Supporting Information
For

Structural diversity and hydrogen storage properties in the system K-Si-H

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Computational details

Full variable-composition predictions were firstly performed within 4000 structures using random structure searches based on the AIRSS code at pressures of 1atm, 50 and 100 GPa. Within the basic AIRSS approach a cell volume and shape is selected at random within a reasonable range; atoms are added at random positions to provide the desired stoichiometry and the system is relaxed until the forces on the atoms are negligible and the pressure takes the required value. Repeating this procedure provides a relatively sparse sampling of the ‘structure space’. We constrained the minimum atomic distances of 1-3 Å in the initial structures, which helps to space out the atoms appropriately and also retain a high degree of randomness. We performed searches with various different symmetry constraints, which is useful because low-energy structures often possess symmetries. The CASTEP code [1] with on-the-fly (OTF) generation of ultrasoft pseudopotentials was used during the AIRSS searches. The cut_off_energy and kpoints_mp_spacing parameters were chosen to be 500 eV and $2\pi \times 0.07$ Å^{-1}. Fixed-composition predictions were employed to further search stable or metastable structures for stable compounds with 1-4 formula units by means of CALYPSO and USPEX codes, during which the geometrical optimizations were performed by VASP (Vienna ab initio simulation packages) code. The cutoff energy and k-point mesh were set as 400 eV and $2\pi \times 0.07$ Å^{-1}. For most of the cases, the fixed-composition structure searches reached convergence after 40 generations, generating about 1600 structures. The predicted low-enthalpy structures were then optimized at a higher accuracy using VASP code.

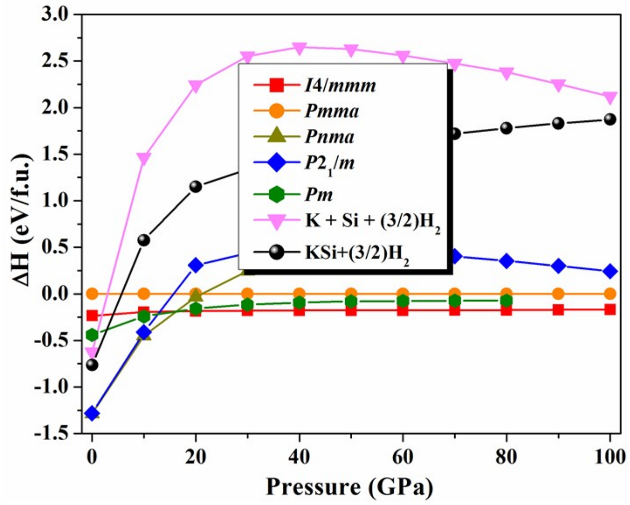

Fig. S1. Enthalpy curves of various structures of $KSiH_3$ relative to *Pmma* structure as a function of pressure. The enthalpies for $KSiH_3$ with respect to K + Si + H_2 are also provided. As shown, two competitive structures of $P2_1/m$ and *Pnma* have lower enthalpies at ambient conditions. The vertical coordinates of $P2_1/m$ and *Pnma* are -1.280 eV/f.u. and -1.287 eV/f.u., respectively, indicating that $KSiH_3$ prefers *Pnma* phase.

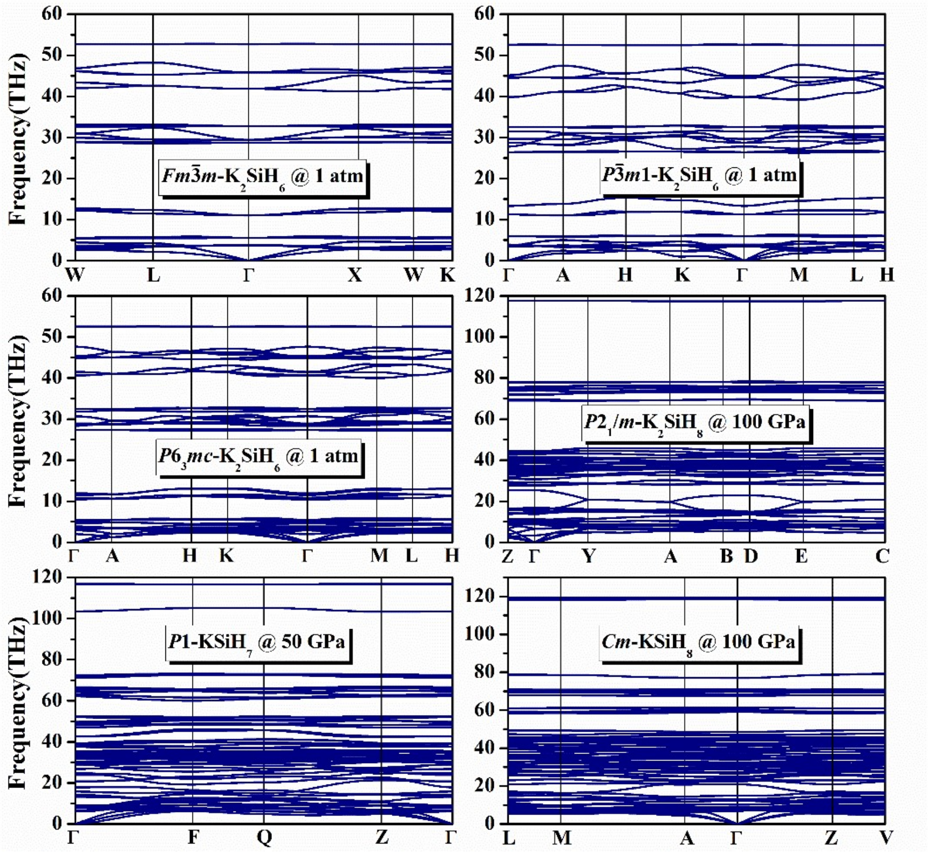

Fig. S2 Calculated phonon dispersion curves for K-Si-H phases at corresponding pressures.

Table S1. Calculated elastic constants for K-Si-H compounds.

Crystal structure	C_{ij} (kBar)
$Fm\bar{3}m$-K_2SiH_6 (1 atm)	$C_{11} = 322$, $C_{44} = 105$, $C_{12} = 106$.
$P\bar{3}m1$-K_2SiH_6 (1 atm)	$C_{11} = 482$, $C_{33} = 214$, $C_{44} = 62$, $C_{66} = 183$, $C_{12} = 116$, $C_{13} = 45$.
$P6_3mc$-K_2SiH_6 (1 atm)	$C_{11} =385$, $C_{33} = 263$, $C_{44} = 95$, $C_{66} = 126$, $C_{12} = 133$, $C_{13} = 86$.
$P2_1/m$-K_2SiH_8 (100 GPa)	$C_{11} =3507$, $C_{22} = 3184$, $C_{33} = 3916$, $C_{44} = 554$, $C_{55} = 1281$, $C_{66} = 1543$, $C_{12} = 1483$, $C_{13} = 1279$, $C_{23} = 1983$, $C_{15} = 109$, $C_{25} = -176$, $C_{35} = 59$, $C_{46} = -71$.
$P1$-$KSiH_7$ (50 GPa)	$C_{11} = 2343$, $C_{12} = 567$, $C_{13} = 829$, $C_{14} = -189$, $C_{15} = -76$, $C_{16} = 87$, $C_{21} = 567$, $C_{22} = 2334$, $C_{23} = 1112$, $C_{24} = -11$, $C_{25} = -55$, $C_{26} = 133$, $C_{31} = 829$, $C_{32} = 1112$, $C_{33} = 2034$, $C_{34} = 149$, $C_{35} = 129$, $C_{36} = -86$, $C_{41} = -189$, $C_{42} = -11$, $C_{43} = 149$, $C_{44} = 1007$, $C_{45} = 140$, $C_{46} = 31$, $C_{51} = -75$, $C_{52} = -55$, $C_{53} = 129$, $C_{54} = 140$, $C_{55} = 551$, $C_{56} = -82$, $C_{61} = 87$, $C_{62} = 133$, $C_{63} = -86$, $C_{64} = 31$, $C_{65} = -82$, $C_{66} = 549$.
Cm-$KSiH_8$ (100 GPa)	$C_{11} =3742$, $C_{22} = 3690$, $C_{33} = 3659$, $C_{44} = 1462$, $C_{55} = 1508$, $C_{66} = 1350$, $C_{12} = 1637$, $C_{13} = 1356$, $C_{23} = 1343$, $C_{15} = -4$, $C_{25} = -58$, $C_{35} = -193$, $C_{46} = 269$.

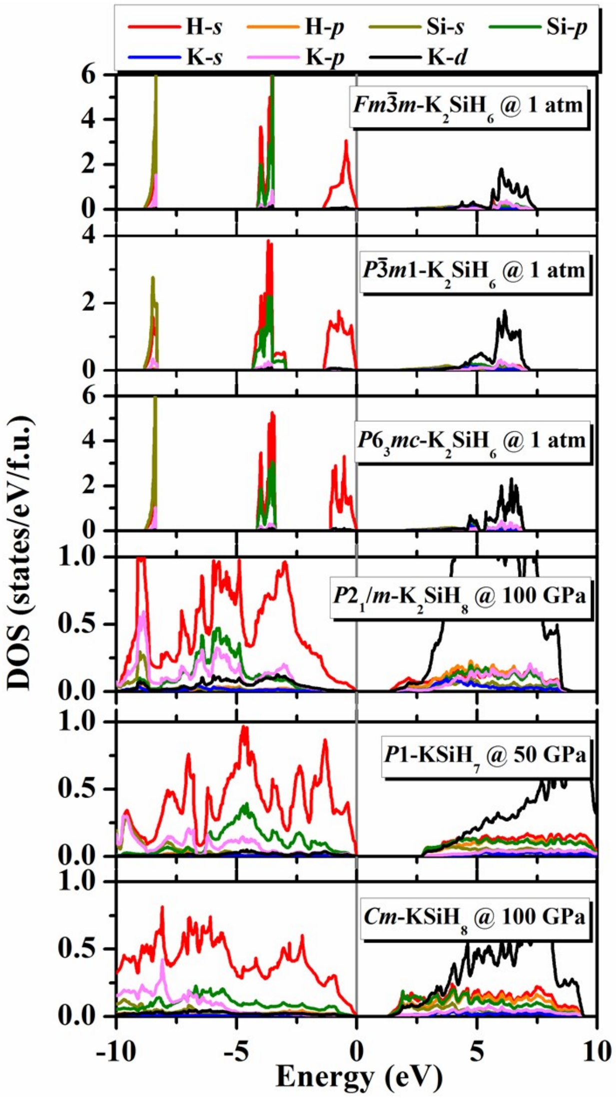

Fig. S3 Calculated projected density of states for K-Si-H phases. Fermi level is set at zero energy and marked by the vertical solid line. It is shown that the gaps between the valence and conduction bands give all studied compounds the properties of insulating materials. In K_2SiH_6 phases, there are quite large contributions of H-*s* orbit on the highest valence bands in comparison to that in other compounds. Furthermore, it is noted that the weak Si-*p* and H-*s* orbital hybridization in the valence band region can be seen, which contributes the weak bonding interactions between Si and H atoms.

Table S2. The calculated charge values of K, Si and H atoms. δ(e) represents the lost charge. It is shown that the charge is transferred from K and Si to H atoms.

Structure Pressure	Atom	Charge value	δ(e)
$Fm\bar{3}m$-K_2SiH_6 1 atm	H1	1.70	-0.70
	Si1	1.41	2.59
	K1	8.19	0.81
$P\bar{3}m1$-K_2SiH_6 1 atm	H1	1.70	-0.70
	Si1	1.42	2.58
	K1	8.20	0.80
$P6_3mc$-K_2SiH_6 1 atm	H1	1.70	-0.7
	H7	1.70	-0.7
	Si1	1.41	2.59
	K1	8.19	0.81
	K3	8.19	0.81
$P2_1/m$- K_2SiH_8 100 GPa	H1	1.66	-0.66
	H2	1.66	-0.66
	H3	1.03	-0.03
	H13	1.65	-0.65
	H15	1.66	-0.66
	Si1	1.18	2.82
	K1	8.42	0.58
	K3	8.41	0.59
$P1$- $KSiH_7$ 50 GPa	H1	1.66	-0.66
	H2	1.73	-0.73
	H3	1.66	-0.66
	H4	1.65	-0.65
	H5	1.70	-0.70
	H6	1.65	-0.65
	H7	1.64	-0.64
	H8	1.07	-0.07
	H9	1.65	-0.65
	H10	0.97	0.03
	H11	1.64	-0.64
	H12	1.66	-0.66
	H13	0.96	0.04
	H14	1.07	-0.07
	Si1	1.31	2.69
	Si2	1.32	2.68
	K1	8.32	0.68
	K2	8.33	0.67

Cm- $KSiH_8$ 100 GPa	H1	1.65	-0.65
	H2	1.00	0.00
	H3	1.62	-0.62
	H4	1.61	-0.61
	H5	1.06	-0.06
	H11	1.70	-0.70
	H12	1.75	-0.75
	H13	1.02	-0.02
	H14	1.59	-1.59
	H15	1.61	-0.61
	H16	1.03	-0.03
	Si1	1.31	2.69
	Si2	1.36	2.64
	K1	8.37	0.63

Table S3. Structural information of K-Si-H compounds under different pressures.

Structure Pressure	Lattice parameters (Å, °)	Atomic coordinates (fractional)				Sites
$Fm\bar{3}m$-K_2SiH_6	a = b = c = 7.867	H1	0.500	-0.205	-0.500	24e
	α = β = γ = 90	Si1	0.000	0.000	0.000	4a
1 atm		K1	0.250	-0.250	-0.250	8c
$P\bar{3}m1$-K_2SiH_6	a = b = 4.531	H1	0.159	0.841	0.745	6i
	c = 3.464	Si1	0.000	0.000	0.500	1b
50 GPa	α = β = 90	K1	0.667	0.333	0.778	2d
	γ = 120					
$P6_3mc$-K_2SiH_6	a = b = 5.490	H1	0.193	0.807	0.868	6c
1 atm	c = 9.074	H7	0.057	0.529	0.073	6c
	α = β = 90	Si1	0.333	0.667	0.969	2b
	γ = 120	K1	0.667	0.333	0.847	2b
		K3	0.000	0.000	0.604	2a
$P2_1/m$- K_2SiH_8	a = 3.112	H1	0.521	0.500	0.838	4f
100 GPa	b = 4.193	H2	0.788	0.994	0.708	4f
	c = 9.616	H3	0.444	0.953	0.461	4f
	α = 90	H13	0.779	0.750	0.373	2e
	β =119.04	H15	0.102	0.250	0.912	2e
	γ = 90	Si1	0.852	0.750	0.232	2e
		K1	0.137	0.750	0.934	2e
		K3	0.826	0.250	0.387	2e
$P1$- $KSiH_7$	a = 5.591	H1	0.015	0.613	0.481	1a
50 GPa	b = 5.264	H2	0.040	0.212	0.487	1a
	c = 3.952	H3	0.461	0.016	0.636	1a
	α = 71.65	H4	0.333	0.077	0.996	1a
	β = 109.37	H5	0.904	0.291	0.878	1a
	γ =76.75	H6	0.196	0.444	0.132	1a
		H7	0.618	0.714	0.451	1a
		H8	0.777	0.040	0.148	1a
		H9	0.141	0.878	0.351	1a
		H10	0.353	0.798	0.933	1a
		H11	0.620	0.318	0.359	1a
		H12	0.708	0.622	0.975	1a
		H13	0.668	0.978	0.131	1a
		H14	0.340	0.664	0.052	1a
		Si1	0.805	0.487	0.406	1a
		Si2	0.212	0.140	0.252	1a
		K1	0.905	0.882	0.774	1a
		K2	0.429	0.438	0.716	1a
Cm- $KSiH_8$	a = 7.377	H1	0.394	0.383	0.115	4b

100 GPa	b = 7.928	H2	0.471	0.134	0.946	4b
	c = 3.041	H3	0.555	0.319	0.391	4b
	α = γ = 90	H4	0.596	0.150	0.294	4b
	β = 66.01	H5	0.462	-0.229	0.965	4b
		K1	0.261	-0.226	0.671	4b
		H11	0.105	-0.000	0.778	2a
		H12	0.849	-0.000	0.710	2a
		H13	0.408	-0.000	0.384	2a
		H14	0.275	-0.000	0.139	2a
		H15	0.608	-0.000	0.796	2a
		H16	0.410	-0.000	0.631	2a
		Si1	0.049	-0.000	0.316	2a
		Si2	0.714	-0.000	0.251	2a

Reference

[1] M. D. Segall, J. D. L. Philip, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark, and M. C. Payne, J. Phys.: Condens. Matter **14**, 2717 (2002).