Supplementary Information:

Solid-state chemistry of glassy antimony oxides

This material provides comprehensive data for the original article. Schematic description of the atomic structures and radial distribution function (RDF) are shown in Fig. . The bonding angle distribution (BAD) function results are shown in Fig. . These results can be compared to the same properties of the amorphous models shown in the main text. The crystalline parameters are listed in Table I. The formation energy values are listed in Table II. Detail k-point settings for the crystalline calculations are listed in Table III. The atomic coordinations and the cell parameters are tabulated in the original format in Tables IV through Table IX. The density of the calculated atomic structures are listed in Table X. Other details about the computational setting are explained in the main text.

TABLE I. Lattice parameters of the optimised crystal structures shown in Fig. 1. The percentage differences with respect to the experimental data referenced in the first column are also given.

Structure	a (Å)	b (Å)	c (Å)	
Sb_2O_3 (α) [a]	11.083(-0.03)	11.083(-0.03)	11.083(-0.03)	$\alpha = 90°$
Sb_2O_3 (β) [b]	4.840(-1.43)	12.379(-0.65)	5.449(+0.72)	$\alpha = 90°$
Sb_2O_3 (γ) [c]	11.523(-1.01)	7.525(-0.55)	7.484(+0.09)	$\alpha = 90°$
Sb_2O_4 (α) [d]	5.500(+0.91)	4.859(+1.01)	11.863(+0.70)	$\alpha = 90°$
Sb_2O_4 (β) [e]	12.204(+1.19)	4.903(+1.50)	5.412(+0.60)	$\beta = 105.6(+0.9)°$
Sb_2O_5 [f]	12.789(+1.18)	4.856(+1.59)	5.483(+1.16)	$\beta = 103.7(-0.2)°$

[a] Ref. 1
[b] Ref. 2
[c] Ref. 3
[d] Ref. 4
[e] Ref. 5
[f] Ref. 6

FIG. 1. The six known crystal structures of the three antimony oxide compositions examined in the text. The radial-distribution functions (RDFs) are shown together with snapshots of the structures. In the latter, The Sb atoms are shown as large white spheres and the O atoms as small red ones.

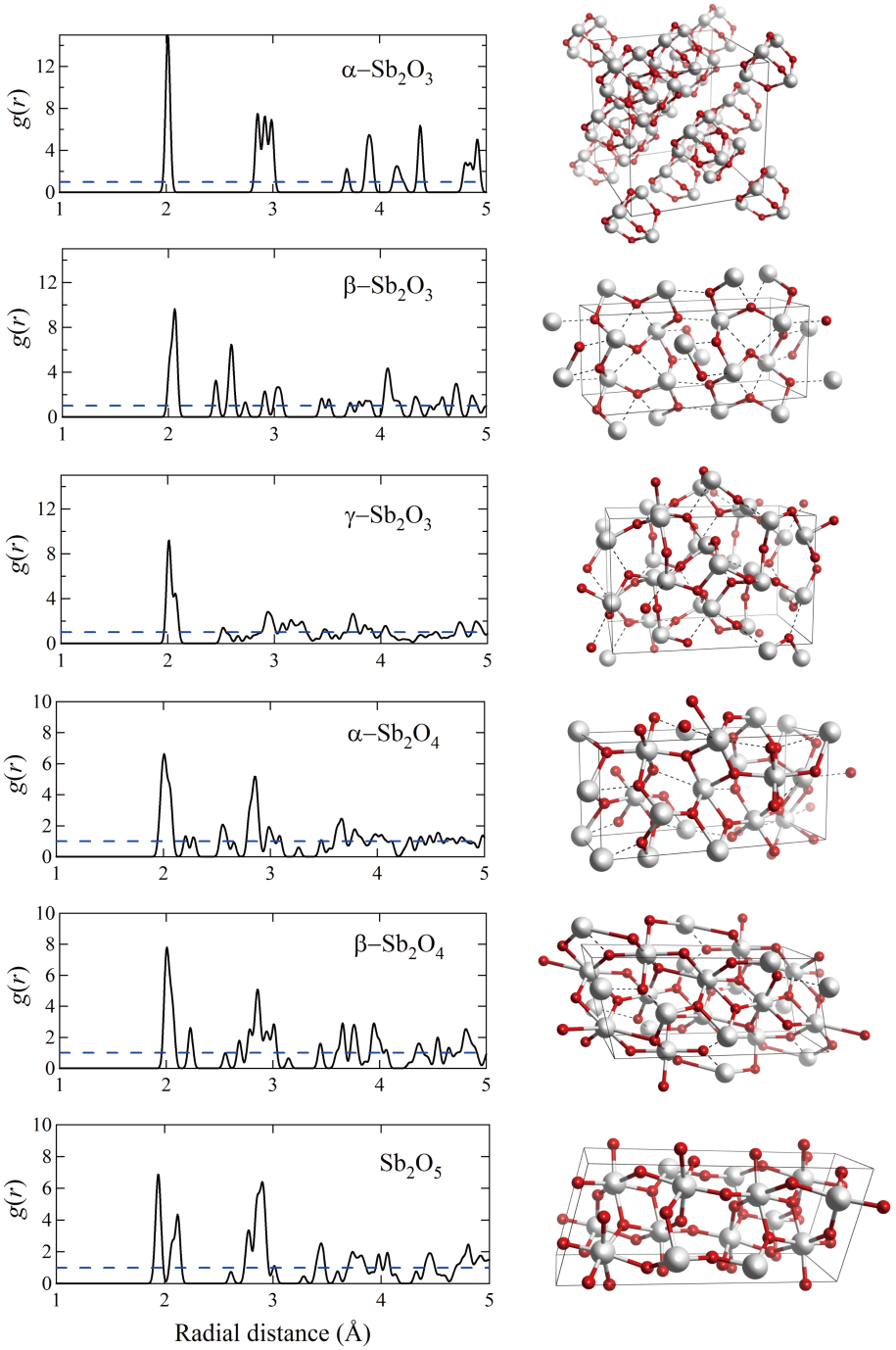

FIG. 2. Calculated bond-angle distribution functions (BADs) of the crystal structures in Fig. 1.

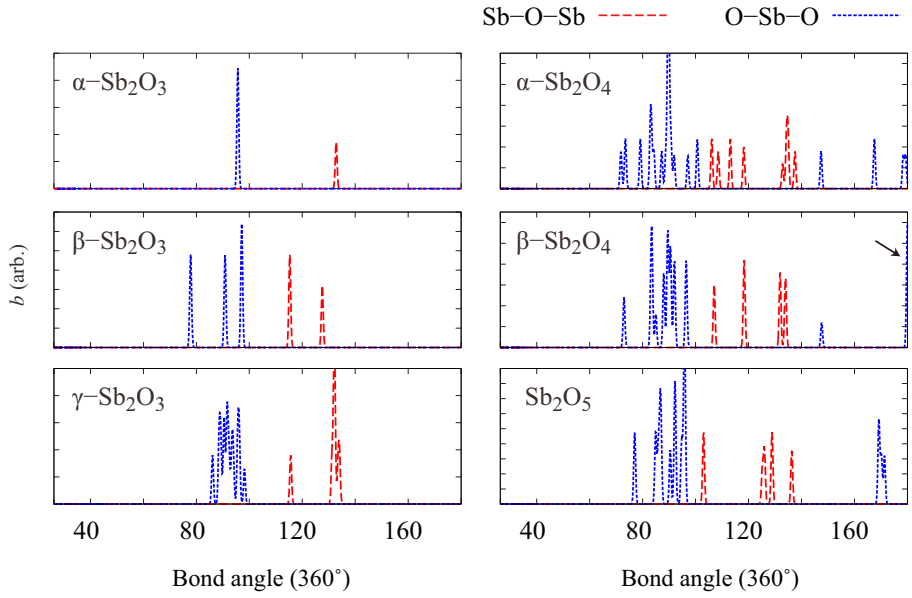

TABLE II. Calculated formation energies of the crystalline antimony oxides. The PBE exchange-correlation functional predicts the β phase of Sb_2O_3 to be more stable than the α phase, contradicting the experimental observations in Ref.[3], but the adding the Grimme DFT-D2 correction for dispersion forces resolved this problem.

Structure	E_f^{PBE} (eV/f.u.)	E_f^{PBE-D2} (eV/f.u.)
Sb_2O_3 (α)	-6.496	-7.031
Sb_2O_3 (β)	-6.541	-7.029
Sb_2O_3 (γ)	-6.388	-7.000
Sb_2O_4 (α)	-8.040	-8.891
Sb_2O_4 (β)	-8.029	-8.913
Sb_2O_5	-8.480	-9.548

TABLE III. Detailed settings of the **k**-points for the crystalline antimony oxides calculations. Gamma-centered grid **k**-points are used for single-point electronic structure calculations using HSE06 functional, and Monkhorst-Pack type grid is used for geometrical relaxation calculations using PBE or PBE-D2 functional.

Structure	**k**-points (HSE06)	**k**-points (PBE-GGA)	**k**-points (PBE-GGA-D2)
Sb_2O_3 (α)	2×2×2	4×4×4	4×4×4
Sb_2O_3 (β)	3×2×3	4×2×4	4×2×4
Sb_2O_3 (γ)	2×4×4	2×4×4	2×4×4
Sb_2O_4 (α)	3×3×2	4×4×2	4×4×2
Sb_2O_4 (β)	2×3×3	2×4×4	2×4×4
Sb_2O_5	2×3×3	2×4×4	2×4×4

TABLE IV. Calculated atomic coordinates of Sb_2O_3 (α) using PBE-GGA-D2 in the VASP POSCAR format.

O	Sb	
1.0		
5.541856489621	-5.541856489621	0.000000000000
-5.541856489621	0.000000000000	-5.541856489621
5.541856489621	5.541856489621	0.000000000000
O	Sb	
12	8	
Direct		
0.190611333787	0.000000000000	0.190611333787
0.809388673213	0.000000000000	0.809388673213
0.809388666213	0.000000000000	0.190611333787
0.190611326787	0.000000000000	0.809388673213
0.809388666213	0.618777332427	0.809388666213
0.190611326787	0.381222653573	0.190611326787
0.559388673213	0.500000000000	0.440611326787
0.940611333787	0.500000000000	0.059388666213
0.940611326787	0.500000000000	0.440611326787
0.559388666213	0.500000000000	0.059388666213
0.940611333787	0.881222667573	0.440611333787
0.559388673213	0.118777346427	0.059388673213
0.117829253667	0.235658507334	0.882170746333
0.117829253667	0.235658507334	0.353487761001
0.117829253667	0.764341492666	0.882170746333
0.646512238999	0.764341492666	0.882170746333
0.632170746333	0.264341492666	0.896512238999
0.632170746333	0.264341492666	0.367829253667
0.632170746333	0.735658507334	0.367829253667
0.103487761001	0.735658507334	0.367829253667

TABLE V. Calculated atomic coordinates of Sb_2O_3 (β) using PBE-GGA-D2 in the VASP POSCAR format.

O	Sb	
1.0		
4.839828977281	0.000000000000	0.000000000000
0.000000000000	12.378897103657	0.000000000000
0.000000000000	0.000000000000	5.449183121942
O	Sb	
12	8	
Direct		
0.250000000000	0.250000000000	0.012971249559
0.750000000000	0.750000000000	0.987028739441
0.750000000000	0.750000000000	0.487028739441
0.250000000000	0.250000000000	0.512971260559
0.145227236115	0.057104809587	0.851452982733
0.854772748885	0.942895194413	0.148547032267
0.354772748885	0.442895194413	0.851452982733
0.645227251115	0.557104805587	0.148547032267
0.854772748885	0.557104805587	0.648547017267
0.145227236115	0.442895194413	0.351452982733
0.645227251115	0.942895194413	0.648547017267
0.354772748885	0.057104809587	0.351452982733
0.031765954051	0.127081182708	0.180376382502
0.968234023949	0.872918832292	0.819623632498
0.468234053949	0.372918832292	0.180376382502
0.531765976051	0.627081167708	0.819623632498
0.968234023949	0.627081167708	0.319623632498
0.031765954051	0.372918832292	0.680376367502
0.531765976051	0.872918832292	0.319623632498
0.468234053949	0.127081182708	0.680376367502

TABLE VI. Calculated atomic coordinates of Sb_2O_3 (γ) using PBE-GGA-D2 in the VASP POSCAR format.

O	Sb	
1.0		
11.522608022841	0.000000000000	0.000000000000
0.000000000000	7.525111471004	-0.000000090517
0.000000000000	-0.000000090081	7.483670041413
O	Sb	
24	16	
Direct		
0.402327135866	0.471253766274	0.131596083063
0.097672758648	0.528746371392	0.631596027294
0.597672728648	0.971253628608	0.368403972706
0.902327165866	0.028746233726	0.868403916937
0.147027546401	0.408668490004	0.268851543231
0.352972478707	0.591331730731	0.768851657944
0.852972478707	0.908668269269	0.231148342056
0.647027531401	0.091331509996	0.731148456769
0.102696746168	0.038665020871	0.173604490096
0.397303297670	0.961335000828	0.673604480301
0.897303267670	0.538664999172	0.326395519699
0.602696776168	0.461334979129	0.826395495904
0.996537137636	0.174294538308	0.494342233708
0.503462734862	0.825705561214	0.994342219511
0.003462734862	0.674294438786	0.005657780489
0.496537135636	0.325705461692	0.505657766292
0.241286584201	0.239446883778	0.607306588842
0.258713507631	0.760553100054	0.107306480707
0.758713507631	0.739446899946	0.892693519293
0.741286569201	0.260553116222	0.392693411158
0.355823305695	0.072652077127	0.297773602758
0.144176802050	0.927347843620	0.797773510796
0.644176802050	0.572652156380	0.202226489204
0.855823305695	0.427347930873	0.702226397242
0.242330677147	0.480587961517	0.491454992119
0.257669320040	0.519412076099	0.991455006098
0.757669320040	0.980587923901	0.008544963902
0.742330677147	0.019412038483	0.508545037881
0.511404081884	0.193786167409	0.273214961119
0.988595889514	0.806213777030	0.773214961478
0.488595889514	0.693786222970	0.226785038522
0.011404081884	0.306213817591	0.726785038881
0.002050276390	0.259715004715	0.239187549760
0.497949719813	0.740285022153	0.739187548410
0.997949719813	0.759714977847	0.260812451590
0.502050271390	0.240284995285	0.760812450240
0.242182376903	0.009708017778	0.015569028410
0.257817644775	0.990291880274	0.515569022028
0.757817644775	0.509708119726	0.484430947972
0.742182391903	0.490291985222	0.984430999590

TABLE VII. Calculated atomic coordinates of Sb_2O_4 (α) using PBE-GGA-D2 in the VASP POSCAR format.

O Sb
1.0
5.499793002946 0.000000000000 0.000000000000
0.000000000000 4.858534753056 0.000000000000
0.000000000000 0.000000000000 11.862525743765
O Sb
16 8
Direct
0.354296969502 0.164357253201 0.090225806556
0.645703001498 0.835642731799 0.590225835556
0.854296998502 0.335642731799 0.090225806556
0.145703030498 0.664357268201 0.590225835556
0.078336574288 0.807229271537 0.189616752473
0.921663432712 0.192770728463 0.689616752473
0.578336567288 0.692770728463 0.189616752473
0.421663432712 0.307229271537 0.689616752473
0.165309048219 0.305216670603 0.307123439314
0.834690981781 0.694783359397 0.807123439314
0.665309018219 0.194783329397 0.307123439314
0.334690951781 0.805216640603 0.807123439314
0.318562436969 0.842754954276 0.403749530460
0.681437593031 0.157245045724 0.903749530460
0.818562406969 0.657245045724 0.403749530460
0.181437563031 0.342754954276 0.903749530460
0.376351229445 0.001164422450 0.248986223423
0.623648770555 0.998835595550 0.748986208423
0.876351229445 0.498835565550 0.248986223423
0.123648770555 0.501164404450 0.748986208423
0.026285827362 0.031172008004 0.997598270774
0.973714172638 0.968828017996 0.497598271774
0.526285827362 0.468827987996 0.997598270774
0.473714172638 0.531171982004 0.497598271774

TABLE VIII. Calculated atomic coordinates of Sb_2O_4 (β) using PBE-GGA-D2 in the VASP POSCAR format.

O	Sb	
1.0		
12.203365743141	0.000000000000	-0.099609248305
0.000000000000	4.902514145949	0.000000000000
-1.413368416445	0.000000000000	5.224277898947
O	Sb	
16	8	
Direct		
0.190549913676	0.063631809448	0.662427923408
0.809450071324	0.936368213552	0.337572076592
0.809450071324	0.063631809448	0.837572076592
0.190549913676	0.936368213552	0.162427923408
0.690549928676	0.563631786448	0.662427923408
0.309450071324	0.436368183552	0.337572076592
0.309450071324	0.563631786448	0.837572076592
0.690549928676	0.436368183552	0.162427923408
0.092918194166	0.408228032198	0.966398509952
0.907081782834	0.591771937802	0.033601490048
0.907081782834	0.408228032198	0.533601490048
0.092918194166	0.591771937802	0.466398509952
0.592918217166	0.908228062198	0.966398509952
0.407081812834	0.091771967802	0.033601490048
0.407081812834	0.908228062198	0.533601490048
0.592918217166	0.091771967802	0.466398509952
0.250000000000	0.250000000000	0.000000000000
0.750000000000	0.750000000000	0.000000000000
0.750000000000	0.250000000000	0.500000000000
0.250000000000	0.750000000000	0.500000000000
0.000000000000	0.281523444357	0.250000000000
0.000000000000	0.718476585643	0.750000000000
0.500000000000	0.781523414357	0.250000000000
0.500000000000	0.218476555643	0.750000000000

TABLE IX. Calculated atomic coordinates of Sb_2O_5 using PBE-GGA-D2 in the VASP POSCAR format.

O	Sb	
1.0		
12.788611630663	0.000000000000	0.023245630659
0.000000000000	4.855775621876	0.000000000000
-1.309123160579	0.000000000000	5.324048017933
O	Sb	
20	8	
Direct		
0.297541158668	0.080474874362	0.375680201470
0.702458841332	0.919525096638	0.624319768530
0.702458841332	0.080474874362	0.124319798530
0.297541158668	0.919525096638	0.875680231470
0.797541158668	0.580474903362	0.375680201470
0.202458841332	0.419525125638	0.624319768530
0.202458841332	0.580474903362	0.124319798530
0.797541158668	0.419525125638	0.875680231470
0.399187421048	0.411121528487	0.054664668567
0.600812608952	0.588878441513	0.945335331433
0.600812608952	0.411121528487	0.445335331433
0.399187421048	0.588878441513	0.554664668567
0.899187391048	0.911121558487	0.054664668567
0.100812578952	0.088878471513	0.945335331433
0.100812578952	0.911121558487	0.445335331433
0.899187391048	0.088878471513	0.554664668567
0.000000000000	0.424672695261	0.250000000000
0.000000000000	0.575327334739	0.750000000000
0.500000000000	0.924672665261	0.250000000000
0.500000000000	0.075327304739	0.750000000000
0.137847296580	0.239880982331	0.279421894129
0.862152673420	0.760119032669	0.720578075871
0.862152673420	0.239880982331	0.220578105871
0.137847296580	0.760119032669	0.779421924129
0.637847326580	0.739880967331	0.279421894129
0.362152703420	0.260119032669	0.720578075871
0.362152703420	0.739880967331	0.220578105871
0.637847326580	0.260119032669	0.779421924129

TABLE X. Relaxed densities of the amorphous and crystalline antimony oxides.

Phase	Density (g/cm^3)
a–Sb_2O_3	5.59
a–Sb_2O_4	6.05
a–Sb_2O_5	6.01
c–$Sb_2O_3(\alpha)$	5.69
c–$Sb_2O_3(\beta)$	5.93
c–$Sb_2O_3(\gamma)$	5.97
c–$Sb_2O_4(\alpha)$	6.44
c–$Sb_2O_4(\beta)$	6.55
c–Sb_2O_5	6.50

REFERENCES

[1]R. M. Bozorth, J. Am. Chem. Soc. **45**, 1621 (1923).

[2]C. Svensson, Acta. Crystallogr. Sect. B-Struct. Sci. **30**, 458 (1974).

[3]D. Orosel, R. E. Dinnebier, V. A. Blatov, and M. Jansen, Acta Crystallogr. B. **68**, 1 (2012).

[4]G. Thornton, Acta. Crystallogr. Sect. B-Struct. Sci. **33**, 1271 (1977).

[5]R. Basso, G. Lucchetti, L. Zefiro, and A. Palenzona, Eur. J. Mineral. **11**, 95 (1999).

[6]M. Jansen, Angew. Chem. **90**, 141 (1978).