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## The C-Er (Carbon-Erbium) System

12.011

167.26

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No phase diagram is available for the Er-C system, although some information has been reported for the compounds and their structures. Tri-erbium carbide,  $\text{Er}_3\text{C}_x$  (where  $0.25 < x < 0.65$ ) forms a cubic  $\text{Fe}_4\text{N}$ -type structure in which the anion sites are partially occupied by C atoms. This structure exists immediately below the melting point, but if  $x$  is close to 0.5, the structure transforms at lower temperatures to a trigonal  $\text{CdCl}_2$ -type structure (see "The Carbon-Rare Earth Systems," in this issue). [81Ato] stated that if  $x$  is much different from 0.5, the cubic structure is retained at all temperatures. Lattice parameters for cubic  $\text{Er}_3\text{C}$  are presented in Table 1, but no values were given for trigonal  $\text{Er}_2\text{C}$ . No melting point or transformation temperature data are available for these compositions.

An intermediate compound of Er having a lower than cubic symmetry can be obtained by arc melting. [58Spe] stated that erbium sesquicarbide is isostructural with  $\text{Y}_2\text{C}_3$ . The structure of the latter compound was eventually determined by [71Bau] to be tetragonal  $\text{Sc}_{15}\text{C}_{19}$  type and the composition to be  $\text{Y}_{15}\text{C}_{19}$  instead of  $\text{Y}_2\text{C}_3$ . [74Bau] determined the equilibrium concentration of erbium

"sesquicarbide" to be  $\text{Er}_{15}\text{C}_{19}$  and reported pseudocubic tetragonal lattice parameters for this structure (Table 1). It was shown by [70Kru1], [70Kru2], and [80Nov] that  $\text{Er}_2\text{C}_3$  can be obtained with the cubic  $\text{Pu}_2\text{C}_3$ -type structure by a solid-state synthesis at elevated temperatures and pressures (30 to 90 kbar, 1200 to 1400 °C). The lattice parameter is included in Table 1. No melting information is available for these Er intermediate compounds.

In the region between 55 and 60 at.% C, the phase relationships in the Er-C phase diagram may be quite similar to those observed in the Y-C system (see "The C-Y (Carbon-Yttrium) System," to be published).

The dicarbide,  $\text{ErC}_2$ , was reported by [58Spe] to have the bct  $\text{CaC}_2$ -type structure. The average value of lattice parameters from several sources is listed in Table 1. An  $\alpha \rightleftharpoons \beta$  transformation from the tetragonal to a cubic form occurs at a temperature above 1300 °C; the lowest of four values is 1275 °C reported by [73McC], and the average of these values is  $1310 \pm 25$  °C. This is in good agreement with the systematic trends of the  $\alpha \rightleftharpoons \beta$  transformation of  $\text{RE}_2\text{C}_2$  compounds. In view of the  $\alpha \rightleftharpoons \beta$  transformation,

Table 1 Er-C Crystal Structure and Lattice Parameter Data

Phase	Composition range, at.% C	Pearson symbol	Space group	Strukturbericht designation	Prototype	Lattice parameters, nm			Density, g/cm <sup>3</sup>	Reference
						a	b	c		
(Er).....	0	<i>hP2</i>	<i>P6<sub>3</sub>/mmc</i>	A3	Mg	0.35592	...	0.55850	9.066	[86Gsc]
Er <sub>3</sub> C.....	~25 to ~33	<i>cF5</i>	<i>Fm3m</i>	<i>L</i> ' <sub>1</sub>	Fe <sub>4</sub> N	0.5034(1)	...	...	9.022	[58Spe]
Er <sub>15</sub> C <sub>19</sub> ....	55.9	<i>tP68</i>	<i>P42<sub>1</sub>c</i>	...	Sc <sub>15</sub> C <sub>19</sub>	0.7989(1)	...	1.579	9.018	[74Bau]
αErC <sub>2</sub> .....	66.7	<i>tI6</i>	<i>I4/mmm</i>	C11 <sub>a</sub>	CaC <sub>2</sub>	0.3619(1)	...	0.6097(1)	7.958	[58Spe, 67Kri, 72Ato, 76Ada, 81Sak]
βErC <sub>2</sub> (a)...	66.7	<i>cF12</i>	<i>Fm3m</i>	C1	CaF <sub>2</sub>	...	...	...	...	[67Kri, 73McC, 76Ada, 76Loe]
α'ErC <sub>2</sub> (b)...	66.7	<i>o??</i>	...	...	LuC <sub>2</sub>	1.328	2.724	0.7020	...	[68Kru]
(C).....	100	<i>hP4</i>	<i>P6<sub>3</sub>/mmc</i>	A9	C (graphite)	0.24612	...	0.67090	2.266	[Pearson2]
<b>Metastable phase</b>										
Er <sub>2</sub> C <sub>3</sub> (c)...	~60	<i>cI40</i>	<i>I43d</i>	D5 <sub>c</sub>	Pu <sub>2</sub> C <sub>3</sub>	0.8137	...	...	9.138	[70Kru1, 70Kru2, 80Nov]

(a) Structure for βErC<sub>2</sub> has not been determined, but its existence and structure are assumed on the basis of the reported α ⇌ β transformation temperature and the known βREC<sub>2</sub> data. (b) Forms from long anneals of αErC<sub>2</sub> at temperatures above 1150 °C. (c) Produced under high pressure and high temperature.

we assume that βErC<sub>2</sub> has the CaF<sub>2</sub>-type structure, similar to that reported for the βREC<sub>2</sub> phase for RE = La, Ce, Eu, Tb, and Lu.

[68Kru] reported that a third form of ErC<sub>2</sub> exists, forming during long anneals at 1305 ± 10 °C (100 to 270 h) from CaC<sub>2</sub>-type αErC<sub>2</sub>. This form (α'ErC<sub>2</sub>) has the LuC<sub>2</sub>-type orthorhombic structure (Table 1).

[67Kri] reported 2255 ± 35 °C as the eutectic temperature for the ErC<sub>2</sub>-C eutectic. Russian investigators reported melting temperatures for ErC<sub>2</sub> both above (2270 °C [71Kos]) and below (2230 °C [70Yup]) the reported eutectic. If these reported melting temperatures are considered actually to be eutectic temperatures, the average value of this eutectic is 2260 ± 25 °C (rounding off the last significant figure to 0). This value for the eutectic temperature is in excellent agreement with the systematic trends of the REC<sub>2</sub>-C eutectic. No reliable data are available for the ErC<sub>2</sub> melting point, the ErC<sub>2</sub>-C eutectic composition, or the solid solubility of Er in (C).

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# The C-Eu (Carbon-Europium) System

12.011

151.96

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No phase diagram is available for the Eu-C system, although some data are available on compounds that are formed in the Eu-C system. [58Spe] did not include Eu in their investigation of the crystal structure of RE-C compounds, but later investigators reported structure data for several Eu-C compounds. [70Lap] reported the preparation of a monocarbide which they designated  $\text{EuC}_{1-x}$ , where  $x$  represents the amount of C that is missing in the compound. They claimed a cubic NaCl-type structure and reported lattice parameters of  $0.5145 \pm 3$  nm in the presence of excess metal and  $0.5141 \pm 1.1$  nm in the presence of excess C. These lattice parameters (Table 1) appear to fit well with those of the cubic  $\text{Fe}_4\text{N}$ -type  $\text{RE}_3\text{C}$  structures.

After unsuccessful attempts to prepare  $\text{Eu}_3\text{C}$ ,  $\text{Eu}_2\text{C}_3$ , and  $\text{EuC}_2$  from the elements, [72Col] reacted >99.9% pure Eu with HCN and  $(\text{CN})_2$  at elevated temperatures and obtained the compounds  $\text{Eu}_2\text{C}_3$ ,  $\text{EuC}_2$ , and  $\text{EuN}_x\text{C}_y$ . X-ray data were obtained with Fe-filtered  $\text{CoK}_\alpha$  radiation using a 114.6 mm Debye-Scherrer camera.  $\text{Eu}_2\text{C}_3$  was found to crystallize with the cubic  $\text{Pu}_2\text{C}_3$ -type structure, in good agreement with the structure of neighboring sesquicarbides. Their data for  $\text{Eu}_2\text{C}_3$  are listed in Table 1.

Other investigators reported some lattice parameter data for  $\text{EuC}_2$ , but a complete structure analysis has not been reported. [68Fai] synthesized  $\text{EuC}_2$  from the elements in sealed Mo bombs in an argon-filled C tube furnace.  $\text{EuC}_2$  gave anomalous X-ray patterns, more complex than those of  $\text{LaC}_2$ ,  $\text{CeC}_2$ , or  $\text{NdC}_2$ , but reproducible with four different samples. This pattern was indexed tentatively as a

bct with  $a = 1.215$  and  $c = 0.7290$  nm, accounting for all but two low index lines. [64Geb] produced  $\text{EuC}_2$  by two methods: (1) reduction of  $\text{Eu}_2\text{O}_3$  (99.9% pure, weight?) with spectrographic grade C (graphite) placed in a graphite crucible; and (2) melting of 2-to-1 mol mixture of C and Eu in a stainless steel bomb in a resistance tube furnace. X-ray powder diffraction patterns of the product using  $\text{CuK}_\alpha$  radiation in both a 114.59-mm powder camera and a Siemens diffractometer showed the bct  $\text{CaC}_2$ -type structure, along with a second phase with a different type of structure. The second phase could be obtained in larger quantities in samples containing a lower C-to-Eu ratio and heated to a somewhat lower temperature.

The low-angle lines of this impurity could be indexed on the basis of an orthorhombic cell with  $a = 0.876$ ,  $b = 1.123$ , and  $c = 0.719$  nm, but the high-angle lines were not indexed satisfactorily [66Geb].

[82Sak] synthesized  $\text{EuC}_2$  by two methods: (1) 99% pure Eu and spectrographic grade C (graphite) were sealed under vacuum in a silica capsule and heated at 1000 °C for 30 h; and (2) 99.999%  $\text{Eu}_2\text{O}_3$  was mixed with C (graphite), pelletized, and heated in Mo under a flow of argon at 1800 °C for 5 h. An excess of 5 at.% C (graphite) was used to remove all of the oxygen. Powder X-ray diffraction patterns were taken using Ni-filtered  $\text{CuK}_\alpha$  radiation with an internal standard of Si. Phase transformation was examined by differential thermal analysis in the temperature range 27 to 727 °C. The dicarbides obtained by each method had bct  $\text{CaC}_2$ -type structure, but each contained a second phase that could not be removed

Table 1 Eu-C Crystal Structure and Lattice Parameter Data

Phase	Composition range, at.% C	Pearson symbol	Space group	Strukturbericht designation	Prototype	Lattice parameters, nm		Density, g/cm <sup>3</sup>	Reference
						a	c		
(Eu) . . . . .	0	<i>cI2</i>	<i>Im3m</i>	A2	W	0.45827	...	5.244	[86Gsc]
$\text{Eu}_3\text{C}$ . . . . .	~25 to ~33	<i>cF5</i>	<i>Fm3m</i>	$L'_1$	$\text{Fe}_4\text{N}$	0.5145(3) (a)	...	7.646(a)	[70Lap]
						0.5141(3) (b)	...	7.722(b)	[70Lap]
$\text{Eu}_2\text{C}_3$ . . . . .	~60	<i>cI40</i>	$\bar{I}43d$	$D5_c$	$\text{Pu}_2\text{C}_3$	0.8368	...	7.530	[72Col]
$\alpha\text{EuC}_2$ . . . . .	66.7	<i>tI6</i>	<i>I4/mmm</i>	$C11_a$	$\text{CaC}_2$	0.4082(36)	0.6701(56)	5.236	[64Geb, 82Sak]
$\beta\text{EuC}_2$ . . . . .	66.7	<i>cF12</i>	<i>Fm3m</i>	C1	$\text{CaF}_2$	0.5961(1)	...	5.519	[68Mat]
$\text{EuC}_6$ . . . . .	85.7	<i>hP14</i>	$P6_3/mmc$	...	$\text{EuC}_6$	0.4314(3)	0.9745(8)	4.737	[75Gue, 80Elm]
(C) . . . . .	100	<i>hP4</i>	$P6_3/mmc$	A9	C (graphite)	0.24612	0.67090	2.266	[Pearson2]

(a) Eu-rich. (b) C-rich.