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Rb-Si (Rubidium-Silicon) System

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Equilibrium Diagram

Information on this system was reviewed by [2001Bor]. The only phase diagram available for this system is a small diagram (no experimental points, unlabelled axes) without further information [1978Chu]. The stated source of this phase diagram is A.N. Kuznetsov, Thesis, Sverdlovsk (1978). Little or no quantitative data is evident in this phase diagram. Nevertheless, [2001Bor] extracted the following qualitative data: there is a liquid miscibility gap in the interval $0.50 > x_{Si} > 0.04$, the montectic temperature is 611 °C and the critical temperature is 800 °C; there is a 1:1 compound that melts at 611 °C (apparently indistinguishable from the montectic temperature); there is a stoichiometric compound of approximately 84 at.% Si of indeterminate melting point. The solubility of Si in liquid Rb at the Rb melting point is apparently negligible (the solubility of Si in liquid Rb, according to [2000Bor], is 4 at.% at 600 °C).

RbSi 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 [1961Bus, 1961Sch]. According to [1948Hoh, 1961Sch], RbSi decomposes upon heating in vacuo at 350-360 °C [1948Hoh] or ~500 °C [1961Sch], forming $RbSi_6$ [1961Sch] or $RbSi_8$ [1948Hoh]. These were identified as new species by their powder diffractograms [1948Hoh, 1961Hoh].

RbSi may be partially decomposed by careful heating under argon. In this way, [1998Sch] identified Rb_6Si_{25}, Rb_8Si_{46} and Rb_xSi_{136} (x = 5 to 12) as transient species.

[1970Cro] partially decomposed RbSi to obtain Rb_5Si_{46}, which was characterized by XRD. This begins to decompose in vacuo at ~530 °C [1970Cro]. The compound of 84 at.% Si, posited by [1978Chu], may have been $RbSi_6$ or one of the transient compounds found by [1998Sch].

$Rb_{12}Si_{17}$ was prepared by synthesis from the elements at 900 °C in sealed Nb containers and jacketed in evacuated ampules of fused silica [1998Que]. Its structure was elucidated from single-crystal XRD data [1998Que].

Crystal Structures and Lattice Parameters

The crystal structures and lattice parameters are presented in Tables 1 and 2, respectively.

RbSi is isotypic with KSi and hence contains isolated Si_4 tetrahedra surrounded by Rb atoms. Each Rb atom has four Si_4 groups associated with it, arranged tetrahedrally [1961Bus]. The Si_4 tetrahedra are entirely analogous to similar 4-atom tetrahedra Sn_4, Ge_4, and Pb_4, found also in compounds with alkali metals [1985Sch]. For this reason, RbSi is sometimes written as Rb_4Si_4 [1998Que].

The compound identified as $RbSi_6$ had a cubic structure, shown by powder XRD [1961Sch].

Rb_5Si_{46} belongs 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], where the water molecules form a number of cavities for up to 8 guest molecules. In Rb_5Si_{46}, the available sites are partially occupied, and the structure is the same as the corresponding Na and K compounds M_xSi_{46} [1970Cro].

Table 1 Rb-Si crystal structure data

Phase	Composition, at.% Si	Pearson symbol	Space group	Strukturbericht designation	Prototype	Reference
Rb	0	*cI*2	$Im\bar{3}m$	*A*2	W	[King1]
RbSi	50.0	*cP*64	$P\bar{4}3n$	…	GeK	[1961Bus, 1961Sch]
$Rb_{12}Si_{17}$	58.6	…	$P2_1/c$	…	…	[1998Que]
Rb_5Si_{46}	90.1	*cP*51	$Pm\bar{3}n$	…	Si	[1970Cro]
Si	100	*cF*8	$Fd\bar{3}m$	*A*4	C (diamond)	[King1]

Table 2 Rb-Si lattice parameter data

Phase	Composition, at.% Si	Lattice parameters, nm			β	Reference
		a	*b*	*c*		
Rb	0	0.5703	…	…	…	[King1]
RbSi	50.0	1.304	…	…	…	[1961Bus, 1961Sch]
$Rb_{12}Si_{17}$	58.6	2.4445	1.4017	4.6038	91.32°	[1998Que]
Rb_5Si_{46}	90.1	1.027	…	…	…	[1970Cro]
Si	100	0.54306	…	…	…	[King1]

$Rb_{12}Si_{17}$ is overall monoclinic with a very large unit cell ($Z = 16$). It was found that the structure of this compound is characterized by both Si_4 tetrahedra and Si_9 clusters; in other words, $Rb_{12}Si_{17}$ can be written as ($Rb_4Si_9 + 2Rb_4Si_4$) [1998Sch, 1998Que]. Experimental Raman spectra due to these clusters were verified by quantum mechanical calculations by these authors.

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