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.
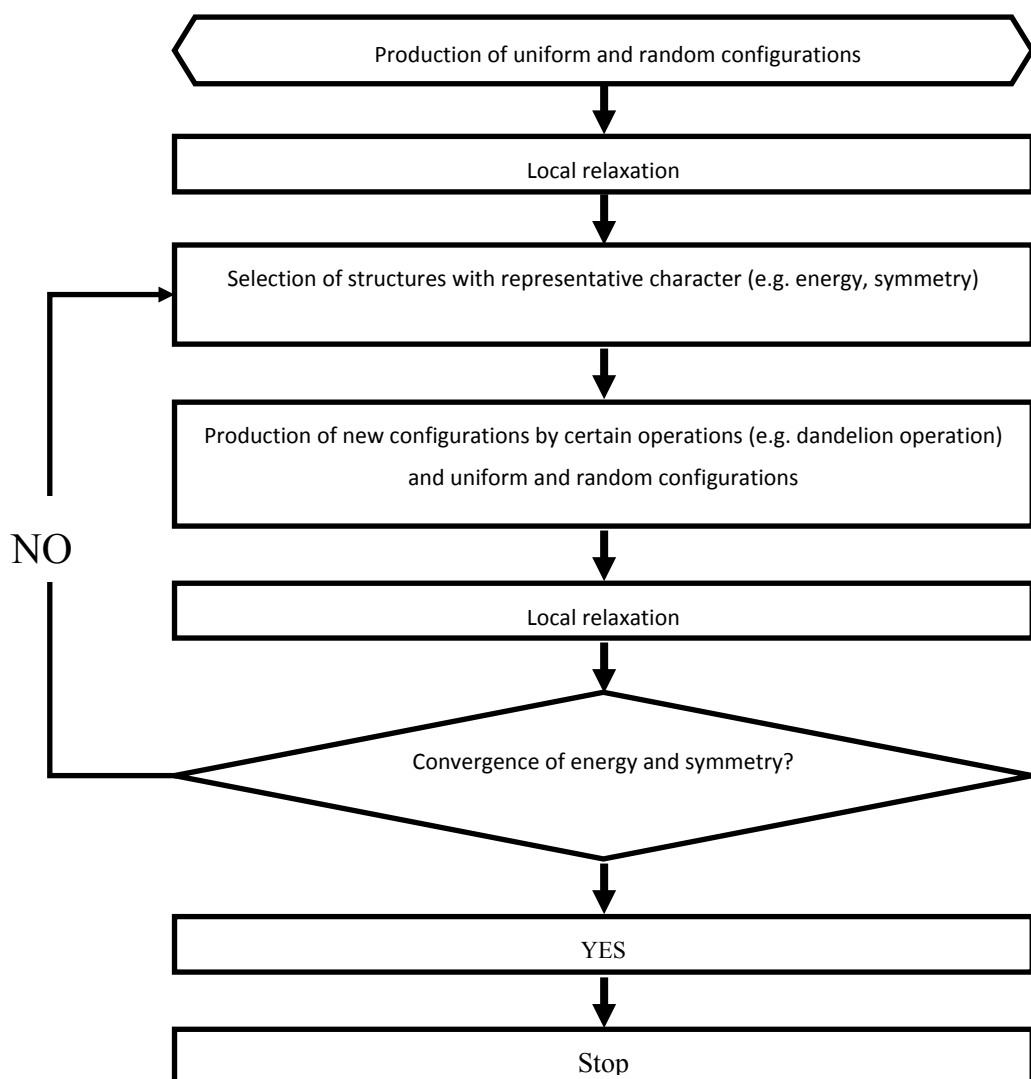
Elastic constants C_{ij} of *Pmma* phase at 4.4 GPa.

C_{11}=-252.887, C_{22}=176.3391, C_{33}=229.4843, C_{44}=26.9919, C_{55}=-77.5387, C_{66}=-7.0655, C_{12}=116.4225, C_{13}=122.7900, C_{23}=122.0376.

$C_{11}<0$, $C_{55}<0$, $C_{66}<0$, $C_{11}+C_{22}+C_{23}+2(C_{12}+C_{13}+C_{23})>0$, $C_{11}+C_{22}-2C_{12}<0$, $C_{11}+C_{33}-2C_{13}<0$, $C_{22}+C_{33}-2C_{23}>0$.

Those do not satisfy Born-Huang criterion, which reflecting the mechanical instability of *Pmma* phase.
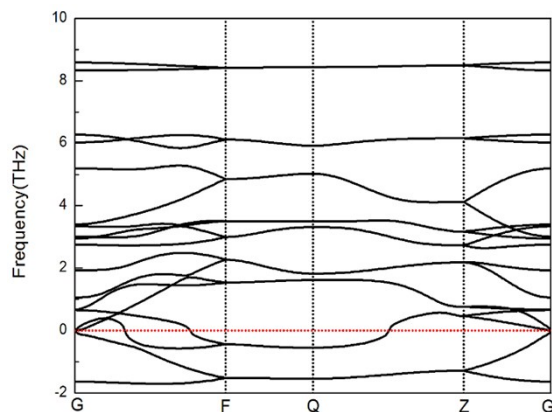
The Phonon band structure of *Pmma* phase.

Figure. 1 The phonon band structure of *Pmma* Phase at 4.4 GPa.

Table 1 Structural coordinates of K2S phases.

Space group	Pressure (GPa)	Atom (Wyckoff)	Atomic	fractional	coordinates	Atomic	cartesian	coordinates
			X	Y	Z	X	Y	Z
$P6_3/mmc$	10	S(2c)	0.33333	0.66667	0.25000	1.43333	2.48263	1.56585
		K(2a)	1.00000	0.00000	1.00000	4.29999	2.48263	6.26340
		K(2d)	0.33333	0.66667	0.75000	1.43333	2.48263	4.69755
Cmcm	100	S(4c)	0.00000	-0.70000	-0.25000	0.00000	3.11192	1.09133
		K(8g)	-0.16510	-0.19323	-0.25000	1.28436	0.85902	1.09133
$P6/mmm$	150	S(1a)	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
		K(2d)	0.33333	0.66667	0.50000	1.14719	1.98700	1.19970
P-3m1	200	S(1b)	1.00000	1.00000	-0.50000	3.37940	1.95110	1.12385
		K(2d)	2.33333	1.66666	-0.90932	7.88528	1.95110	-2.04388