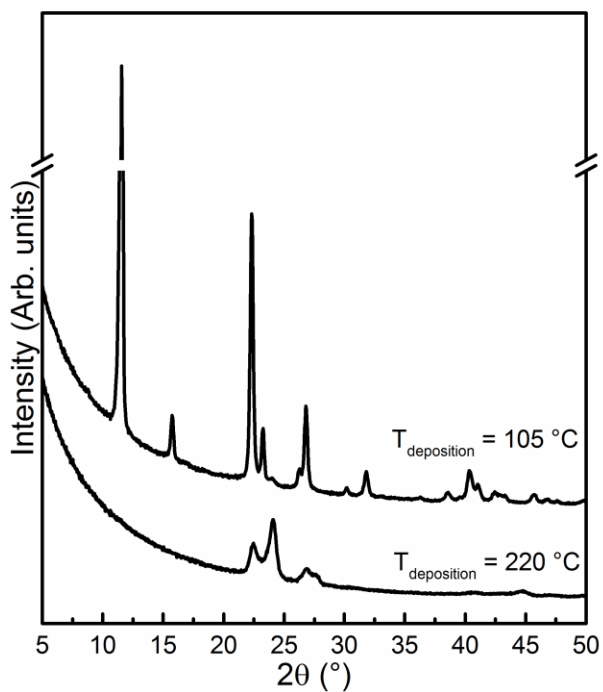


Figure S2. GIXRD patterns of Li_2Q samples deposited at 105 and 220 °C using 1600 ALD/MLD cycles with pulse/purge lengths of 2.0s/2.0s and 10s/20s for LiHMDS and HQ, respectively. Full range of y-axis not shown for clarity.

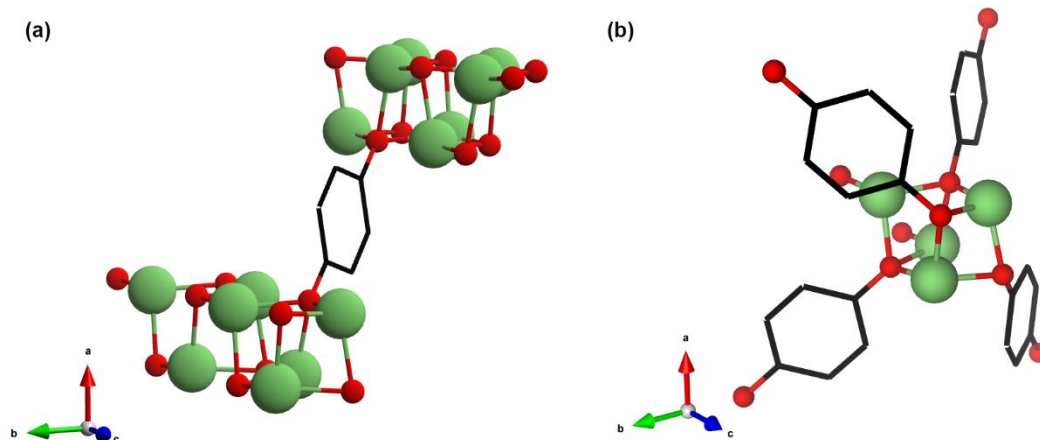


Figure S3. (a) The interconnectivity of the Li_2O_2 chains through a $[\text{C}_6\text{H}_4\text{O}_2]^{2-}$ unit (b) The secondary building unit resembling a lithium cubane cluster with the 3-coordinated lithium sites evident.

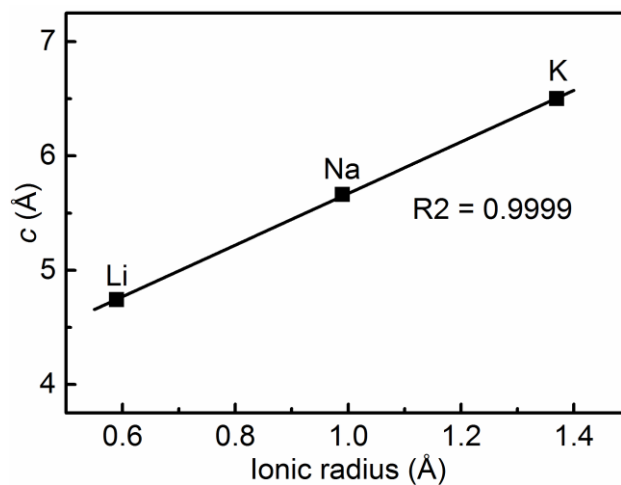


Figure S4. c -axis of the M_2Q compounds plotted against the ionic radii. Li: this work; Na, K from Couhorn and Dronkowski, *Z. Anorg. Allg. Chem.* 2003, **629**, 647-652

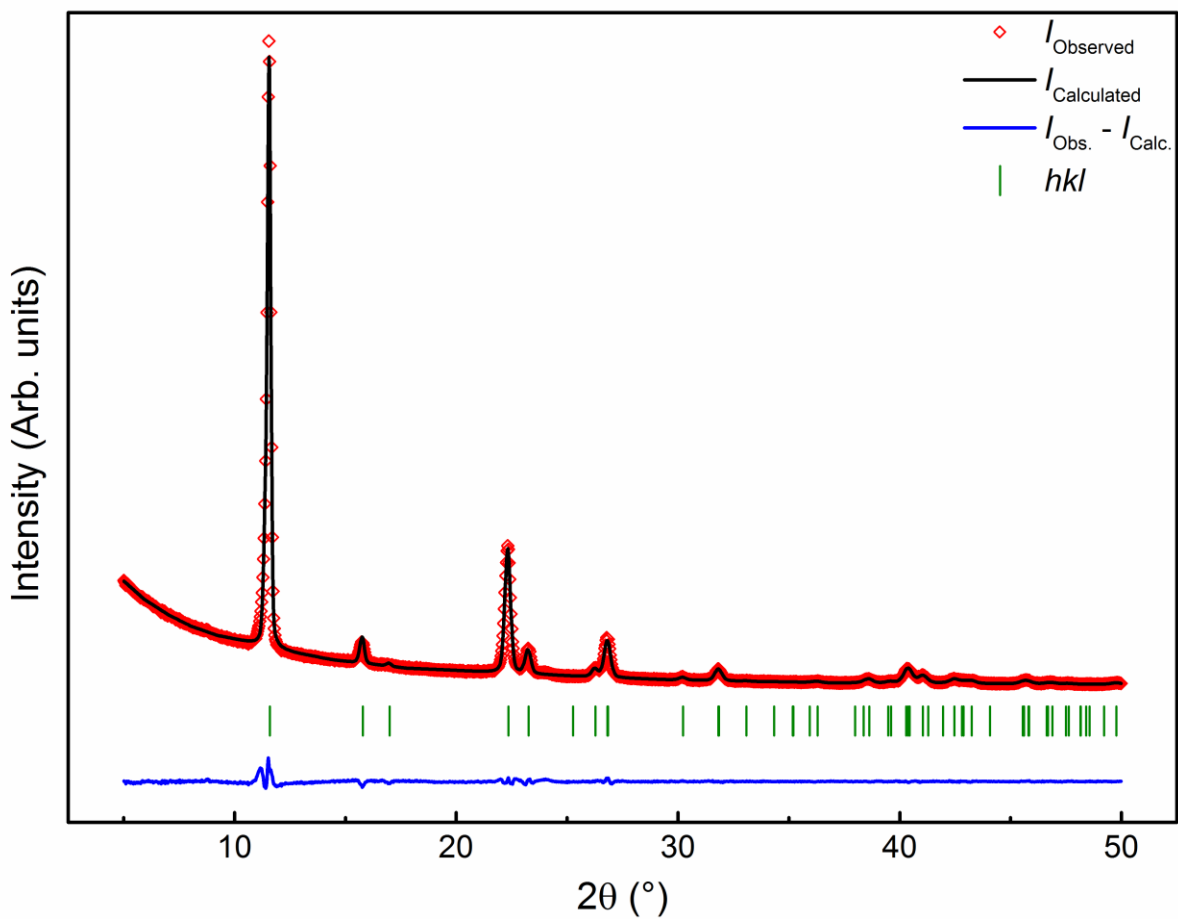


Figure S5. LeBail fit of the Li_2Q GIXRD pattern (deposition temperature: $105\text{ }^\circ\text{C}$) using the calculated orthorhombic $Pccn$ space group. $a = 11.25\text{ \AA}$, $b = 10.45\text{ \AA}$, $c = 4.66\text{ \AA}$. $R_p = 11.6$, $R_{wp} = 9.44$, $\chi^2 = 5.75$

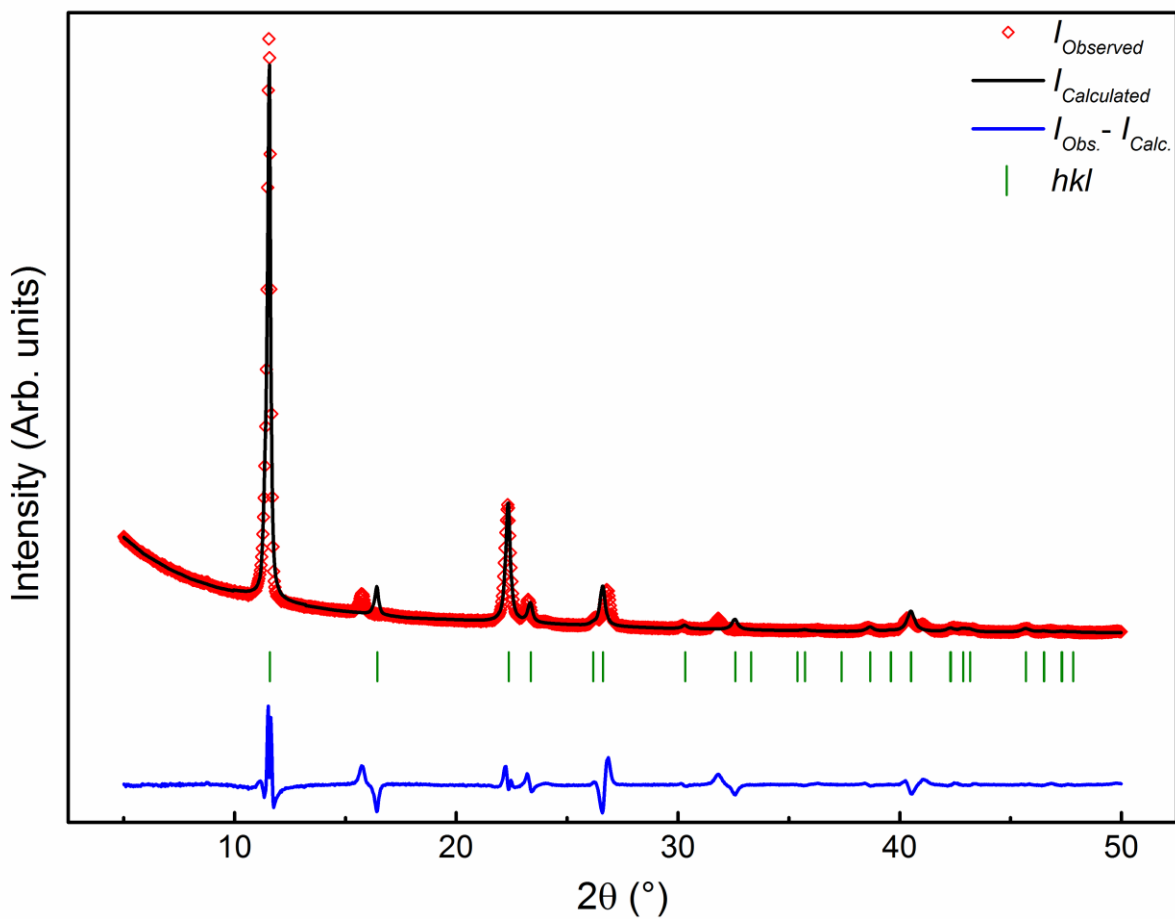


Figure S6. LeBail fit of the Li_2Q GIXRD pattern (deposition temperature: $105\text{ }^\circ\text{C}$) using the space group $P4_2/nm$ of Na_2Q shown here to demonstrate the inadequacy of the tetragonal symmetry to explain the observed GIXRD pattern. $a = 10.74\text{ \AA}$, $c = 4.65\text{ \AA}$. $R_p = 35.3$, $R_{wp} = 41.3$, $\chi^2 = 110$

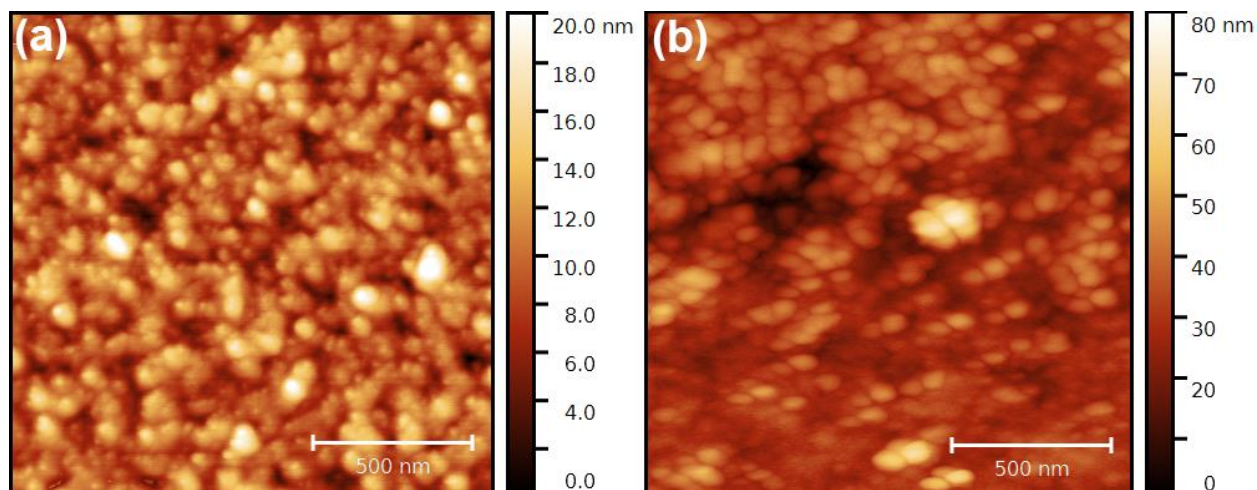


Figure S7. The AFM images obtained from (a) pristine, and (b) exposed samples. Note the differing depth scale.

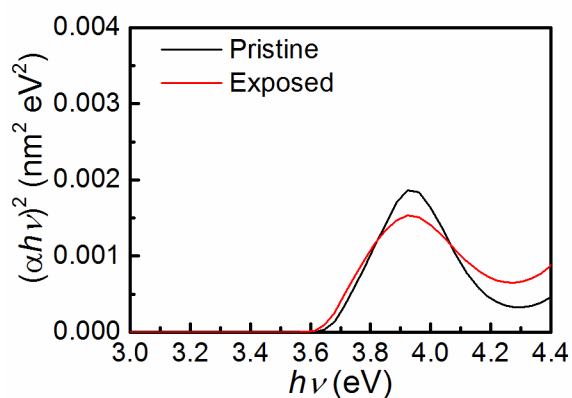


Figure S8. $(\alpha h\nu)^2$ vs $h\nu$ plots for the pristine (black line) and exposed (red line) Li_2Q samples obtained from the UV-VIS measurements.

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