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# Cs-Si (Cesium-Silicon) System

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## Equilibrium Diagram

Information on this system was reviewed by [2001Bor]. No phase diagram has been reported. A number of studies [1962Hol, 1963Hol, 1963Ked, 1965 Win] investigated the corrosion of materials (including Si) by Cs at high temperature in the context of ion propulsion. The purpose of these studies was not the determination of solubility, and no solubility data are available from them. In cesium ion bombardment of silicon experiments [1963Mcc], the maximum solubility of Cs in solid Si at 500 °C was estimated to be $10^{15}$ atoms $cm^{-3}$. Based on a density of solid Si of 2.32 g $cm^{-3}$, this is equivalent to a Cs atom fraction of $2 \times 10^{-8}$.

CsSi was prepared by direct combination of the elements at 600-650 °C [1948Hoh, 1961 Sch] and was characterized by single-crystal x-ray diffraction (XRD) [1948Hoh, 1961Bus, 1961 Sch]. The thermal decomposition of CsSi above 350 °C [1948Hoh, 1961Sch] yielded a compound of approximate stoichiometry $CsSi_8$. That this was a species different from the starting material was verified by its unindexed powder XRD pattern [1948Hoh]. More careful decomposition [1998Sch] led to the identification of a number of transient phases, such as $Cs_4Si_9$, $Cs_{12}Si_{17}$, and clathrate phases $Cs_8Si_{46}$ and $Cs_xSi_{136}$. These phases were identified by a combination of thermogravimetric and Raman spectroscopic methods and quantum chemical calculations [1998Sch].

Like NaSi and KSi, CsSi was partially decomposed by heating under argon to prepare $Cs_7Si_{136}$ [1970Cro], which was characterized by XRD [1970Cro].

## Crystal Structures and Lattice Parameters

Crystal structure and lattice parameters are presented in Tables 1 and 2, respectively.

CsSi is isostructural with KSi and RbSi and contains isolated $Si_4$ tetrahedra surrounded by Cs atoms. Each Cs atom has four $Si_4$ groups associated with it, arranged tetrahedrally [1961Bus]. The $Si_4$ groups are entirely analogous to those of other Group IV A elements $Ge_4$, $Sn_4$, and $Pb_4$ [1985Sch]. For this reason, CsSi is sometimes written as $Cs_4Si_4$.

$Cs_7Si_{136}$ is analogous to one member of the series of compounds $Na_xSi_{136}$ ($0 < x < 24$). Such a series is structurally similar to gas and liquid hydrate calathrate compounds, for example $16H_2S \cdot 8CHCl_3 \cdot 136H_2O$ [1970Cro]. The Si atoms form "cages," which may contain (to varying extent) guest molecules. The unit cubic cell of $Me_{24}Si_{136}$ may be described [1970Cro] as arising from the juxtaposition of 16 pentagonal dodecahedra and eight 16-sided polyhedra. In $Cs_7Si_{136}$, the Si cages are of two types, the larger of which can accommodate Cs atoms to a maximum of eight. The 16 smaller cages apparently remain unoccupied [1970Cro].

**Table 2 Cs-Si lattice parameter data**

| Phase | Composition, at.% Si | Lattice parameter, nm *a* | Reference |
|---|---|---|---|
| Cs | 0 | 0.6141 | [King1] |
| CsSi | 50.0 | 1.350 | [1961Bus, 1961Sch] |
| $Cs_7Si_{136}$ | 95.1 | 1.464 | [1970Cro] |
| Si | 100 | 0.54306 | [King1] |

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**Table 1 Cs-Si crystal structure data**

| Phase | Composition, at.% Si | Pearson symbol | Space group | Strukturbericht designation | Prototype | Reference |
|---|---|---|---|---|---|---|
| Cs | 0 | *cI*2 | $Im\bar{3}m$ | A2 | W | [King1] |
| CsSi | 50.0 | *cP*64 | $P\bar{4}3n$ | … | GeK | [1961Bus, 1961Sch] |
| $Cs_7Si_{136}$ | 95.1 | *cF*143 | $Fd\bar{3}n$ | … | … | [1970Cro] |
| Si | 100 | *cF*8 | $Fd\bar{3}m$ | A4 | C (diamond) | [King1] |

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