Polymorphism and structural diversities of $LiClO_4$ - β-alanine ionic co-crystals

Paulina H. Marek[a,b], Grzegorz J. Cichowicz[b], Dorota M. Osowicka[a], Izabela D. Madura[a]*, Łukasz Dobrzycki[b], Michał K. Cyranski[b], Arkadiusz Ciesielski[b]*

[a] Warsaw University of Technology, Faculty of Chemistry, Noakowskiego 3, 00-664 Warsaw, Poland

[b] University of Warsaw, Faculty of Chemistry, Faculty of Chemistry, Pasteura 1, 02-093 Warsaw, Poland

pmarek@ch.pw.edu.pl, izabela@ch.pw.edu.pl

Electronic Supplementary Information (ESI)

Contents:

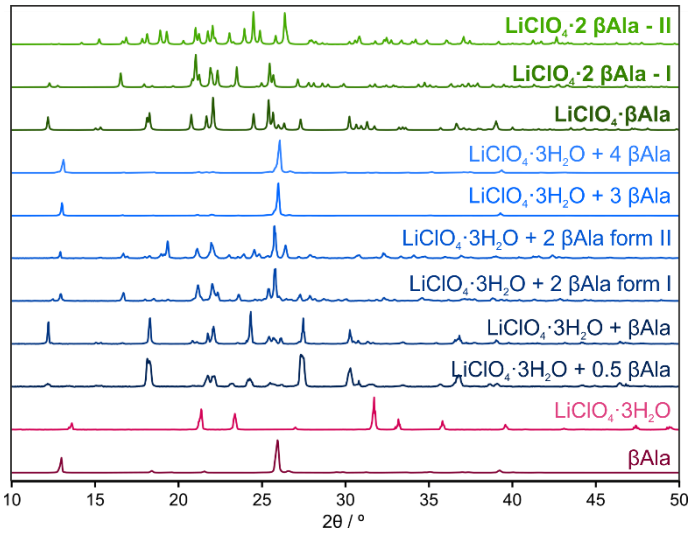


Figure S1. Experimental powder patterns of components (in pink) and tested mixtures (in blue). Simulated from crystal structures diffractograms of obtained crystal structures presented in green.

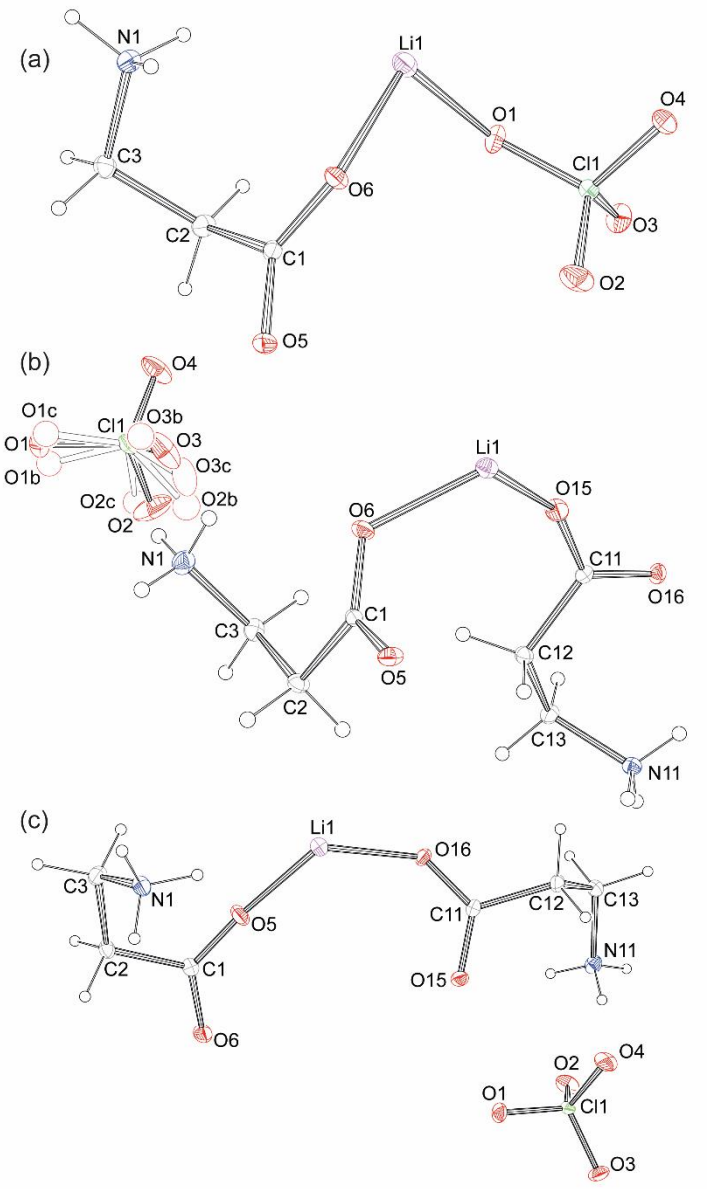
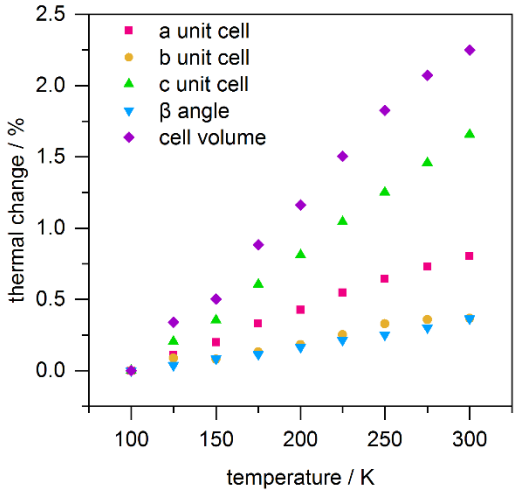


Figure S2. ORTEP drawings of an asymmetric part of the unit cells for (a) **$LiClO_4$·βAla**, (b) **$LiClO_4$·2βAla-I** and (c) **$LiClO_4$·2βAla-II**.

(a)



(b) (c)

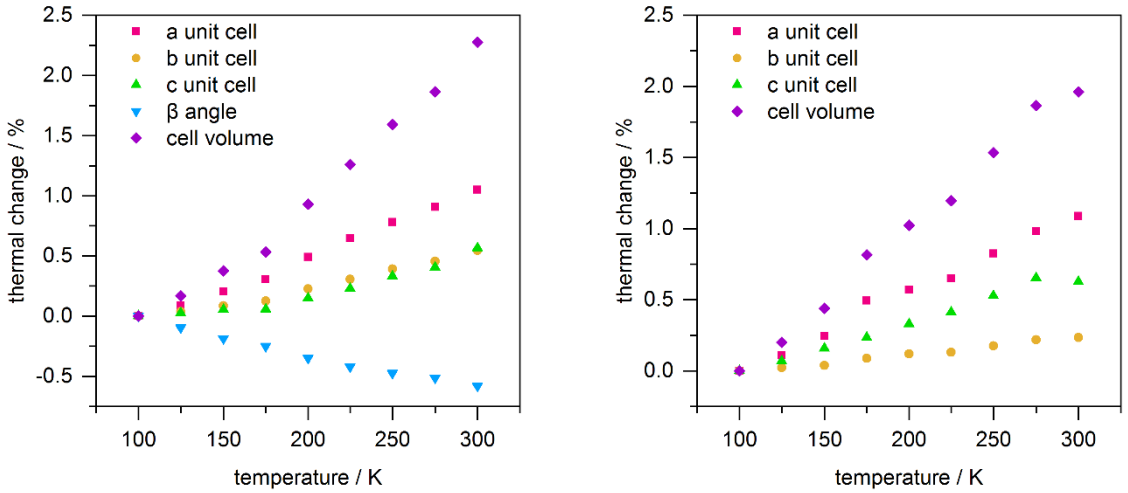


Figure S3. Cell parameters changes with temperature in structure of (a) **$LiClO_4$·βAla**, (b) **$LiClO_4$·2βAla-I** (c) **$LiClO_4$·2βAla-II**.

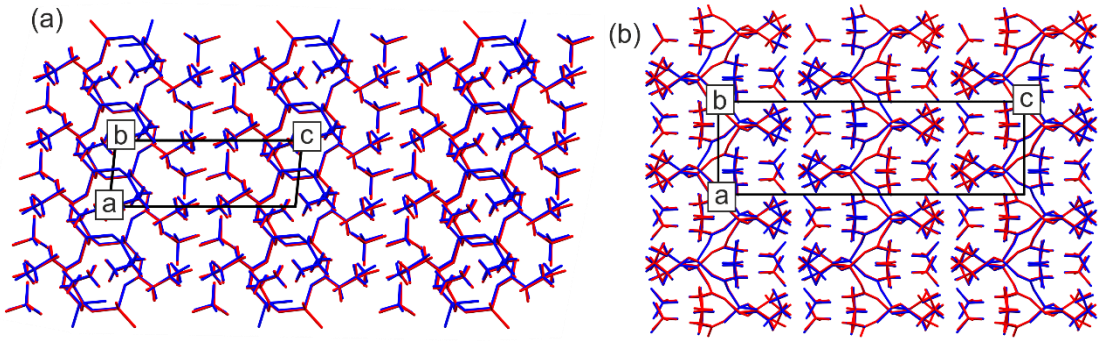


Figure S4. An overlay of experimental (blue) and optimized in CRYSTAL09 program (red) crystal structures for (a) **$LiClO_4$·2βAla-I** and (b) **$LiClO_4$·2βAla-II**.

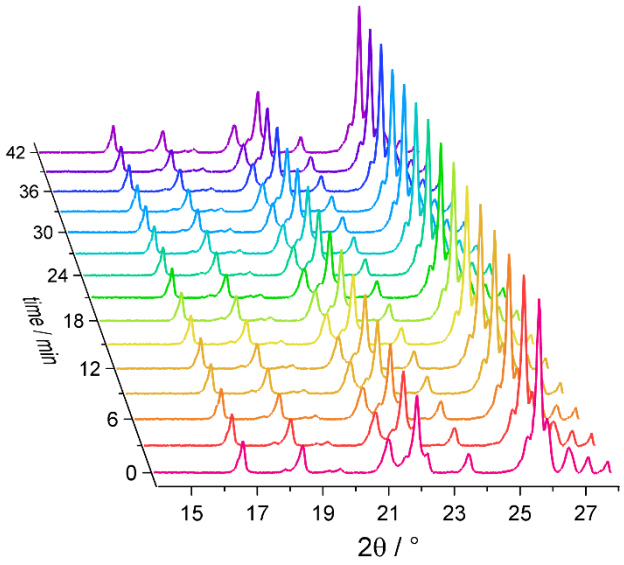


Figure S5. Powder diffraction patterns of dried crystals of **$LiClO_4$·2βAla-I** phase. No transition is observed. Measurements taken in 3 minutes interval.

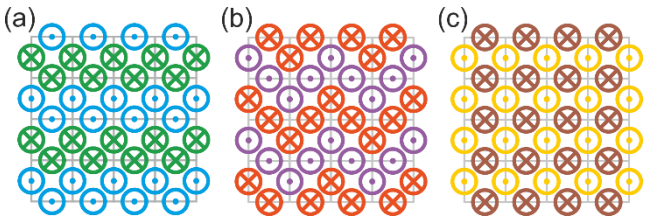


Figure S6. Observed types of grids considering amino acid side chain positions. (a) Network corresponding to **$LiClO_4$·βAla-I**, (b) **$LiClO_4$·βAla-II**, EVUWAU, EVUWEY and (c) ROZTUW. Direction of the amino acid side chain facing forward and backward was marked with a spot and a cross, respectively.

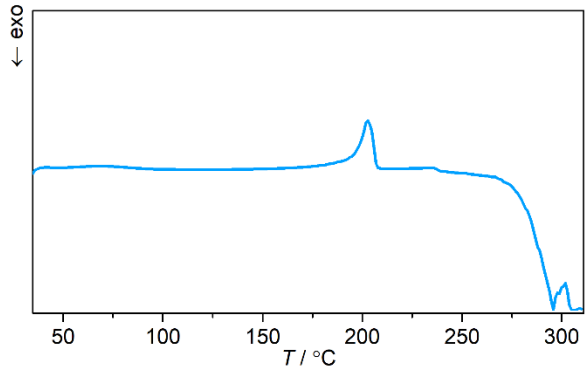


Figure S7. DSC profiles of $LiClO_4$·βAla. Melting point temperature melting point temperature (T_m) and Fusion Enthalpy (ΔH) are equal 198.8°C and 19.96 kJ/mol, respectively.

Table S1. Temperature changes of unit cell parameters observed for single crystal of **$LiClO_4$·βAla**

T/ K	**100**	**125**	**150**	**175**	**200**	**225**	**250**	**275**	**300**
a/ Å	24.142(2)	24.168(2)	24.1895(18)	24.2220(12)	24.2449(10)	24.2738(11)	24.2971(13)	24.3181(13)	24.3358(15)
b/ Å	5.0158(5)	5.0202(5)	5.0199(4)	5.0223(3)	5.0250(2)	5.0285(3)	5.0323(3)	5.0338(3)	5.0342(3)
c/ Å	14.5186(13)	14.5481(13)	14.5700(11)	14.6062(7)	14.6364(6)	14.6699(7)	14.7002(8)	14.7301(8)	14.7589(9)
β/ °	125.826(3)	125.873(3)	125.930(2)	125.970(2)	126.0330(10)	126.095(2)	126.143(2)	126.205(2)	126.284(2)
V/ Å	1425.4(2)	1430.3(2)	1432.60(19)	1438.04(13)	1442.00(10)	1446.89(13)	1451.48(14)	1454.97(14)	1457.52(16)

Table S2. Temperature changes of unit cell parameters observed for single crystal of **$LiClO_4$·2βAla-I**

T/ K	**100**	**125**	**150**	**175**	**200**	**225**	**250**	**275**	**300**
a/ Å	4.9651(5)	4.9695(5)	4.9751(5)	4.9806(6)	4.9877(5)	4.9950(4)	5.0019(3)	5.0070(4)	5.0148(4)
b/ Å	8.4352(6)	8.4373(6)	8.4418(7)	8.4459(7)	8.4513(6)	8.4590(4)	8.4670(4)	8.4718(5)	8.4785(5)
c/ Å	13.9521(13)	13.9520(13)	13.9552(13)	13.9599(15)	13.9671(12)	13.9822(9)	13.9973(9)	14.0090(10)	14.0278(10)
β/ °	95.970(4)	95.884(4)	95.792(4)	95.731(5)	95.635(4)	95.562(3)	95.504(2)	95.460(3)	95.410(3)
V/ Å	581.17(9)	581.91(9)	583.11(9)	584.30(11)	585.90(9)	588.00(7)	590.07(6)	591.54(7)	593.78(7)

Table S3. Temperature changes of unit cell parameters observed for single crystal of **$LiClO_4$·2βAla-II**

T/ K	**100**	**125**	**150**	**175**	**200**	**225**	**250**	**275**	**300**
a/ Å	8.3654(6)	8.3746(6)	8.3857(8)	8.4066(10)	8.4131(5)	8.4197(4)	8.4344(4)	8.4476(4)	8.4564(7)
b/ Å	9.9427(7)	9.9449(7)	9.9466(10)	9.9514(12)	9.9546(5)	9.9556(5)	9.9602(4)	9.9645(5)	9.9661(8)
c/ Å	27.587(2)	27.6060(19)	27.630(3)	27.652(3)	27.6779(16)	27.7010(14)	27.7324(13)	27.7670(13)	27.760(2)
V/ Å	2294.5(3)	2299.2(3)	2304.6(4)	2313.3(5)	2318.0(2)	2322.0(2)	2329.75(18)	2337.32(19)	2339.5(3)

Table S4. Parameters of the functions fitted to atomic parameters used for determination of thermal expansion tensor.

structure	atomic parameter	fitted function
$LiClO_4$·βAla	a	$f(T)=24.048 + 9.8612\cdot10^{-4}\cdot T$
	b	$f(T)=5.0056 + 1.0014\cdot10^{-4}\cdot T$

	c	$f(T)=14.392 + 0.0012289 \cdot T$
	β	$f(T)=125.58 + 0.0022873 \cdot T$
$LiClO_4$·2βAla-I	a	$f(T)=4.9337 + 2.6977 \cdot 10^{-4} \cdot T$
	b	$f(T)=8.4073 + 2.287 \cdot 10^{-4} \cdot T$
	c	$f(T)=13.959 -2.5543 \cdot 10^{-4} \cdot T + 1.5722 \cdot 10^{-6} \cdot T^2$
	β	$f(T)=96.209 -0.0027546 \cdot T$
$LiClO_4$·2βAla-II	a	$f(T)=8.3177 + 4.6673 \cdot 10^{-4} \cdot T$
	b	$f(T)=9.9295 + 1.2296 \cdot 10^{-4} \cdot T$
	c	$f(T)=27.483 + 9.9243 \cdot 10^{-4} \cdot T$

Table S5. Diagonalized thermal expansion tensor element / 10-5 K-1 for obtained ICCs calculated at 100 K.

element	**$LiClO_4$·βAla**	**$LiClO_4$·2βAla-I**	**$LiClO_4$·2βAla-II**
S_{11}	1.18020	-0.31203	5.58000
S_{22}	1.99660	2.71290	1.23680
S_{33}	8.49040	6.67290	3.59810

Table S6. Deviations of all atoms engaged in formation of the 16- or 6-membered rings from the mean plane and τ4' parameter for structures reported herein and structures from CSD database.

		mean deviation / Å		τ_4' parameter
16-membered rings	ROZTUW	**0.839**		0.918
	$LiClO_4$·2βAla-I	**0.695**		0.833
	EVUWEY	0.281	*mean:*	0.891
		0.341	0.311	
	EVUWAU	0.210	*mean:*	0.854
		0.497	0.353	
	$LiClO_4$·2βAla-II	0.346	*mean:*	0.844
		0.301	0.323	
6-membered rings	AZIPIK	0.144		0.889
	AZIPOQ	0.138		0.901
	AZIPUW	0.140		0.905
	AZIQAD	0.106		0.862
	GLYLIB	0.251		0.874
	HEFWUK	0.139		0.923
	NOCXIO	0.140		0.901
	NOCXIO01	0.139		0.897
	$LiClO_4$·βAla	0.155		0.904
	YOXBET	0.143		0.912

Table S7. Bond lengths present in **$LiClO_4$·βAla**, **$LiClO_4$·2βAla-I** and **$LiClO_4$·2βAla-II** crystal structures.

Bond / Å	**$LiClO_4$·βAla**	**$LiClO_4$·2βAla-I**		**$LiClO_4$·2βAla-II**	
	x = 0	x = 0	x = 1	x = 0	x = 1
Cx1 – Ox5	1.2589(14)	1.263(2)	1.252(2)	1.2459(16)	1.2576(16)
Cx1 – Ox6	1.2632(13)	1.255(2)	1.264(2)	1.2674(16)	1.2624(16)
Cx1 – Cx2	1.5203(15)	1.525(3)	1.522(3)	1.5244(18)	1.5244(18)
Cx2 – Cx3	1.5284(16)	1.519(3)	1.519(3)	1.5197(18)	1.5204(19)
C3 – Nx1	1.4954(15)	1.499(3)	1.494(2)	1.4959(18)	1.4982(18)
Li1 – Ox6	1.929(2)	1.920(4)	1.947(4) [3]	1.910(3) [4]	1.943(3)
Li1 – Ox5	1.918(2) [1]	1.909(4) [2]	1.898(4)	1.877(3)	1.940(3) [5]
Cl1 – O1	1.4495(9)	1.422(2)		1.4437(10)	
Cl1 – O2	1.4331(10)	1.419(2)		1.4468(10)	
Cl1 – O3	1.4480(9)	1.431(2)		1.4464(10)	
Cl1 – O4	1.4430(9)	1.4356(16)		1.4377(11)	
Li1 – O1	1.999(2)				

[1] +x, 1+y, +z; [2] 1+x, +y, +z; [3] 1-x, 1/2+y, 2-z; [4] -1/2+x, 3/2-y, 1-z; [5] 1/2-x, 1/2+y, +z

Coordinates of **LiClO4·2βAla-I** after optimization in CRYSTAL09 at DFT(B3LYP)/TZVP level of theory (only asymmetric unit is presented).

Cl	0.0296573154679	-0.270517889115	0.386800815978
O	0.0728898818156	0.315741170272	-0.0317475335325
O	0.321899599167	-0.140984214627	-0.127052967208
O	-0.305138866457	-0.160551698212	-0.202793741833
O	0.0565731843247	-0.439264129306	-0.090764231225
O	0.36231322345	-0.250923371485	0.395699881948
N	-0.46027702026	0.143741322856	-0.0643396577593
N	0.49802489345	-0.140306885045	-0.405599788511
C	0.448171421017	-0.187520008036	-0.196297632274
C	-0.0385313075442	0.423343672592	-0.0851963259544
C	-0.301781989201	0.386452000302	-0.145642711571
H	-0.286782000834	0.434050009507	-0.217226799027
H	-0.463594172731	0.452443307542	-0.116208520618
C	0.292328183448	-0.28165046772	-0.275901504312
H	0.0945579691458	-0.227445811989	-0.292887355322
H	0.252324029652	-0.398298156325	-0.247207809702
C	0.439882707566	-0.30027274388	-0.364309990199
H	0.317754351704	-0.3649618651	-0.419743675627
H	-0.36666353395	-0.359173493366	-0.348793372767
C	-0.373721122425	0.212652777076	-0.155049398914
H	-0.205344493706	0.142109230398	-0.174593183076
H	0.458144438779	0.197586261068	-0.210177551148
Li	-0.0284105810793	-0.218085191387	-0.103649727752
O	-0.114070095469	-0.146082761111	0.307678251947
O	-0.0759515252636	-0.236727644743	0.493332750645
O	-0.0404679158806	-0.456430884241	0.353505159396
H	-0.301906007908	0.133011304601	-0.0109022155106
H	0.386627303009	0.212081182578	-0.0411983783485
H	0.330072273476	-0.0686370527894	-0.408093372472
H	-0.445382408367	-0.15461155863	-0.47354632855
H	0.463643182002	0.0303882291193	-0.0797492282032
H	-0.348784226171	-0.0855046408042	-0.363318238176

Coordinates of **LiClO4·2βAla-II** after optimization in CRYSTAL09 at DFT(B3LYP)/TZVP level of theory (only asymmetric unit is presented).

Cl	-0.167438093101	-0.18244623236	-0.318309912075
O	0.313764565793	-0.494057137549	-0.403513584063
O	0.235865439532	0.306248516114	-0.375111703689
O	-0.472298516685	0.279569351235	0.467635174336
O	0.374499096801	0.173639867217	-0.478941464317
O	-0.160933899319	-0.281913467817	-0.366116424906
O	-0.15961086069	-0.0238953612669	-0.336188329791
O	-0.0159024653647	-0.213784030884	-0.281284715157
O	-0.334542152861	-0.206148113373	-0.288249701057
N	0.0978673630289	0.0940860546319	0.445717012429
H	0.115427022712	0.165807747482	0.419547598273
H	0.0746658685123	0.142869188781	0.478597552121
H	-0.00515271777434	0.0443238994087	0.435007385629
N	0.377233383359	-0.3642004453	-0.305438282465
H	0.33856435694	-0.293657036907	-0.331307309432
H	0.472261741433	-0.416546099124	-0.319490715665
H	0.416626667315	-0.312907669873	-0.275461705049
C	0.236245630662	0.433602208891	-0.374145483758
C	0.433069807598	0.185125543114	0.479508943603
C	0.39488812042	0.0799399359998	0.441384254892
H	0.397278693929	0.127037117228	0.405849590287
H	0.492647080811	0.00729219634084	0.442350121426
C	0.244165354796	-0.458105295508	-0.291624998887
H	0.172904815432	-0.405482453861	-0.264911983709
H	0.29875894861	0.454807235461	-0.274674689268
C	0.240547052839	0.00341216996677	0.449087743339
H	0.227359678404	-0.0731494967504	0.421413634138
H	0.237254014729	-0.0441932971941	0.48443849666
C	0.141245051428	-0.495795650435	-0.334863702648
H	0.0863914497997	-0.405809352658	-0.349789862305
H	0.0457747345262	0.439309606396	-0.321836811944
Li	0.216625785894	0.185145904389	-0.430381485275