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K-Si (Potassium-Silicon) System

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Equilibrium Diagram

No original K-Si phase diagram is available. Information on this system was reviewed by [2001Bor].

The solubility of K in solid Si was measured from the point of view of semiconductor doping [1967Svo] in the range 550-1100 °C. The K diffused into the Si either by direct contact with liquid K or from K obtained by the electrolysis of KI. The analytical method was flame emission photometry. Single crystal *p*-type Si with a resistivity of 100 Ω cm was used. The authors claim that boron was the only impurity. The Li content of the K was below detection limits. Table 1 presents the results. The existence of compounds was not mentioned in this work [1967Svo].

The solubility of Si in liquid K was investigated by contacting the two metals for 1 h at 600-650 °C, followed by analysis by spectroscopy [1982Ale]. It was concluded that Si was "insoluble" in liquid K (the limit of detection was not stated).

KSi was prepared by heating the elements in a corundum crucible in a sealed steel bomb to 650 °C [1948Hoh, 1961Bus, 1961Sch]. It was characterized by x-ray diffraction (XRD) on powder [1948Hoh] and single-crystal samples [1961Bius, 1961Sch]. KSi is unstable to heat, losing K; upon heating in vacuo, nonstoichiometric compounds corresponding to KSi_8 [1948Hoh] or KSi_6 [1961Sch] were obtained at temperatures up to ~500 °C. That these were new species was established from their powder diffractograms [1948Hoh, 1961Sch].

Like NaSi, KSi may be partially decomposed by heating under Ar to yield K_7Si_{46} [1970Cro], which was characterized by XRD [1970Cro]. A similar compound K_8Si_{46} was prepared by reaction of K vapor with solid Si under a low pressure Ar atmosphere at 600-700 °C [1967Gal, 1969Gal]. As described in the next section, K_8Si_{46} and K_7Si_{46} belong to the same series of nonstoichiometric compounds of special common structure; it is possible, therefore, that KSi_6 and KSi_8, obtained earlier [1948Hoh, 1961Sch], were mixtures of compounds K_xSi_{46} ($x = 7, 8$).

$K_{12}Si_{17}$ was prepared by direct combination of the elements at 900 °C in sealed Nb containers jacketed in evacuated ampules of fused silica. It was characterized by single-crystal XRD [1998Sch].

Table 1 Solubility of K in Si

Temperature, °C	Atoms, cm^{-3}	Atom fraction of K(a)
550	7.0×10^{17}	1.4×10^{-5}
600	1.2×10^{18}	2.4×10^{-5}
650	1.6×10^{18}	3.2×10^{-5}
700	2.5×10^{18}	5.0×10^{-5}
750	3.4×10^{18}	6.8×10^{-5}
900	5.5×10^{18}	1.1×10^{-4}
1100	7.6×10^{18}	1.5×10^{-4}

(a) Assuming density of solid Si = 2.32 g cm^{-3} [1967Svo]

Crystal Structures and Lattice Parameters

Crystal structures and lattice parameters are presented in Tables 2 and 3.

KSi, with 32 molecules per unit cell, contains isolated Si_4 tetrahedra surrounded by K atoms. Each K atom has four Si_4 groups associated with it, arranged tetrahedrally [1961Bus]. These Si_4 tetrahedra are similar to Sn_4, Ge_4, and Pb_4 groups also found in intermetallic compounds with alkali metals [1985Sch]. For this reason KSi is sometimes written as K_4Si_4.The compound identified as KSi_6 was indicated by powder XRD to have a cubic structure [1948Hoh].

The compounds K_7Si_{46} and K_8Si_{46} both belong to a series of cage or clathrate structures, strictly analogous to the well-known gas or liquid hydrates, such as $8Cl_2 \cdot 46H_2O$ [1970Cro]. The K compounds are analogous to the Na compounds Na_xSi_{46}, in which the Si atoms form cages for the guest metal atoms. In K_8Si_{46}, all the cages are occupied by metal atoms, but in K_7Si_{46} there is incomplete occupation.

Table 2 K-Si crystal structure data

Phase	Composition, at.% Si	Pearson symbol	Space group	Strukturbericht designation	Prototype	Reference
K	0	*cI*2	$Im\bar{3}m$	A2	W	[King1]
KSi	50.0	*cP*64	$P\bar{4}3n$	…	GeK	[1961Sch]
KSi(a)	50.0	*tI*64	$I4_1/acd$	…	NaPb	[1984Eve]
$K_{12}Si_{17}$	58.6	…	$P2_1/c$	…	…	[1998Que]
K_7Si_{46}	85.2	…	$Pm\bar{3}n$	…	K_7Si_{46}	[1969Gal]
K_8Si_{46}	86.8	*cP*54	$Pm\bar{3}n$	…	K_8Si_{46}	[1967Gal] [1969Gal]
Si	100	*cF*8	$Fd\bar{3}m$	A4	C (diamond)	[King1]

(a) at 4 GPa

Table 3 K-Si lattice parameter data

Phase	Composition, at.% Si	Lattice parameter, nm			β	Reference
		a	*b*	*c*		
K	0	0.5321	…	…	…	[King1]
KSi	50.0	1.262	…	…	…	[1961Bus, 1961Sch]
KSi(a)	50.0	1.057	…	1.710	…	[1984Eve]
$K_{12}Si_{17}$	58.6	2.571	1.4770	4.819	91.64°	[1998Que]
K_8Si_{46}	85.2	1.030	…	…	…	[1967Gal, 1969Gal]
K_7Si_{46}	86.8	1.026	…	…	…	[1970Cro]
Si	100	0.54306	…	…	…	[King1]

(a) at 4 GPa

The clathrate structure may be described as a tetrahedral network of pentagonal dodecahedra combined with 14-face polyhedra [1967Gal, 1969Gal].

$K_{12}Si_{17}$ is monoclinic overall with a large unit cell (Z = 16). This compound contains the cluster Si_9^{4-} [1998Sch] and may be written (K_4Si_9 + $2K_4Si_4$) [1998Que]. Experimental Raman spectra due to Si_9^{4-} clusters were verified by quantum chemical calculations [1998Sch].

Pressure

KSi was prepared by direct reaction of the elements at 4 GPa and 600-700 °C in boron nitride crucibles with a Belt-type apparatus [1984Eve]. After quenching to ambient temperature, XRD on powder samples was taken. The high-pressure form of KSi is tetragonal of the NaPb type.

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