

**Supplementary Information** for the paper entitled “*Unexpected Stable Stoichiometries and Superconductivity of Potassium-rich Sulfides*”

Ying Li, Xilian Jin\*, Tian Cui\*, Quan Zhuang, Die Zhang, Xing Meng, Kuo Bao, Bingbing Liu, and Qiang Zhou.

College of Physics, State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, China

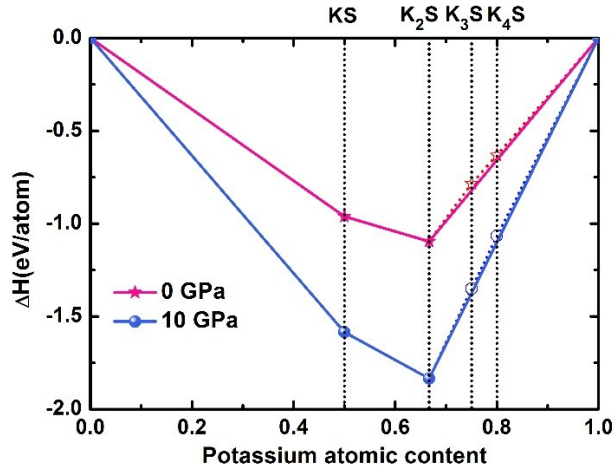


Fig. S1 Enthalpy difference curves of  $K_xS$  with respect to K and S at selected pressures.

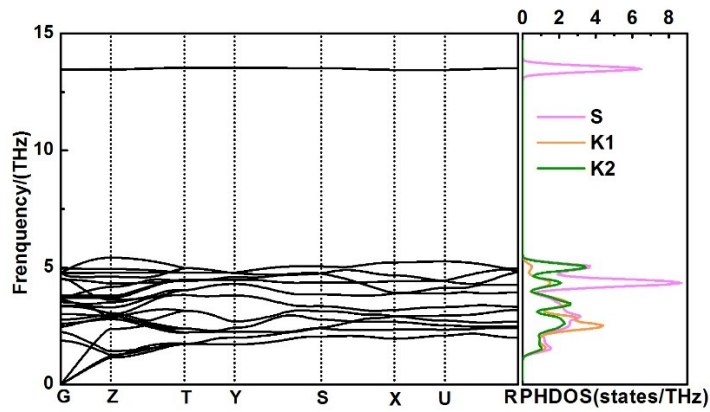


Fig. S2 The phonon band structure and partial phonon density of states (PDOS) charts of  $Pmmn$  (KS) at ambient pressure.

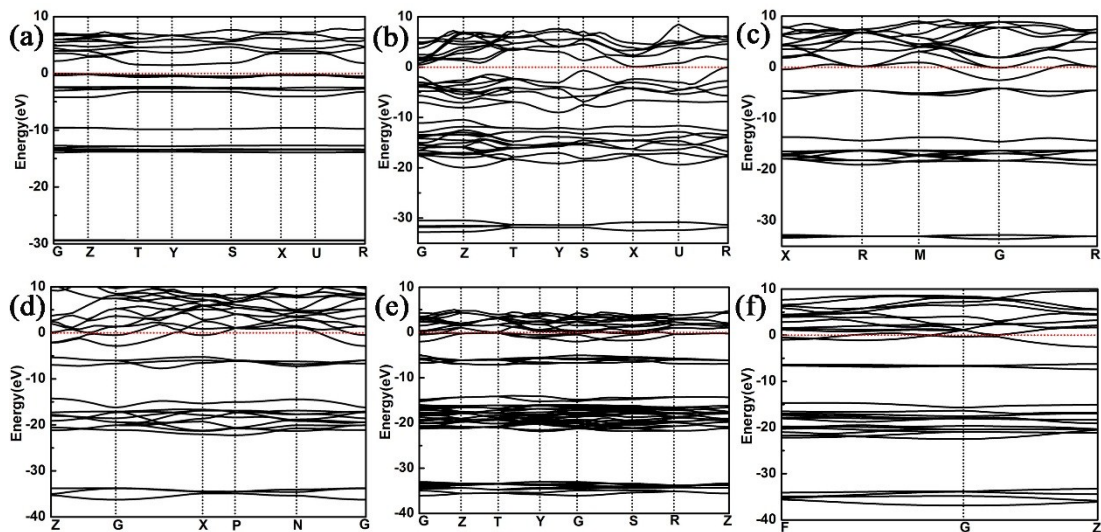


Fig. S3 The electronic band structure of  $K_xS$  compounds. (a) The electronic band structure of  $Pmmn$  (KS) at ambient pressure, (b) the electronic band structure of  $Pbam$  (KS) at 100 GPa, (c) the electronic band structure of  $Pm-3m$  ( $K_3S$ ) at 50 GPa, (d) the electronic band structure of  $I4/mmm$  ( $K_3S$ ) at 100 GPa, (e) the electronic band structure of  $Cmcm$  ( $K_4S$ ) at 30 GPa, (f) the electronic band structure of  $R-3m$  ( $K_4S$ ) at 100 GPa. The dotted line indicates the Fermi energy.

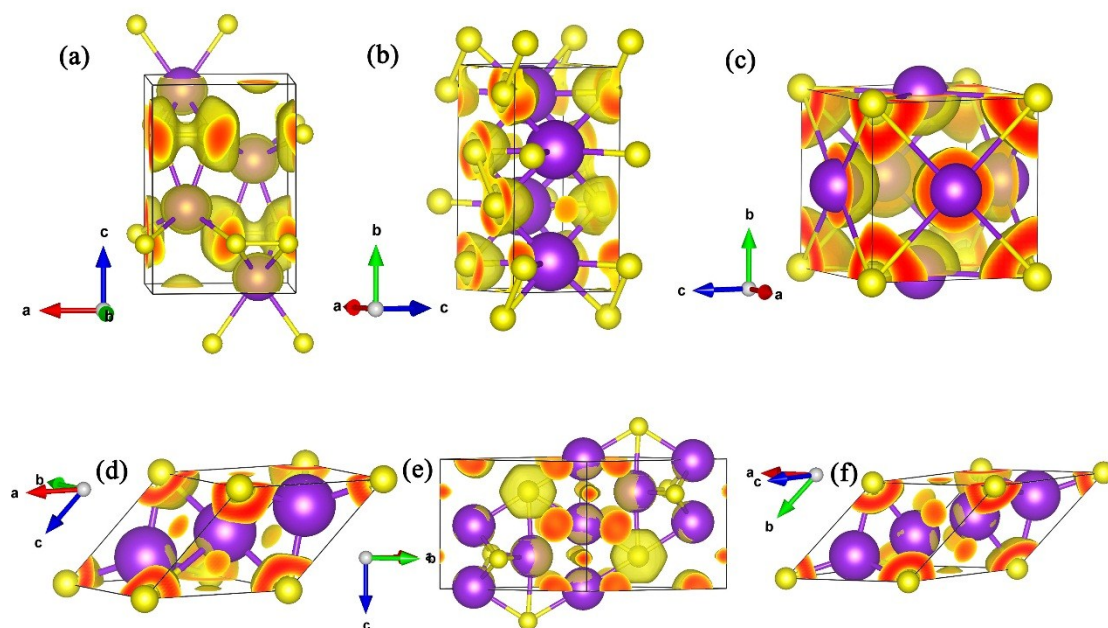


Fig. S4 Crystal structure and isosurface (0.65) of the ELF  $K_xS$  system. (a)  $Pmmn$  (KS) at ambient pressure, (b)  $Pbam$  (KS) at 100 GPa, (c)  $Pm-3m$  ( $K_3S$ ) at 50 GPa, (d)  $I4/mmm$  ( $K_3S$ ) at 100 GPa, (e)  $Cmcm$  ( $K_4S$ ) at 50 GPa, (f)  $R-3m$  ( $K_4S$ ) at 100 GPa. Purple and yellow atoms are K and S, respectively.

**Table S1** Detailed structural information of the  $K_xS$  compounds.

Space group	Pressure (GPa)	Lattice parameter (Å)	Atom	Atomic coordinates		
				X	Y	Z
$Pmmn$	0	a=5.89500	S(4f)	-0.18285	0.50000	0.25052
		b=4.97450	K(2b)	-0.00000	0.50000	0.59911
		c=8.63760	K(2a)	0.00000	1.00000	0.06262
$Pbam$	100		S(4g)	0.68357	0.61517	0.00000
			K(4h)	0.70981	0.86932	0.50000
$Pm-3m$	50	a=b=c= 3.95830	S(1a)	0.00000	0.00000	0.00000
			K(3c)	0.00000	0.50000	0.50000

<i>I4/mmm</i>	100	a=b=3.75560	S(2a)	-0.00000	-1.00000	0.00000
		c=7.03500	K(4d)	-0.00000	-0.50000	-0.25000
			K(2b)	-0.00000	-1.00000	-0.50000
<i>Cmcm</i>	50	a=4.45390	S(4c)	-0.00000	0.69227	0.75000
		b= 12.52340	K(4c)	0.00000	0.31925	0.75000
		c=5.65380	K(4b)	-0.00000	0.50000	0.50000
			K(8f)	-0.00000	0.88170	1.01298
<i>R-3m</i>	100	a=b=c=4.78090	S(1a)	0.00000	0.00000	0.00000
			K(2c)	0.40604	0.40604	0.40604
			K(2c)	0.78458	0.78458	0.78458

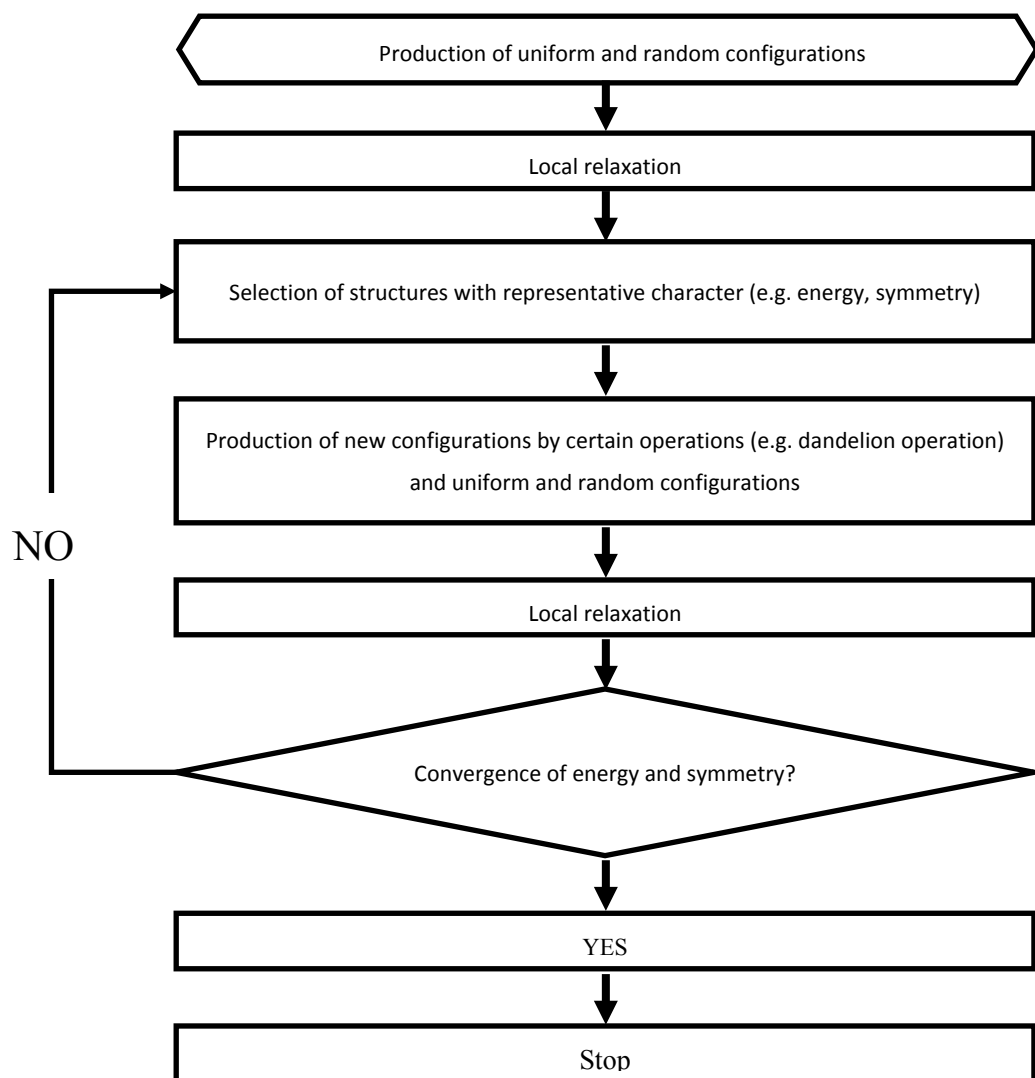
**Table S2** The calculated elastic constant  $C_{ij}$  (GPa) of  $K_xS$  compounds at relevant pressure.

Space group	Pressure (GPa)	$C_{11}$	$C_{12}$	$C_{13}$	$C_{33}$	$C_{44}$
		$C_{22}$	$C_{23}$	$C_{55}$	$C_{66}$	
<i>Pmmn</i>	0.0001	11.75	6.77	9.45	33.06	8.87
		30.61	11.48	10.36	8.72	
<i>Pbam</i>	100	285.51	128.88	250.18	465.84	228.43
		345.64	212.26	243.65	210.28	
<i>Pm-3m</i>	50	180.08	103.87	103.87	180.08	67.41
		180.08	103.87	67.41	67.41	
<i>I4/mmm</i>	100	442.98	274.23	293.73	364.38	142.08
		442.98	293.73	142.08	97.03	
<i>Cmcm</i>	50	173.96	65.31	58.44	148.16	51.72
		147.16	63.15	52.60	49.08	
<i>R-3m</i>	100	457.31	188.90	72.96	579.53	34.94
		188.90	72.96	34.94	134.20	

#### The detailed descriptions of ELocR code.

We have developed a software code ELocR (Crystal Structure Analysis by Evolutional Local Random Computational Method) for crystal structure prediction combined with ab initio energy calculational codes, e.g. VASP, and a special evolutional strategy. The approach only requires chemical compositions for a given compound to predict stable or metastable

structures at given external conditions, e.g. pressure. In the first generation, the unit cell is built and constrained by axis lengths, cell angles, and cell volume to the target values. Atoms or atomic groups are distributed uniformly and randomly but must meet the criteria of distance or bond length between atoms in the unit cell. The ab initio code is adopted to relax the configuration to the optimized structure with a local minimum in the energy. Subsequently, a number of optimized structures with certain representative character, for example lower energy, higher symmetry etc. are selected as the seeds for next generations to produce new configurations. Then partial atoms are deviated from the original positions by certain operations, e.g. dandelion operation, and satisfied certain distribution, e.g. Gaussian distribution. At the same time, a proportion of configurations as mentioned in the first generation are adopted to enhance structural diversity. Repeated the steps described above until the convergence of energy and symmetry have been reached. The flow chart of ELocR can be found in figure below.



Those information of ELocR code mentioned above has been published in *RSC Advances* (Y. Li, X. Jin, T. Cui, et al. *RSC Adv.*, 2017, 7, 7424-7430.)

We have used ELocR code to predict the thermodynamically stable structures of

various stoichiometries of  $\text{SnH}_n$  ( $n = 1/4, 1/3, 1/2, 1, 2, 3, 4, 5, 6, 7, 8$ ) using ELocR code, and checked by the USPEX successfully. (H. Zhang, X. Jin, et al. *RSC Adv.*, 2015, **5**, 107637-107641.) Some calculated data on crystal structure of ELocR code agreed well with corresponding experimental X-ray diffraction (XRD) data [Q. Zhuang, X. Jin, T. Cui, et al. *Inorg. Chem.*, 2017, **56**, 3901-3908; Y. Li, X. Jin, T. Cui, et al. *RSC Adv.*, 2017, **7**, 7424-7430].