Supplementary Information

Ionisation of atoms determined by kappa refinement against 3D electron diffraction data

Ashwin Suresh *et al.*

*Corresponding author. Email: palat@fzu.cz

This file includes:

Supplementary Materials and Methods

XRD data collection & processing

The samples natrolite and borane were measured using Rigaku OD Supernova equipped with Atlas S2 CCD detector, using Mo-Kα radiation (λ = 0.71073 Å) from the microfocused sealed X-ray tube. The samples were cooled during the measurement using open-flow Cryostream 800 from Oxford Cryosystems to 100 K. The data collection, integration, scaling and absorption correction were handled in CrysAlis PRO[1]. Given the weaker high-angle diffraction maxima in borane, the data collection was set up to a resolution of 0.50 Å, while in the case of sample natrolite, the data was collected up to 0.40 Å resolution. Both datasets had considerable average redundancy of 9.4 and 11.3 for natrolite and borane respectively.

DFT calculations

To ensure a comprehensive understanding of the structure of investigated materials, we employed a range of exchange-correlation functionals and basis sets. The selected combinations and their justifications are as follows:

Functionals

B3LYP (Becke, 3-parameter, Lee-Yang-Parr)[2]:

B3LYP is a widely used hybrid functional that combines Hartree-Fock exchange with DFT exchange correlation. It has been extensively validated for various materials and is known for providing a good balance between accuracy and computational cost, therefore we employed it for quartz, borane and natrolite.

HSE06 (Heyd-Scuseria-Ernzerhof)[3]:

The HSE06 functional is a screened hybrid functional that improves upon the long-range exchange interactions by introducing a range-separation parameter. This functional is particularly effective for systems with localized states, therefore we choose to test its performance with quartz and natrolite.

PBESOL (Perdew-Burke-Ernzerhof for solids)[4]:

PBESOL is a variant of the PBE functional optimized for solid-state systems. It modifies the original PBE functional to better reproduce the equilibrium properties of densely packed solids

and is often used for materials with strong periodicity, therefore we picked it for quartz, borane and natrolite.

wB97-X (ωB97X)[5]:

The ωB97X functional is a range-separated hybrid functional that includes both long-range and short-range exchange interactions. It is known for its accuracy in predicting molecular properties, therefore we expected its application to borane to provide accurate electronic properties and insight into the nature of bonding in this molecule.

M05-2X (M052X)[6]:

M052X is a meta-hybrid functional incorporating both Hartree-Fock exchange and density functional theory (DFT) exchange-correlation. It is designed to accurately predict thermochemical properties and reaction barriers. For borane, which is a small molecule with significant electron correlation effects, M052X offers a good balance of accuracy and computational cost.

Basis Sets

POB-TZVP-REV2[7]:

The POB-TZVP-REV2 basis set is an optimized triple-zeta valence basis set designed for periodic systems. It provides a balanced approach to computational efficiency and accuracy, making it suitable for large-scale calculations in solid-state chemistry. We chose this basis set for quartz, borane and natrolite.

cc-pVDZ (Correlation Consistent polarized Valence Double Zeta)[8]:

The cc-pVDZ basis set is designed to accurately describe valence electrons while maintaining computational efficiency. It's a rather broad and non-specialized basis set, therefore we choose it for quartz, borane and natrolite.

AhlrichsVDZ[9]:

The AhlrichsVDZ basis set is another commonly used double-zeta basis set known for its computational efficiency and reliable performance in DFT calculations. Its inclusion in this study was justified by the low computational cost of using this basis set, therefore we tried to employ it for quartz, borane and natrolite.

Justification

We based our choice of functional/basis set pair on a few criteria. First was a sensible, low total energy obtained from the optimization of charges of the molecules. Second was the sensibility of the charges themselves, and third was the values of P_{val} and kappas obtained during the refinement.

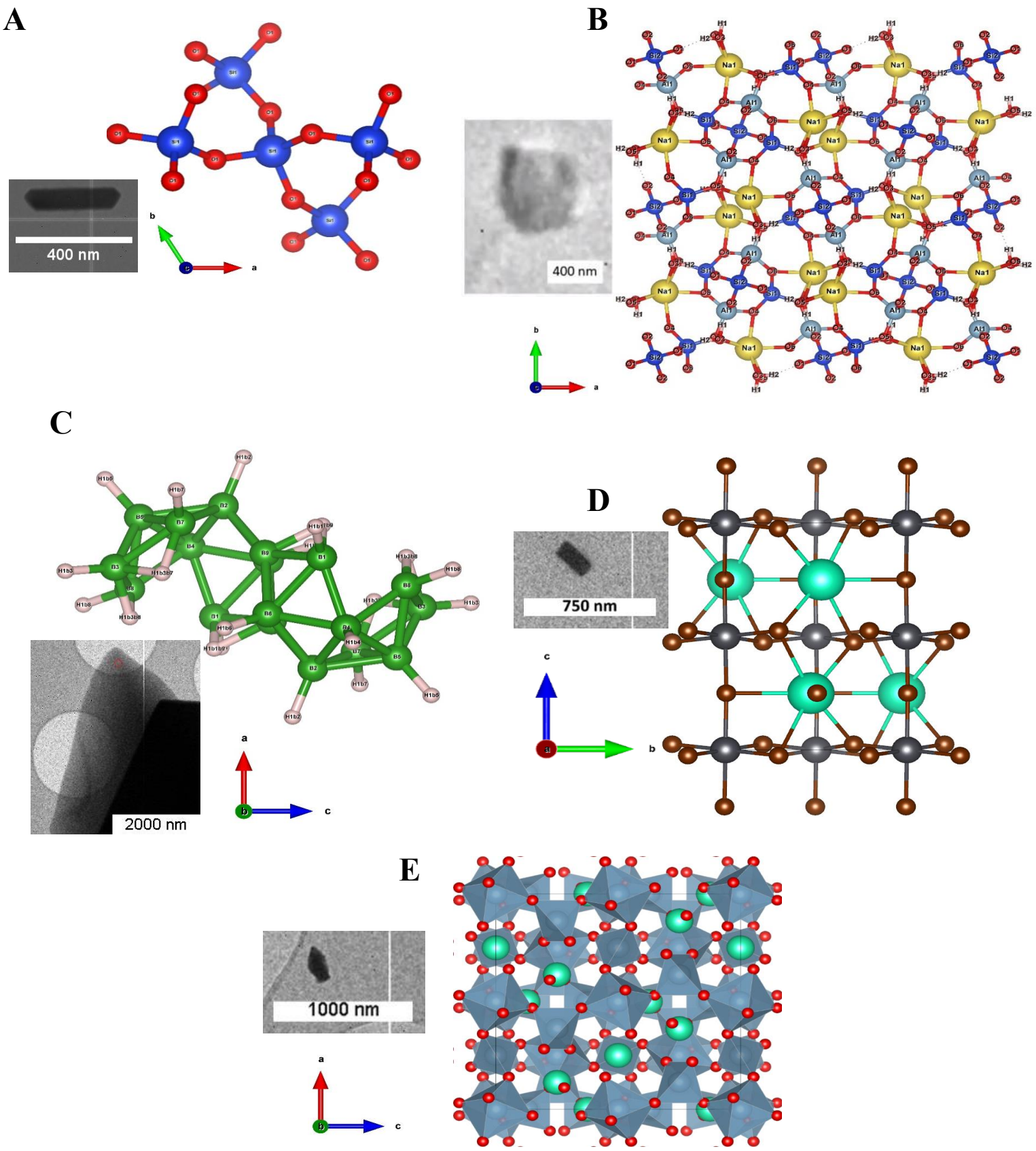
We did not pick R-factors as the criterion of our evaluation, as the differences in R-factors were small.

For quartz and natrolite, the evaluation was straightforward. Calculations yielded results that had low energy, with charges, Pvals and kappas all having reasonable values. Different sets of calculations were in agreement with each other, we therefore chose those with the lowest energies.

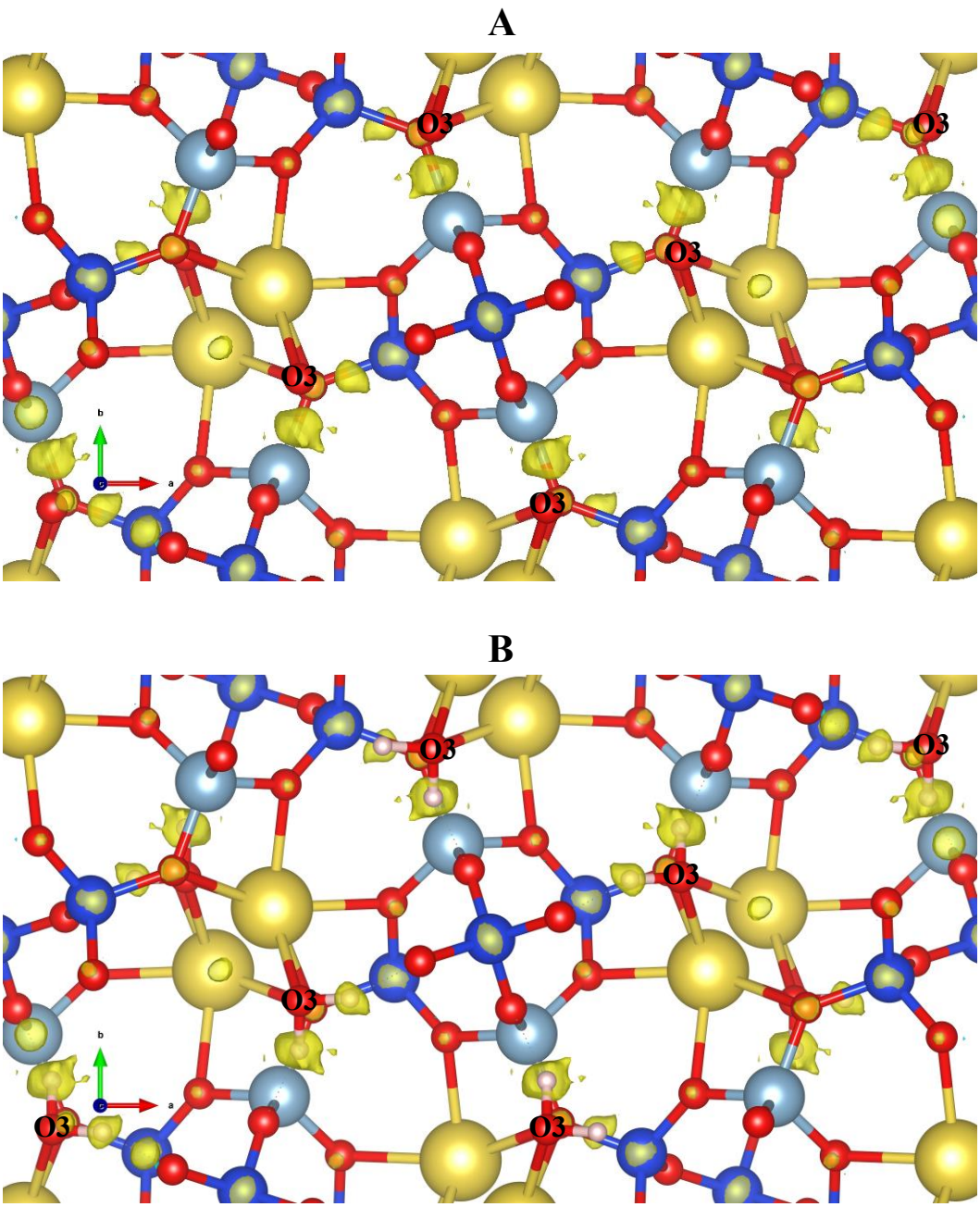
For Borane, the results differed noticeably with the basis set used. Using the AhlrichsVDZ basis set yielded the lowest energies, but unfortunately, the calculations failed to correctly predict the distribution of charges in the molecule, giving physically non-meaningful results. Similar results were obtained with the cc-pVDZ basis set. POB-TZVP 79 basis set gave the best results in terms of the quality of the refinements in providing meaningful charge density values

An alternative (to Crystal23) *ab initio* approach (all-electron augmented plane wave + local orbitals) implemented in Wien2k code was used to work with systems containing heavier atoms and given its larger computational cost, we focused only on cases with a smaller number of atoms per unit cell: we first tested form factors for quartz and found good agreement with results from Crystal23; here we used generalised gradient approximation (GGA) as starting point and checked that differences to local density approximation (LDA) are small. Convergence with respect to the number of k-points in the Brillouin zone and increased values of the plane-wave expansion parameter (RKMAX was increased from the recommended value up to 9.0) were tested. Cut-off of the plane-wave expansion G_{max}[10] was kept at default values Next, we evaluated the form factors for Cs-perovskite and LuAG and found only moderate change in form factors upon increasing RKMAX from default recommended values. Control calculations were performed also for natrolite.

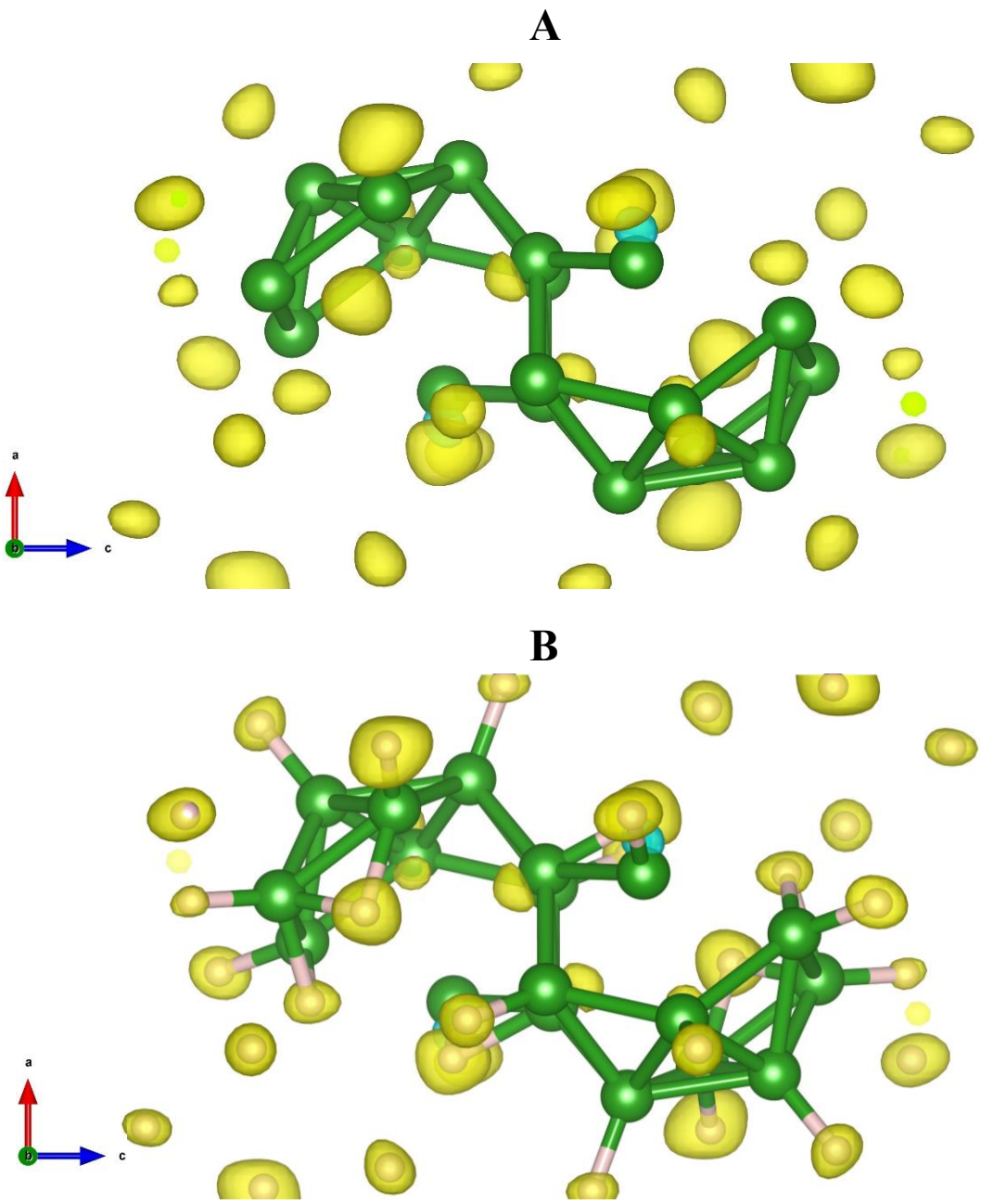
Supplementary Tables 7 to 11 show a comparison between some of the combinations of functionals and basis sets employed for the different data sets.



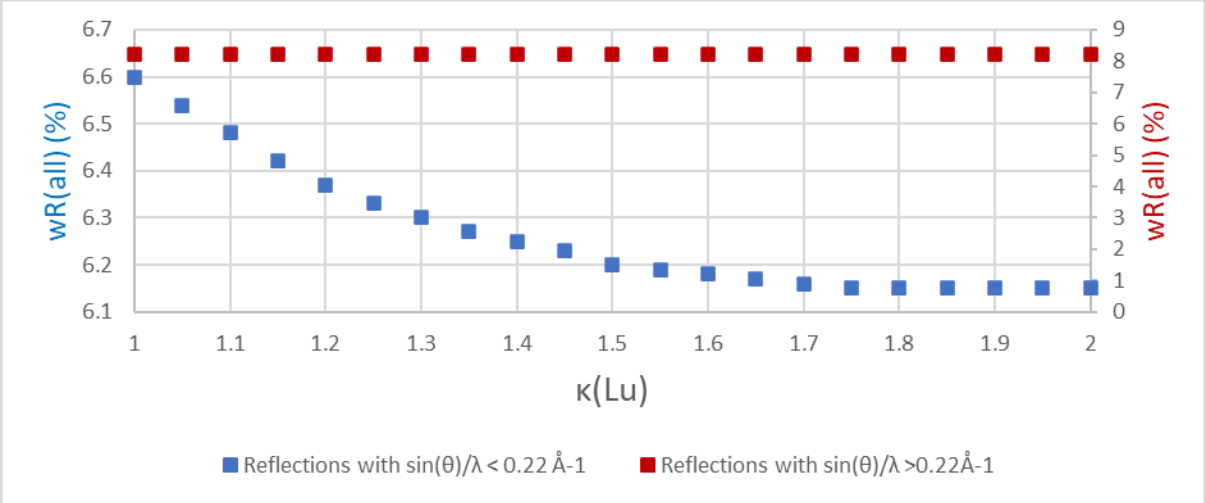
Supplementary Fig.1. Projections of crystal structures of the compound chosen for this study. (**A**) Quartz, (**B**) Natrolite, (**C**) Borane, (**D**) Cs-perovskite, (**E**) LuAG



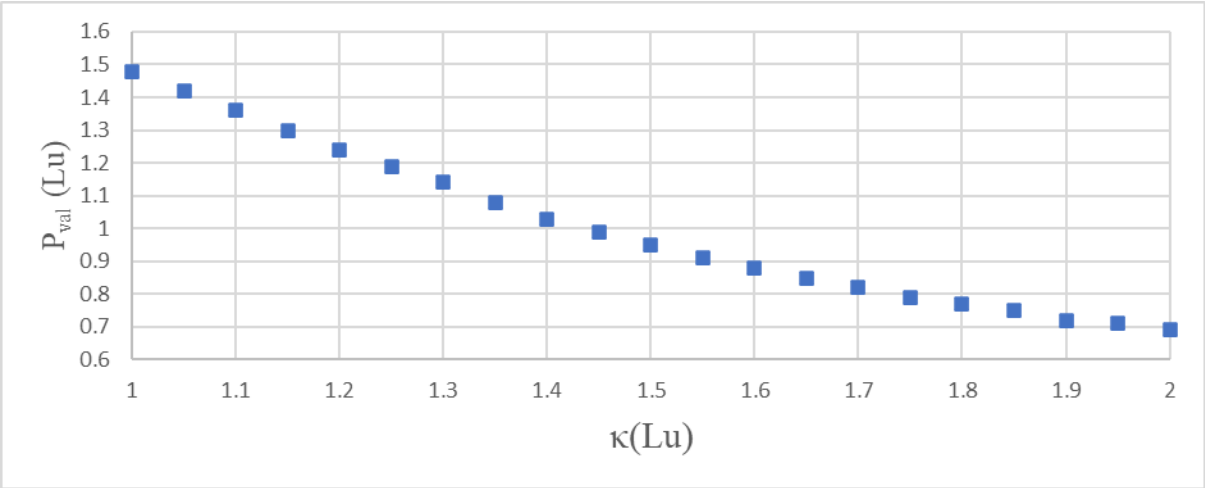
Supplementary Fig.2. Determination of Hydrogen atoms in Natrolite. 3D difference Fourier maps without hydrogen atoms (A) and with hydrogen atoms added (B) at 1.5 σ (ΔV(r)) isosurface drawn in vesta. 2 hydrogen atoms (drawn in white) were identified from the local maxima (plotted in yellow) near the oxygen atom labelled O3 (drawn in red).



Supplementary Fig.3. Determination of Hydrogen atoms in Borane. 3D difference Fourier maps without hydrogen atoms (A) and with hydrogen atoms added (B) at 1.5 σ (ΔV(r)) isosurface drawn in vesta. 11 hydrogen atoms (drawn in white) in each of the two cages were identified from the local maxima (plotted in yellow) near the boron atoms (drawn in green).



Supplementary Fig.4. The plot of wR(all) as a function of κ(Lu) for high- and low-resolution reflections separated at sin(θ) /λ = 0.22 Å^{-1}. At each step, all parameters except for κ(Lu) were refined.



Supplementary Fig.5. The Plot of Pval (Lu) as a function of κ(Lu). At each step, all parameters except for κ(Lu) were refined.

Crystal data						
Sample	Quartz	Natrolite	Natrolite	Borane	Cs-perovskite	LuAG
Chemical formula	SiO_2	$Na_2Al_2Si_3O_{12}H_4$	$Na_2Al_2Si_3O_{12}H_4$	$B_{18}H_{22}$	$CsPbBr_3$	$Lu_3Al_5O_{12}$
M_r	60.1	380.2	380.2	108.4	579.8	851.8
Crystal system, space group	Trigonal, $P3_221$	Orthorhombic, *Fdd*2	Orthorhombic, *Fdd*2	Orthorhombic, *Pccn*	Orthorhombic, *Pbnm*	Cubic, $Ia\bar{3}d$
Temperature (K)	293	95	95	100	153	153
a, *b*, *c* (Å)	4.9012(24), 4.9012, 5.4068(26)	18.3885(1), 18.7183(32), 6.6569(11)	18.4125(9), 18.7073(7), 6.6306(2)	10.7789(17), 11.9869(16), 10.7338(17)	8.1189(4), 8.359(4), 11.7593(1)	11.9105(4), 11.9105(4), 11.9105(4)
α, β, γ (°)	90, 90, 120	90, 90, 90	90, 90, 90	90, 90, 90	90, 90, 90	90, 90, 90
V (Å^3)	112.48(8)	2291.31(54)	2283.90(16)	1386.87(36)	798.1(1)	1689.6(1)
Z	3	8	8	4	4	8
Radiation type	Electron, λ = 0.0251 Å	Electron, λ = 0.0251 Å	Electron, λ = 0.0251 Å	Electron, λ = 0.0251 Å	Electron, λ = 0.0251 Å	Electron, λ = 0.0251 Å
Crystal size (mm)	0.0004	0.0005	0.0005	0.0016	0.0004	0.0003
Estimated crystal dimensions (nm*nm*nm)	312.25* 64.26* 40.14	341.64 * 281.08 * 82.72	380.21 * 255.32 * 102.87	$$	84.49 * 67.05 * 67.45	84.67 * 47.75 * 26.36
Data collection						
Diffractometer	TEM FEI Tecnai G2 20	TEM FEI Tecnai G2 20	TEM FEI Tecnai G2 20	TEM FEI Tecnai G2 20	TEM FEI Tecnai G2 20	TEM FEI Tecnai G2 20
3D ED method	Precession	Precession	Continuous Rotation	Precession	Continuous Rotation	Continuous Rotation
No. of measured, independent and observed [$I > 3\sigma(I)$] reflections	3631, 1076, 1004	15767, 6018, 4419	12368, 4546, 4422	6806, 2204, 1997	16736, 422, 363	23256, 1562, 1363
Tilt range, tilt step	-55° to +55°, 1°	-60° to +60°, 1°	-60° to +60°, 0.5°	-31° to +63.5°, 0.3°	-60° to +60°, 0.5°	-60° to +40°, 0.5°
Exposure time per frame (ms)	1000	482	500	405	567	987
Completeness	89%	94%	95%	85%	94%	94%
Flux (e/Å^2/s)	1.0922	0.8992	0.8992	0.0199	1.6955	0.6171
R_{int}	0.110	0.113	0.194	0.122	0.241	0.314
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	1.25	1.1	1.00	0.85	1.00	1.4
Limiting Miller indices	-10<h<10, -10<k<10, -12<l<11	-36<h<38, -41<k<40, -14<l<14	-35<h<35, -37<k<37, -13<l<13	-16<h<16, -17<k<17, -16<l<15	-15<h<15, -16<k<16, -23<l<23	-30<h<30, -26<k<26, -30<l<30
Kinematical Refinement						
$R[F > 3\sigma(F)]$, $wR(F)$, S	0.147, 0.243, 12.07	0.181, 0.233, 2.70	0.179, 0.231, 11.10	0.187, 0.262, 2.59	0.185, 0.255, 3.37	0.244, 0.356, 4.42
No. of reflections	1076	6018	4546	2204	422	1562
No. of parameters	15	38	38	81	13	9
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.34, −0.66	2.46, −1.59	0.29, −0.40	0.24, −0.30	1.06, −1.17	3.00, −2.99
$$ We couldn't estimate the crystal dimensions for the borane sample because it was not possible to calculate from the crystal projections due to the size of the crystal and the presence of other crystals nearby during tracking.						

Supplementary Table 1. Summary of crystallographic information, data collection, and kinematical refinement

	Quartz	Natrolite (Precession)	Natrolite (Continuous rotation)	Borane	Cs-perovskite	LuAG
Estimated crystal thickness from TEM images (Å)	401	827	1029	**	675	264
Without thickness model						
RSg(max), DSg(max)	0.7, 0.0	0.66, 0.0	0.66, 0.0015	0.8, 0.0	0.66, 0.0015	0.66, 0.0015
No. of reflections (Nobs/ Nall)	5364/ 7491	10475/ 25820	10849/ 11952	3296/ 9446	2709/16345	7493/21544
No. of reflections after symmetry averaging (MNobs/ MNall)	960/ 1074	3224/ 4365	4395/ 4516	823/ 1261	1086/ 3314	1016/ 1302
No. of parameters	126	219	157	190	87	66
Robs/ MRobs	4.30/ 2.87	6.93/ 5.36	6.68/ 5.27	6.82/ 7.44	6.46/ 5.44	8.33/ 5.10
Rall/ MRall	5.17/ 3.08	10.66/ 6.52	6.88/ 5.33	12.88/ 9.49	16.87/ 9.63	13.08/ 5.83
wRall/ MwRall	5.28/ 3.63	8.13/ 5.97	8.07/ 6.29	7.78/ 7.46	7.93/ 5.60	9.46/ 5.68
GoFobs/ GoFall	1.62/ 1.41	1.84/ 1.27	3.15/ 3.01	2.52/ 1.60	1.76/ 0.82	2.02/ 1.31
ED thickness (Å)	394	496	565	1677	415	298
With thickness model						
Thickness model used	thickmodel cylinder thickcorr 0.25	thickmodel wedge thickcorr 0.4	thickmodel wedge thickcorr 0.4	thickmodel wedge thickcorr 0.8	thickmodel wedge thickcorr 0	thickmodel wedge thickcorr 0
RSg(max), DSg(max)	0.7, 0.0	0.66, 0	0.66, 0.0015	0.8, 0.0	0.66, 0.0015	0.66, 0.0015
No. of reflections (Nobs/Nall)	5364/ 7491	10475/ 25820	10849/ 11952	3296/ 9446	2709/16345	7493/21544
No. of reflections after symmetry averaging (MNobs/ MNall)	960/ 1074	3224/ 4565	4395/ 4516	823/1261	1086/ 3314	1016/ 1302
No. of parameters	126	219	157	190	87	66
Robs/ MRobs	3.73/ 2.52	6.48/ 5.12	5.67/ 4.51	6.30/ 7.02	5.48/ 4.64	7.25/ 4.42
Rall/ MRall	4.61/ 2.74	10.19/ 6.27	5.85/ 4.56	12.46/ 9.12	16.10/ 9.00	11.94/ 5.16
wRall/ MwRall	4.54/ 3.30	7.61/ 5.75	6.87/ 5.42	7.08/ 7.02	6.79/ 4.90	8.20/ 4.87
GoFobs/ GoFall	1.38/ 1.22	1.71/ 1.19	2.68/ 2.56	2.25/ 1.46	1.45/ 0.70	1.73/ 1.14
ED thickness (Å)	505	857	925	2339	691	470

**We couldn't estimate the crystal thickness for the borane sample because it was not possible to calculate from the crystal projections due to the size of the crystal and the presence of other crystals nearby during tracking.

Supplementary Table 2. The IAM refinement statistics before and after the introduction of the thickness model

Sample	**Enantiomorph 1**	**Enantiomorph 2**
Quartz (SiO_2)		
Resolution $\sin\theta/\lambda$ ($Å^{-1}$)	1.25	1.25
Space group	$P3_121$	$P3_221$
RSg(max), DSg(max)	0.7, 0.0	0.7, 0.0
No. of reflections (Nobs/ Nall)	5364/ 7491	5364/ 7491
No. of reflections after symmetry averaging (MNobs/ MNall)	960/ 1074	960/ 1074
No. of parameters	126	126
Robs/ MRobs	6.95/ 5.42	4.30/ 2.87
Rall/ MRall	8.02/ 5.66	5.17/ 3.08
wRall/ MwRall	8.68/ 6.98	5.28/ 3.63
GoFobs/ GoFall	2.69/ 2.32	1.62/ 1.41
Z-score	-23.4 σ	23.4 σ *
*Enantiomorph 2 was chosen as the absolute structure		

Supplementary Table 3. Determination of absolute structure of quartz by dynamical refinement

Sample	**Enantiomorph 1**	**Enantiomorph 2**
Natrolite [$Na_2Al_2Si_3O_{12}H_4$] (Precession)		
Resolution sinθ/λ ($Å^{-1}$)	1	1
Space group	Fdd2	Fdd2
RSg(max), DSg(max)	0.66, 0.0	0.66, 0.0
No. of reflections (Nobs/ Nall)	10475/ 25820	10475/ 25820
No. of reflections after symmetry averaging (MNobs/ MNall)	3224/ 4365	3224/ 4365
No. of parameters	219	219
Robs/ MRobs	13.56/ 9.63	6.93/ 5.36
Rall/ MRall	17.59/ 11.01	10.66/ 6.52
wRall/ MwRall	15.88/ 10.90	8.13/ 5.97
GoFobs/ GoFall	3.73/ 2.48	1.84/ 1.27
Z-score	-47.5 σ	47.5 σ *
Sample	Enantiomorph 1	Enantiomorph 2
Natrolite [$Na_2Al_2Si_3O_{12}H_4$] (Continuous Rotation)		
Resolution sinθ/λ ($Å^{-1}$)	1	1
Space group	Fdd2	Fdd2
RSg(max), DSg(max)	0.66, 0.0015	0.66, 0.0015
No. of reflections (Nobs/ Nall)	10849/ 11952	10849/ 11952
No. of reflections after symmetry averaging (MNobs/ MNall)	4395/ 4516	4395/ 4516
No. of parameters	157	157
Robs/ MRobs	17.71/ 13.33	6.68/ 5.27
Rall/ MRall	18.02/ 13.43	6.88/ 5.33
wRall/ MwRall	23.04/ 17.22	8.07/ 6.29
GoFobs/ GoFall	8.99/ 8.59	3.15/ 3.01
Z-score	-57.8 σ	57.8 σ *
* Enantiomorph 2 was chosen as the absolute structure		

Supplementary Table 4. Determination of absolute structure of natrolite by dynamical refinement

Sample		**Experiment**		
Natrolite [$Na_2Al_2Si_3O_{12}H_4$]				
Method/Program		Precession	Continuous Rotation	X-ray
Resolution sinθ/λ ($Å^{-1}$)		1.0	1.0	1.3
IAM Refinement				
RSg(max), DSg(max)		0.66, 0.00	0.66, 0.0015	
No. of reflections (Nobs/ Nall)		10475/ 25820	10849/ 11952	9023/ 9300
No. of reflections after symmetry averaging (MNobs/ MNall)		3224/ 4565	4395/ 4516	9023/ 9300
No. of parameters		219	157	98
Robs/ MRobs		6.48/ 5.12	5.67/ 4.51	1.48/ 1.48
Rall/ MRall		10.19/ 6.27	5.85/ 4.56	1.56/ 1.56
wRall/ MwRall		7.61/ 5.75	6.87/ 5.42	1.99/ 1.99
GoFobs/ GoFall		1.71/ 1.19	2.68/ 2.56	1.17/ 1.16
Kappa Refinement				
RSg(max), DSg(max)		0.66, 0.00	0.66, 0.0015	
No. of reflections (Nobs/ Nall)		10475/ 25820	10849/ 11952	9023/ 9300
No. of reflections after symmetry averaging (MNobs/ MNall)		3224/ 4565	4395/ 4516	9023/ 9300
No. of parameters		235	173	114
Robs/ MRobs		5.68/ 4.27	4.91/ 3.74	1.40/ 1.40
Rall/ MRall		9.48/ 5.41	5.11/ 3.80	1.48/ 1.48
wRall/ MwRall		6.42/ 4.41	5.83/ 4.48	1.80/ 1.80
GoFobs/ GoFall		1.38/ 1.00	2.27/ 2.17	1.05/ 1.06
Charge density parameters				
Atom label				
Si1, Si2 * (N_{val} =4)	P_{val}	2.836 (50)	2.824 (68)	2.903 (82)
	Kappa	1.068 (8)	1.061 (11)	1.001 (10)
	q = N_{val} - P_{val}	**1.164 (50)**	**1.176 (68)**	**1.097 (82)**
Al1 (N_{val} =3)	P_{val}	1.986 (62)	1.769 (82)	2.543 (131)
	Kappa	1.062 (14)	1.064 (22)	0.942 (18)
	q = N_{val} - P_{val}	**1.014 (62)**	**1.231 (82)**	**0.457 (131)**
Na1 (N_{val} =1)	P_{val}	0.261 (53)	0.254 (68)	0.253 (118)
	Kappa	1.398 (183)	1.269 (220)	1.505 (304)
	q = N_{val} - P_{val}	**0.739 (53)**	**0.746 (68)**	**0.747 (118)**
O1 (N_{val} =6)	P_{val}	6.735 (31)	6.660 (41)	6.594 (41)
	Kappa	0.951 (5)	0.977 (6)	0.975 (3)
	q = N_{val} - P_{val}	**-0.735 (31)**	**-0.660 (41)**	**-0.594 (41)**
O2 (N_{val} =6)	P_{val}	6.714 (28)	6.877 (34)	6.644 (41)
	Kappa	0.959 (5)	0.949 (5)	0.968 (1)
	q = N_{val} - P_{val}	**-0.714 (28)**	**-0.877 (34)**	**-0.644 (41)**
O3 (N_{val} =6)	P_{val}	6.713 (44)	6.717 (54)	6.567 (53)
	Kappa	1.040 (7)	1.029 (8)	0.968 (3)
	q = N_{val} - P_{val}	**-0.713 (41)**	**-0.717 (54)**	**-0.567 (53)**
O5, O4, O6 * (N_{val} =6)	P_{val}	6.749 (28)	6.786 (34)	6.702 (24)
	Kappa	0.964 (4)	0.962 (4)	0.967 (2)
	q = N_{val} - P_{val}	**-0.749 (26)**	**-0.786 (34)**	**-0.702 (24)**
H2, H1 * † (N_{val} =1)	P_{val}	0.544 (25)	0.564 (26)	0.469 (32)
	Kappa	1.167 (82)	1.817 (166)	2.221 (673)
	q = N_{val} - P_{val}	**0.456 (26)**	**0.436 (26)**	**0.531 (32)**

* The Pval and k parameters of atoms in similar chemical environments were constrained to be equal.
† The ADPs were constrained to be equal.

Supplementary Table 5. Refinement statistics and refined charge density parameters against experimental 3DED and X-ray measurements for natrolite

Sample		**Experiment**	
Borane ($B_{18}H_{22}$)			
Method/Program		Precession	X-ray
Resolution $\sin\theta/\lambda$ ($Å^{-1}$)		0.85	1.0
IAM Refinement			
RSg(max), DSg(max)		0.66, 0.00	
No. of reflections (Nobs/ Nall)		4779 / 13809	4924/ 5672
No. of reflections after symmetry averaging (MNobs/ MNall)		1906 / 3179	4924/ 5672
No. of parameters		233	126
Robs/ MRobs		7.56/ 6.51	2.86/ 2.86
Rall/ MRall		12.99/ 8.46	3.47/ 3.47
wRall/ MwRall		8.45/ 7.11	5.09/ 5.09
GoFobs/ GoFall		2.27/ 1.44	3.03/ 2.86
Kappa Refinement			
RSg(max), DSg(max)		0.66, 0.00	
No. of reflections (Nobs/ Nall)		4779 / 13809	4924/ 5672
No. of reflections after symmetry averaging (MNobs/ MNall)		1906/3179	4924/ 5672
No. of parameters		249	142
Robs/ MRobs		6.04/4.89	2.91/ 2.91
Rall/ MRall		11.44/6.82	3.53/ 3.53
wRall/ MwRall		7.08/5.21	5.54/ 5.54
GoFobs/ GoFall		1.85/1.20	3.32/ 3.12
Charge density parameters			
Atom labels			
B3 (N_{val} =3)	P_{val}	3.231 (44)	3.190 (88)
	Kappa	1.054 (9)	1.014 (10)
	q = N_{val} - P_{val}	**-0.231 (44)**	**-0.190 (88)**
B5, B4, B6, B2 * (N_{val} =3)	P_{val}	3.153 (16)	3.274 (23)
	Kappa	1.063 (6)	1.022 (5)
	q = N_{val} - P_{val}	**-0.153 (16)**	**-0.274 (23)**
B8, B7, B1 * (N_{val} =3)	P_{val}	3.06 (19)	3.213 (43)
	Kappa	1.081 (6)	1.009 (6)
	q = N_{val} - P_{val}	**-0.06 (19)**	**-0.213 (43)**
B9 (N_{val} =3)	P_{val}	3.037 (25)	3.115 (59)
	Kappa	1.067 (9)	1.043 (9)
	q = N_{val} - P_{val}	**-0.037 (25)**	**-0.115 (59)**
H1b3 (N_{val} =1)	P_{val}	0.957 (24)	0.861 (39)
	Kappa	1.249 (45)	05.541 (34885)
	q = N_{val} - P_{val}	**0.043 (24)**	**0.139 (39)**
H1b3b7, H1b1b9, H1b3b8 * (N_{val} =1)	P_{val}	0.772 (14)	0.698 (30)
	Kappa	1.46 (4)	04.701 (16152)
	q = N_{val} - P_{val}	**0.228 (14)**	**0.302 (30)**
H1b5, H1b4, H1b6, H1b2 * (N_{val} =1)	P_{val}	0.923 (10)	0.811 (16)
	Kappa	1.394 (23)	3.692 (2238)
	q = N_{val} - P_{val}	**0.077 (10)**	**-0.023 (3)**
H1b7, H1b8, H1b1 * (N_{val} =1)	P_{val}	0.992 (8)	0.921 (26)
	Kappa	1.28 (2)	1.510 (97)
	q = N_{val} - P_{val}	**0.008 (8)**	**0.079 (26)**

* The Pval and k parameters of atoms in similar chemical environments were constrained to be equal.

Supplementary Table 6. Refinement statistics and refined charge density parameters against experimental 3DED and X-ray for borane

Sample		**Theory**							
Quartz (SiO_2)									
Program		WIEN2k_reported	WIEN2k_2000GGA	WIEN2k_1000 LDA	WIEN2k_rkmax8	Crystal23_reported	Crystal23_B3LYP_ccpVDZ	Crystal_HSE06	Crystal_PBESOL
Resolution $\sin\theta/\lambda$ ($Å^{-1}$)		1.0	1.0	1.0	1.0	1.25	1.25	1.25	1.25
IAM refinement									
No. of reflections (Nobs/ Nall)		600/ 629	600/ 629	600/ 629	600/ 629	1175/ 1218	1175/ 1218	1175/ 1218	1175/ 1218
No. of parameters		1	1	1	1	1	1	1	1
Robs		1.89	1.89	1.78	1.89	1.27	1.12	1.22	1.17
Rall		1.90	1.89	1.78	1.89	1.29	1.13	1.24	1.19
wRall		3.42	3.41	3.21	3.41	3.02	2.93	2.92	2.85
GoFobs/ GoFall		2.02/ 1.98	2.02/ 1.98	1.90/ 1.86	2.02/ 1.98	3.40/ 3.34	3.30/3.25	3.30/ 3.24	3.22/ 3.16
Kappa Refinement									
No. of reflections (Nobs/ Nall)		600/629	600/629	600/629	600/629	1175/ 1218	1175/ 1218	1175/ 1218	1175/ 1218
No. of parameters		5	5	5	5	5	5	5	5
Robs		0.96	0.95	0.91	0.96	0.57	0.51	0.61	0.60
Rall		0.97	0.97	0.92	0.97	0.59	0.53	0.62	0.62
wRall		1.68	1.66	1.63	1.68	0.89	0.82	0.94	0.93
GoFobs/ GoFall		1.00/ 0.98	1.00/ 0.98	0.97/ 0.94	1.00/ 0.98	1.00/ 0.99	0.93/ 0.92	1.06/ 1.04	1.05/ 1.03
Charge density parameters									
Atom label									
Si1 (N_{val} =4)	P_{val}	2.952 (60)	2.954 (60)	3.023 (59)	2.957 (61)	2.781 (26)	2.786 (24)	2.804 (28)	2.833 (27)
	Kappa	1.097 (7)	1.096 (7)	1.088 (6)	1.097 (7)	1.073 (3)	1.056 (3)	1.075 (3)	1.072 (3)
	q = N_{val} - P_{val}	**1.048 (60)**	**1.046 (60)**	**0.977(59)**	**1.043 (61)**	**1.219 (26)**	**1.214 (24)**	**1.196 (28)**	1.167 (27)
O1 (Nval =6)	Pval	6.524 (30)	6.523 (30)	6.488 (29)	6.521 (30)	6.609 (13)	6.607 (12)	6.598 (14)	6.584 (14)
	Kappa	0.999 (4)	0.999 (4)	0.999 (4)	0.999 (4)	0.994 (1)	0.993 (1)	0.993 (2)	0.993 (2)
	q = N_{val} - P_{val}	**-0.524 (30)**	**-0.523 (30)**	**-0.488 (29)**	**-0.521 (30)**	**-0.609 (13)**	**-0.607 (12)**	**-0.598 (14)**	**-0.584 (14)**

Supplementary Table 7. Refinement statistics and refined charge density parameters against theoretical data for Quartz

Sample		**Theory**				
Natrolite [$Na_2Al_2Si_3O_{12}H_4$]						
Method/Program		Crystal23 (reported)	Crystal23_B3LYP_ccpVDZ	Crystal23_HSE06_POB-TZVP-REV2	Crystal23_PBESOL0_POB-TZVP-REV2	WIEN2k (reported)
Resolution $\sin\theta/\lambda$ ($Å^{-1}$)		1.0	1.0	1.0	1.0	1.0
IAM Refinement						
No. of reflections (Nobs/ Nall)		4748/ 4776	4748/ 4776	4748/ 4776	4748/ 4776	4747/ 4799
No. of parameters		1	1	1	1	1
Robs		1.99	2.08	2.05	1.99	1.99/ 1.99
Rall		1.99	2.09	2.06	1.99	1.99/ 1.99
wRall		4.48	5.05	4.54	4.44	4.32/ 4.32
GoFobs/ GoFall		6.71/ 6.70	6.39/ 6.37	5.74/ 5.72	5.62/5.60	4.21/ 4.19
Kappa Refinement						
No. of reflections (Nobs/ Nall)		4748/ 4776	4748/ 4776	4748/ 4776	4748/ 4776	4747/ 4799
No. of parameters		17	17	17	17	17
Robs		0.43	0.33	0.44	0.44	0.55/ 0.55
Rall		0.43	0.33	0.45	0.45	0.55/ 0.55
wRall		0.67	0.53	0.69	0.69	1.03/ 1.03
GoFobs/ GoFall		1.00/ 1.00	0.66/ 0.65	0.88/ 0.88	0.87/ 0.87	1.00/ 1.00
Charge density parameters						
Atom label						
Si1, Si2 * (N_{val} =4)	P_{val}	2.781 (10)	2.226 (10)	2.812 (10)	2.827 (10)	2.813 (14)
	Kappa	1.029 (2)	1.039 (2)	1.025 (2)	1.024 (2)	1.067 (2)
	$q = N_{val} - P_{val}$	**1.219 (10)**	**1.774 (10)**	**1.188 (10)**	**1.173 (10)**	**1.187 (14)**
Al1 (N_{val} =3)	P_{val}	1.742 (12)	1.751 (13)	1.744 (12)	1.779 (13)	1.836 (18)
	Kappa	1.074 (4)	0.978 (3)	1.074 (4)	1.069 (4)	1.084 (5)
	$q = N_{val} - P_{val}$	**1.258 (12)**	**1.249 (13)**	**1.256 (12)**	**1.221 (13)**	**1.164 (18)**
Na1 (N_{val} =1)	P_{val}	0.020 (6)	-0.757 (16)	0.010 (4)	0.010 (5)	0.021 (9)
	Kappa	2.204 (578)	0.590 (10)	3.057 (1567)	2.734 (1349)	2.307 (903)
	$q = N_{val} - P_{val}$	**0.98 (6)**	**1.757 (16)**	**0.99 (4)**	**0.99 (5)**	**0.979 (9)**
O1 (N_{val} =6)	P_{val}	6.681 (6)	7.034 (5)	6.678 (6)	6.671 (6)	6.663 (9)
	Kappa	0.979 (1)	0.949 (1)	0.978 (1)	0.976 (1)	0.968(1)
	$q = N_{val} - P_{val}$	**-0.681 (6)**	**-1.034 (41)**	**-0.678 (6)**	**-0.671 (6)**	**-0.663 (9)**
O2 (N_{val} =6)	P_{val}	6.824 (5)	7.052 (4)	6.824 (5)	6.812 (5)	6.791 (8)
	Kappa	0.964 (1)	0.944 (1)	0.962 (1)	0.962 (1)	0.955 (1)
	$q = N_{val} - P_{val}$	**-0.824 (5)**	**-1.052 (4)**	**-0.824 (5)**	**-0.812 (5)**	**-0.791 (8)**
O3 (N_{val} =6)	P_{val}	6.994 (9)	7.093 (6)	7.021 (8)	7.022 (8)	6.986 (13)
	Kappa	0.948 (1)	0.940 (1)	0.946 (1)	0.945 (1)	0.941 (2)
	$q = N_{val} - P_{val}$	**-0.994 (9)**	**-1.093 (6)**	**-1.021 (8)**	**1.022 (8)**	**-0.986 (13)**
O5, O4, O6 * (N_{val} =6)	P_{val}	6.859 (5)	7.128 (4)	6.853 (4)	6.840 (4)	6.827 (7)
	Kappa	0.962 (1)	0.940 (1)	0.960 (1)	0.959 (1)	0.953 (1)
	$q = N_{val} - P_{val}$	**-0.859 (5)**	**-1.128 (4)**	**-0.853 (4)**	**-0.840 (4)**	**-0.827 (7)**
H2, H1 * (N_{val} =1)	P_{val}	0.494 (4)	0.551 (3)	0.473 (3)	0.472 (4)	0.501 (5)
	Kappa	1.549 (15)	1.404 (10)	1.648 (17)	1.627 (17)	1.605 (23)
	$q = N_{val} - P_{val}$	**0.506 (4)**	**0.436 (3)**	**0.527 (3)**	**0.528 (4)**	**0.499 (5)**

* The Pval and k parameters of atoms in similar chemical environments were constrained to be equal.

Supplementary Table 8. Refinement statistics and refined charge density parameters against theoretical data for natrolite

Sample		**Theory**			
Borane ($B_{18}H_{22}$)					
Method/Program		Crystal23 (reported)	Crystal23_PBESOL_POB-TZVP-REV2	Crystal23_ M052X_POB-TZVP-REV2	Crystal23_ wB97-X_POB-TZVP-REV2
Resolution sinθ/λ ($Å^{-1}$)		1.25	1.25	1.25	1.25
IAM Refinement					
No. of reflections (Nobs/ Nall)		3873/ 4775	3871/ 4775	3871/ 4775	3871/ 4775
No. of parameters		1	1	1	1
Robs		6.63	6.58	6.61	6.33
Rall		6.69	6.63	6.67	6.39
wRall		8.66	8.78	8.78	8.45
GoFobs/ GoFall		4.30/ 3.88	4.38/ 3.95	4.37/ 3.94	4.22/ 3.81
Kappa Refinement					
No. of reflections (Nobs/ Nall)		3873/ 4775	3871/ 4775	3871/ 4775	3871/ 4775
No. of parameters		17	17	17	17
Robs		1.78	1.76	1.80	1.82
Rall		1.86	1.84	1.88	1.90
wRall		2.23	2.22	2.29	2.27
GoFobs/ GoFall		1.10/ 1.00	1.09/ 1.00	1.13/ 1.03	1.12/ 1.02
Charge density parameters					
Atom labels					
B3 (N_{val} =3)	P_{val}	3.119 (11)	3.143 (11)	3.139 (12)	3.147 (12)
	Kappa	1.117 (3)	1.109 (3)	1.109 (3)	1.105 (3)
	q = N_{val} - P_{val}	**-0.119 (11)**	**-0.143 (11)**	**-0.139 (11)**	**-0.147 (12)**
B5, B4, B6, B2 * (N_{val} =3)	P_{val}	3.002 (5)	3.014 (5)	3.010 (5)	3.008 (5)
	Kappa	1.145 (2)	1.134 (2)	1.138 (2)	1.135 (2)
	q = N_{val} - P_{val}	**-0.002 (5)**	**-0.014 (5)**	**-0.010 (5)**	**-0.008 (5)**
B8, B7, B1 * (N_{val} =3)	P_{val}	3.065 (7)	3.086 (7)	3.077 (7)	3.074 (7)
	Kappa	1.116 (2)	1.106 (2)	1.109 (2)	1.106 (2)
	q = N_{val} - P_{val}	**-0.065 (7)**	**-0.086 (7)**	**0.077 (7)**	**-0.074 (7)**
B9 (N_{val} =3)	P_{val}	3.039 (7)	3.048 (7)	3.043 (7)	3.053 (7)
	Kappa	1.116 (3)	1.103 (3)	1.106 (3)	1.102 (3)
	q = N_{val} - P_{val}	**-0.039 (7)**	**-0.048 (7)**	**-0.043 (7)**	**-0.053 (7)**
H1b3 (N_{val} =1)	P_{val}	0.970 (6)	0.951 (6)	0.953 (6)	0.956 (6)
	Kappa	1.317 (12)	1.313 (12)	1.315 (12)	1.317 (12)
	q = N_{val} - P_{val}	**0.030 (6)**	**0.049 (6)**	**0.047 (6)**	**0.044 (6)**
H1b3b7, H1b1b9, H1b3b8 * (N_{val} =1)	P_{val}	0.847 (4)	0.838 (4)	0.844 (4)	0.834 (4)
	Kappa	1.323 (8)	1.293 (8)	1.295 (9)	1.317 (9)
	q = N_{val} - P_{val}	**0.153 (4)**	**0.162 (4)**	**0.156 (4)**	**0.166 (4)**
H1b5, H1b4, H1b6, H1b2 * (N_{val} =1)	P_{val}	1.023 (3)	1.010 (3)	1.015 (3)	1.017 (3)
	Kappa	1.272 (5)	1.257 (5)	1.257 (5)	1.263 (5)
	q = N_{val} - P_{val}	**-0.023 (3)**	**0.010 (3)**	**-0.015 (3)**	**-0.017 (3)**
H1b7, H1b8, H1b1 * (N_{val} =1)	P_{val}	1.012 (3)	0.996 (3)	1.001 (3)	1.006 (3)
	Kappa	1.268 (5)	1.258 (5)	1.257 (5)	1.259 (5)
	q = N_{val} - P_{val}	**-0.012 (3)**	**0.004 (3)**	**-0.001 (3)**	**-0.006 (3)**

* The Pval and k parameters of atoms in similar chemical environments were constrained to be equal.

Supplementary Table 9. Refinement statistics and refined charge density parameters against theoretical data for borane

Sample		**Theory**			
Caesium lead bromide ($CsPbBr_3$)					
Method/Program		WIEN2k (reported)	WIEN2k(finer k mesh)	WIEN2k (LDA)	WIEN2k (incr. Rkmax)
Resolution sinθ/λ (Å-1)		1.0	1.0	1.0	1.0
IAM Refinement					
No. of reflections (Nobs/ Nall)		3271/3366	3271/3366	3271/3366	3271/3366
No. of parameters		1	1	1	1
Robs		0.23	0.23	0.23	0.23
Rall		0.24	0.23	0.23	0.23
wRall		1.17	0.24	0.24	0.24
GoFobs/ GoFall		9.59/ 9.45	1.20	1.15	1.20
Kappa Refinement					
No. of reflections (Nobs/ Nall)		3271/3366	3271/3366	3271/3366	3271/3366
No. of parameters		9	9	9	9
Robs		0.08	0.1	0.12	0.1
Rall		0.09	0.11	0.13	0.11
wRall		0.12	0.29	0.31	0.29
GoFobs/ GoFall		1.01/ 1.00	0.03/0.04	0.04/0.04	0.03/0.04
Charge density parameters					
Atom labels					
Cs (N_{val} =1)	P_{val}	0.220 (4)	0.187 (7)	0.291 (14)	0.189 (7)
	Kappa	1.647(17)	1.932 (60)	1.509 (41)	1.932 (60)
	$q = N_{val} - P_{val}$	**0.780 (4)**	**0.813 (7)**	**0.709 (14)**	**0.811 (7)**
Pb (N_{val} =4)	P_{val}	3.243(4)	3.202 (10)	3.309 (11)	3.197 (10)
	Kappa	1.084 (1)	1.091 (2)	1.073 (3)	1.092 (2)
	$q = N_{val} - P_{val}$	**0.757 (4)**	**0.793 (10)**	**0.691 (11)**	**0.803 (10)**
Br1 (N_{val} =7)	P_{val}	7.512 (3)	7.523 (5)	7.454 (6)	7.524 (5)
	Kappa	0.9758 (3)	0.981 (1)	0.985 (1)	0.982 (1)
	$q = N_{val} - P_{val}$	**-0.512 (3)**	**-0.523 (5)**	**-0.454 (6)**	**-0.524 (5)**
Br2 (N_{val} =7)	P_{val}	7.512 (3)	7.544 (5)	7.473 (6)	7.545 (5)
	Kappa	0.9758 (3)	0.979	0.983 (1)	0.980
	$q = N_{val} - P_{val}$	**-0.512 (3)**	**-0.544 (5)**	**-0.473 (6)**	**-0.545 (5)**

Supplementary Table 10. Refinement statistics and refined charge density parameters against theoretical data for Cs-perovskite

Sample		**Theory**	
Lutetium Aluminium Garnet ($Lu_3Al_5O_{12}$)			
Method/Program		WIEN2k (reported)	WIEN2k (LDA)
Resolution sinθ/λ ($Å^{-1}$)		1.0	1.0
IAM Refinement			
No. of reflections (Nobs/ Nall)		434/599	434/599
No. of parameters		1	1
Robs		1.05	0.63
Rall		1.13	0.63
wRall		3.90	2.07
GoFobs/ GoFall		1.30/ 1.18	8.28/7.87
Kappa Refinement			
No. of reflections (Nobs/ Nall)		434/599	434/599
No. of parameters		9	9
Robs		0.72	0.26
Rall		0.73	0.26
wRall		3.30	0.58
GoFobs/ GoFall		1.18/ 1.00	
Charge density parameters			
Atom labels			
Lu (N_{val} =3)	P_{val}	1.302 (291)	1.531 (47)
	Kappa	1.336(291)	1.224 (25)
	$q = N_{val} - P_{val}$	**1.698 (291)**	**1.469 (47)**
Al1 (N_{val} =3)	P_{val}	1.732 (227)	1.857 (21)
	Kappa	1.131 (70)	1.129 (11)
	$q = N_{val} - P_{val}$	**1.268 (227)**	**1.143 (21)**
Al2 (N_{val} =3)	P_{val}	1.340 (344)	1.783 (57)
	Kappa	1.245 (146)	1.089 (17)
	$q = N_{val} - P_{val}$	**1.660 (344)**	**1.217 (57)**
O (N_{val} =6)	P_{val}	7.018 (165)	6.856 (17)
	Kappa	0.933 (17)	0.950 (2)
	$q = N_{val} - P_{val}$	**-1.018 (165)**	**-0.856 (17)**

Supplementary Table 11. Refinement statistics and refined charge density parameters against theoretical data for LuAG

Supplementary references

1. Rigaku OD (2024). CrysAlis PRO. Rigaku Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.
2. Becke, A. D. (1993). Density-functional thermochemistry. III. The role of exact exchange. The Journal of Chemical Physics, 98(7), 5648-5652. doi: 10.1063/1.464913
3. Heyd, J., Scuseria, G. E., & Ernzerhof, M. (2003). Hybrid functionals based on a screened Coulomb potential. The Journal of Chemical Physics, 118(18), 8207-8215. doi: 10.1063/1.1564060
4. Perdew, J. P., Ruzsinszky, A., Csonka, G. I., Vydrov, O. A., Scuseria, G. E., Constantin, L. A., Zhou, X., & Burke, K. (2008). Restoring the Density-Gradient Expansion for Exchange in Solids and Surfaces. Physical Review Letters, 100(13), 136406. doi: 10.1103/PhysRevLett.100.136406
5. Chai, J.-D., & Head-Gordon, M. (2008). Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections. Physical Chemistry Chemical Physics, 10(44), 6615-6620. doi: 10.1039/B810189B
6. Zhao, Y., & Truhlar, D. G. (2008). The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. Theoretical Chemistry Accounts, 120(1-3), 215-241. doi: 10.1007/s00214-007-0310-x
7. D. Vilela Oliveira, M. F. Peintinger, J. Laun, and T. Bredow, "BSSE-correction scheme for consistent gaussian basis sets of double- and triple-zeta valence with polarization quality for solid-state calculations",Journal of Computational Chemistry 2019, 40, DOI: 10.1002/jcc.26013
8. Dunning, T. H. (1989). Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. The Journal of Chemical Physics, 90(2), 1007-1023. doi: 10.1063/1.456153
9. Schäfer, A., Horn, H., & Ahlrichs, R. (1992). Fully optimized contracted Gaussian basis sets for atoms Li to Kr. The Journal of Chemical Physics, 97(4), 2571-2577. doi: 10.1063/1.463096
10. Tran, F., Stelzl, J., Koller, D., Ruh, T. & Blaha, P. (2017). Simple way to apply nonlocal van der Waals functionals within all-electron methods. Physical Review. B./Physical Review. B 96. doi: 10.1103/PhysRevB.96.054103