Supporting Information

Simple Guanidinium Salts Revisited: Room-Temperature Ferroelectricity in Hydrogen-Bonded Supramolecular Structures

Marek Szafrański

Faculty of Physics, Adam Mickiewicz University, Umultowska 85, 61-614 Poznań, Poland

E-mail: masza@amu.edu.pl

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Table S1. Crystal data and structure refinement details for $GHBF_4$ at several temperatures from the temperature range between 100 and 400 K.

Temperature (K)	100	150	200	250	295
Crystal system, space group			Hexagonal, *R*3*m*		
Unit cell dimensions: *a* (Å)	7.40437(9)	7.41170(17)	7.4172(2)	7.4301(2)	7.4535(6)
c(Å)	8.75770(13)	8.8351(2)	8.9126(3)	9.0154(4)	9.1038(9)
Volume ($Å^3$)	415.812(9)	420.32(2)	424.74(2)	431.02(3)	438.00(7)
Z, Calculated density (g/cm^3)	3, 1.760	3, 1.741	3, 1.723	3, 1.698	3, 1.671
Absorption coefficient (mm^{-1})	0.207	0.205	0.202	0.200	0.196
Crystal size (mm)	0.38×0.34×0.27	0.29×0.28×0.23	0.33×0.30×0.25	0.29×0.28×0.23	0.38×0.34×0.27
Θ range (^{o})	3.94 to 41.01	3.92 to 30.09	3.91 to 45.50	3.89 to 30.00	3.87 to 37.47
Max/min limiting indices h, k, l	-13/13,-13/13,-16/15	-10/10,-10/10,-12/12	-14/14,-14/13,-17/9	-10/10,-10/10,-12/12	-12/12,-12/12,-15/15
Reflections collected/unique (R_{int})	8848/708(0.0234)	2845/325(0.0179)	1583/729(0.0082)	2929/331(0.0216)	5848/589(0.0192)
Completeness to θ_{max} (%)	99.4	97.1	99.1	97.2	98.7
Refinement method			Full-matrix least-squares on F^2		
Data/restrains/parameters	708/1/26	321/1/26	729/1/26	331/1/27	589/1/27
Goodness-of-fit on F^2	1.210	1.134	1.016	1.086	1.072
R_1/wR_2 indices [$I>2\sigma_I$]	0.0189/0.0522	0.0199/0.0542	0.0316/0.0813	0.0249/0.0659	0.0387/0.1165
R_1/wR_2 indices [all data]	0.0191/0.0523	0.0199/0.0542	0.0340/0.0826	0.0252/0.0662	0.0489/0.1280
Max/min ΔF ($e.Å^{-3}$)	0.280/-0.182	0.176/-0.114	0.363/-0.134	0.189/-0.083	0.249/-0.124

Table S1. continued

Temperature (K)	320	350	370	400
Crystal system, space group		Hexagonal, *R*3*m*		
Unit cell dimensions: *a* (Å)	7.4793(3)	7.51121(6)	7.5381(4)	7.5823(7)
c(Å)	9.1760(5)	9.2294(11)	9.2589(8)	9.2887(12)
Volume (Å^3)	444.54(3)	451.05(7)	455.63(5)	462.48(8)
Z, Calculated density (g/cm^3)	3, 1.646	3, 1.622	3, 1.606	3, 1.582
Absorption coefficient (mm^{-1})	0.193	0.191	0.189	0.186
Crystal size (mm)	0.29×0.28×0.23	0.29×0.28×0.23	0.29×0.28×0.23	0.29×0.28×0.23
Θ range (^{o})	3.85 to 30.19	3.83 to 30.04	3.82 to 28.43	3.80 to 30.31
Max/min limiting indices h, k, l	-10/10,-10/10,-12/12	-10/10,-10/10,-12/12	-10/10,-9/10,-12/12	-10/10,-10/10,-12/13
Reflections collected/unique (R_{int})	3097/349(0.0219)	3066/315(0.0205)	3265/310(0.0257)	2848/365(0.0176)
Completeness to θ_{max} (%)	98.4	98.9	98.8	98.4
Refinement method		Full-matrix least-squares on F^2		
Data/restrains/parameters	349/1/26	351/1/22	310/3/29	365/3/29
Goodness-of-fit on F^2	1.143	1.178	1.131	1.101
R_1/wR_2 indices [$I>2\sigma_I$]	0.043/0.01330	0.0539/0.1656	0.0449/0.1263	0.0563/0.1797
R_1/wR_2 indices [all data]	0.0457/0.1365	0.0622/0.1790	0.0563/0.1374	0.0803/0.2078
Max/min ΔF (e.Å^{-3})	0.278/-0.141	0.266/-0.149	0.130/-0.118	0.139/-0.111

Table S2. Crystal data and structure refinement details for $GHClO_4$ at several temperatures from the temperature range between 100 and 375 K.

Temperature (K)	100	125	150	175	210	250
Crystal system, space group			Hexagonal, *R*3*m*			
Unit cell dimensions: *a* (Å)	7.5566(2)	7.5590(2)	7.56586(15)	7.5643(3)	7.57142(15)	7.5826(3)
c(Å)	8.8263(3)	8.8937(3)	8.8972(3)	8.9165(4)	8.9748(32)	9.0356(4)
Volume ($Å^3$)	436.47(2)	438.11(2)	441.065(18)	441.84(3)	445.565(17)	449.91(3)
Z, Calculated density (g/cm^3)	3, 1.821	3, 1.814	3, 1.802	3, 1.799	3, 1.784	3, 1.766
Absorption coefficient (mm^{-1})	0.606	0.604	0.600	0.599	0.594	0.588
Crystal size (mm)	0.37×0.30×0.28	0.37×0.30×0.28	0.44×0.33×0.29	0.37×0.30×0.28	0.36×0.34×0.26	0.44×0.33×0.29
Θ range (^{o})	3.88 to 31.92	3.87 to 31.88	3.86 to 54.01	3.86 to 31.81	3.85 to 37.36	3.84 to 54.01
Max/min limiting indices h, k, l	-11/11,-11/11,-12/13	-11/11,-11/11,-13/13	-17/14,-11/15,-19/13	-11/11,-11/11,-13/13	-12/12,-12/12,-15/15	-16/10,-8/17,-8/20
Reflections collected/unique (R_{int})	5444/403(0.0197)	2826/401(0.0246)	1703/997(0.0213)	2848/402(0.0235)	4380/592(0.0214)	1820/815(0.0190)
Completeness to θ_{max} (%)	100	100	92.4	100	98.4	96.1
Refinement method			Full-matrix least-squares on F^2			
Data/restrains/parameters	403/1/26	401/1/26	997/1/26	402/1/26	592/1/26	815/1/27
Goodness-of-fit on F^2	1.200	1.135	1.010	1.213	1.149	0.998
R_1/wR_2 indices [$I>2\sigma_I$]	0.0134/0.0373	0.0153/0.0402	0.0221/0.0561	0.0157/0.0415	0.0151/0.0411	0.0278/0.0707
R_1/wR_2 indices [all data]	0.0134/0.0373	0.0153/0.0402	0.0225/0.0562	0.0157/0.0415	0.0152/0.0412	0.0339/0.0740
Max/min ΔF ($e.Å^{-3}$)	0.217/-0.232	0.363/-0.194	0.325/-0.471	0.281/-0.195	0.219/-0.217	0.226/-0.292

Table S2. continued

Temperature (K)	270	295	325	350	375
Crystal system, space group			Hexagonal, *R*3*m*		
Unit cell dimensions: *a* (Å)	7.58491(19)	7.5590(2)	7.6045(3)	7.6180(4))	7.6428(15)
c(Å)	9.0692(3)	8.8937(3)	9.1725(5)	9.2288(7)	9.277(4)
Volume (Å^3)	451.86(2)	438.11(2)	459.37(4)	463.83(5)	469.3(2)
Z, Calculated density (g/cm^3)	3, 1.759	3, 1.814	3, 1.730	3, 1.713	3, 1.693
Absorption coefficient (mm^{-1})	0.586	0.604	0.576	0.5971	0.564
Crystal size (mm)	0.37×0.30×0.28	0.44×0.33×0.29	0.37×0.30×0.28	0.37×0.30×0.28	0.37×0.30×0.28
Θ range (^{o})	3.83 to 32.11	3.87 to 31.88	3.81 to 32.10	3.80 to 32.15	3.78 to 32.32
Max/min limiting indices h, k, l	-11/11,-11/11,-13/13	-11/11,-11/11,-13/13	-11/11,-11/11,-13/13	-11/11,-11/11,-13/13	-11/11,-11/11,-13/13
Reflections collected/unique (R_{int})	5607/417(0.0285)	2826/401(0.0246)	1950/415(0.0200)	1971/419(0.0204)	1992/423(0.0293)
Completeness to θ_{max} (%)	100	100	99.1	99.1	96.4
Refinement method			Full-matrix least-squares on F^2		
Data/restrains/parameters	417/1/27	401/1/26	415/1/27	419/1/27	423/1/27
Goodness-of-fit on F^2	1.115	1.135	1.182	1.221	1.098
R_1/wR_2 indices [$I>2\sigma_I$]	0.0166/0.0465	0.0153/0.0402	0.0193/0.0554	0.0209/0.0604	0.0327/0.0900
R_1/wR_2 indices [all data]	0.0167/0.0466	0.0153/0.0402	0.0193/0.0554	0.0209/0.0605	0.0334/0.0906
Max/min ΔF (e.Å^{-3})	0.217/-0.292	0.363/-0.194	0.220/-0.128	0.201/-0.134	0.229/-0.152

Table S3. Geometry of hydrogen bonds in $GHBF_4$.

T (K)	N–H	F···H	N···F	∠NHF
100	0.875(10)	2.087(10)	2.9581(3)	173.7(10)
150	0.856(15)	2.111(15)	2.9651(6)	175.0(13)
200	0.877(14)	2.110(13)	2.9714(5)	167.2(15)
250	0.865(17)	2.125(17)	2.9850(8)	172.7(14)
295	0.89(2)	2.11(2)	3.0014(7)	174.7(18)
320	0.95(3)	2.07(3)	3.0173(13)	176(2)
350	0.86	2.20	3.055(2)	171.9
370	0.86	2.23	3.0806(19)	169.7
400	0.86	2.27	3.115(3)	168.4

Table S4. Geometry of hydrogen bonds in $GHClO_4$

T (K)	N–H	O···H	N···O	∠NHO
100	0.814(10)	2.213(10)	3.0238(6)	173.7(13)
125	0.831(10)	2.199(10)	3.0259(6)	173.6(14)
150	0.840(12)	2.194(12)	3.0308(4)	173.9(16)
175	0.833(10)	2.201(11)	3.0312(7)	174.3(14)
210	0.821(9)	2.220(9)	3.0371(5)	174.2(13)
250	0.847(16)	2.198(16)	3.0448(7)	177(2)
270	0.820(12)	2.230(12)	3.0483(8)	175.1(16)
300	0.842(19)	2.213(19)	3.0535(8)	176(2)
325	0.781(15)	2.284(15)	3.0638(10)	175.8(19)
350	0.741(17)	2.337(17)	3.0761(12)	175(2)
375	0.71(3)	2.39(3)	3.095(2)	175(4)

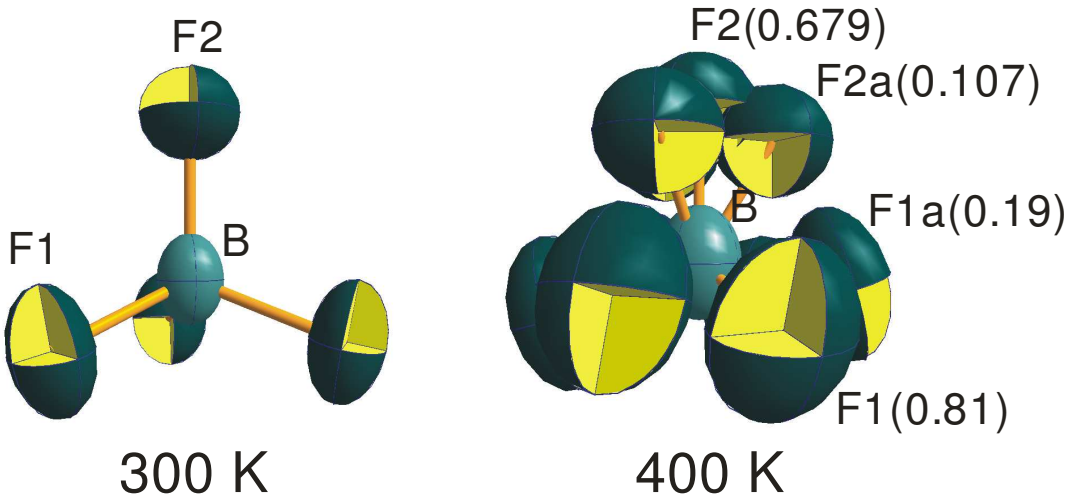

Figure S1. The BF_4^- anion: ordered at 300 K and partially disordered at 400 K. The occupancy factors are listed in brackets.

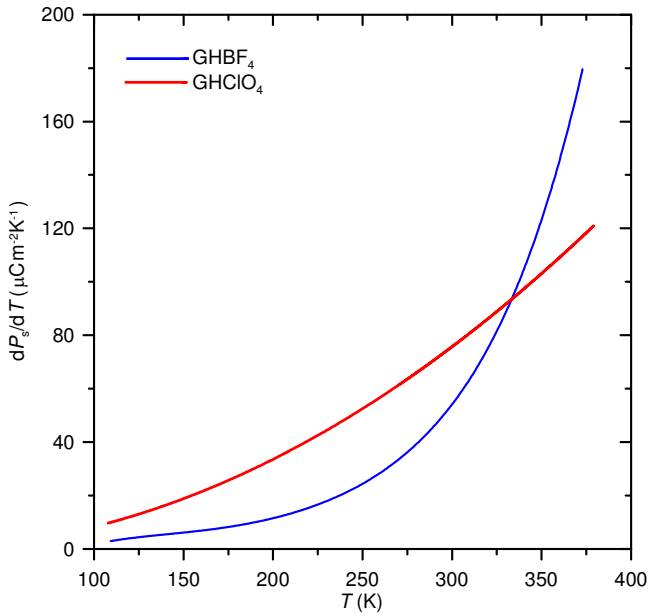

Figure S2. Temperature dependences of pyroelectric coefficients of $GHBF_4$ and $GHClO_4$.