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Diversities of Stoichiometry and Electrical Conductivity in Sodium Sulfides

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Table S1. Lattice parameters and space group (SG) of experimental phases: Na_2S_5, Na_2S_4, Na_2S_2 and Na_2S, which derived using PBE and optB86-vdW methods and compared with experimental values at 0 GPa

Phase	SG	Method	a	b	C
		Exp.	7.654	14.51	5.846
Na_2S_5	*Pnma*	PBE	7.797	14.723	5.913
		optB86-vdW	7.605	14.471	5.778
		Exp.	9.5965		11.7885
Na_2S_4	$I\text{-}4_2d$	PBE	9.698		11.975
		optB86-vdW	9.552		11.626
		Exp.	4.489		10.227
Na_2S_2	$P6_3/mmc$	PBE	4.501		10.277
		optB86-vdW	4.445		10.210
		Exp.	7.629		5.394
Na_2S_2	$P\text{-}6_2m$	PBE	7.676		5.397
		optB86-vdW	7.581		5.371
		Exp.	6.547		
Na_2S	*Fm*-3*m*	PBE	6.567		
		optB86-vdW	6.514		

Table S2. Lattice parameters, space group (SG) and atomic position of predicted phases: Na_3S, Na_5S_3, Na_2S_2 and Na_2S_3

Compound	SG	Lattice parameters			Site		Special position		
		a	b	c			x	y	z
Na_3S	*P6₃/mmc*	6.831		4.512	Na	6h	0.8183	0.1817	0.2500
					S	2c	0.6667	0.3333	0.7500
Na_5S_3	*I*4/*mcm*	10.938		5.333	Na1	4b	0.0000	0.5000	0.7500
					Na2	16k	0.7840	0.0873	0.0000
					S1	8h	0.3458	0.8458	0.5000
					S2	4a	0.0000	0.0000	0.2500
Na_2S_2	*Pbam*	9.156	4.432	3.814	Na	4g	0.8648	0.3347	0.0000
					S	4h	0.3985	0.6338	0.5000
Na_2S_3	*Pnma*	13.087	7.964	4.073	Na	8d	0.3795	0.9742	0.3211
					S1	4c	0.4811	0.7500	0.8779
					S2	4c	0.2444	0.7500	0.6304
					S3	4c	0.1144	0.7500	0.3189

Table S3. Calculated elastic constants (C_{ij} in GPa) for Na_3S, Na_5S_3, Na_2S_2 and Na_2S_3, respectively. Na_2S_2 are calculated at 7GPa; all the other phases are calculated at 0 GPa

Phases	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}
Na_3S	19.3		57.7	0.87			17.5	19.4	
Na_5S_3	67.5		61.7	26.1		8.75	25.7	19.2	
Na_2S_2	76.5	76.3	121.4	43.0	17.6	7.5	53.0	21.9	30.3
Na_2S_3	55.1	54.8	25.9	96.7	69.3	14.9	9.0	10.8	9.2

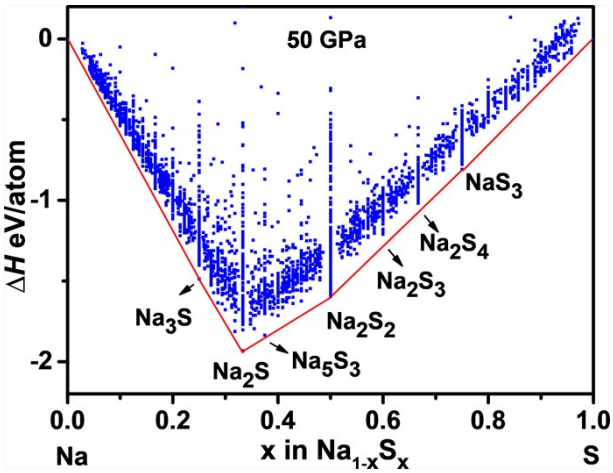

Figure S1. Convex hull constructed by structure searches using variable compositions at 50 GPa.

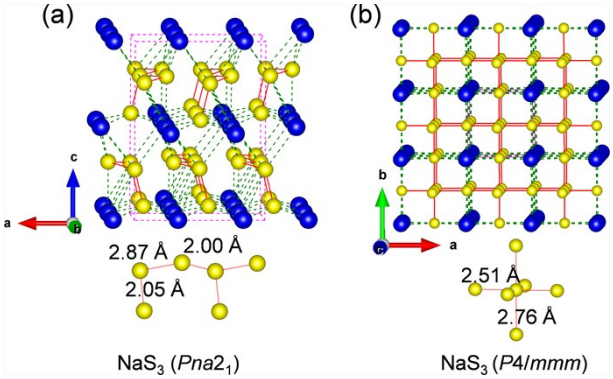

Figure S2. Crystal structure for predicted NaS_3 ($Pna2_1$) (a) and NaS_3 ($P4/mmm$) (b); the blue and yellow spheres represent Na and S atoms, respectively.

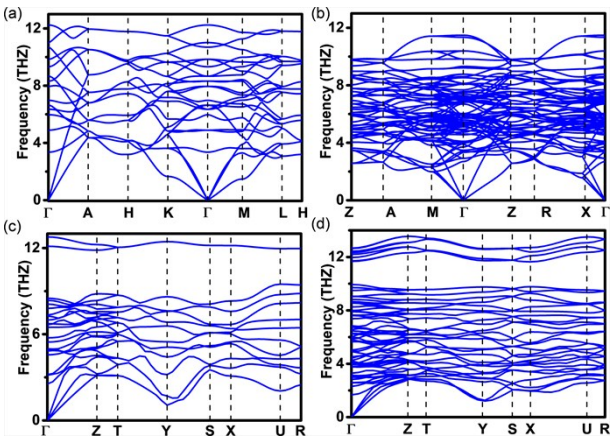

Figure S3. Phonon dispersion for predicted Na_3S calculated at 30 GPa (a). Na_5S_3 (b), Na_2S_3 (c) and Na_2S_2 (d) are calculated at 10 GPa.

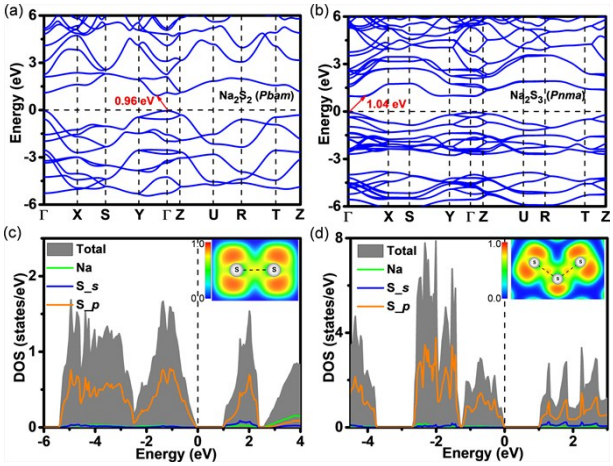

Figure S4. Band structure for predicted phases: Na_2S_2 (*Pbam*) (a) and Na_2S_3 (*Pnma*) (b). Total and partial density for Na_2S_2 (*Pbam*) (c) and Na_2S_3 (*Pnma*) (d). The inserts in density of states are the ELF maps around the S_2^{2-} and S_3^{2-} polyanions.