The Investigation of Phase Diagrams of Erbium Pnictides

M. N. Abdusalyamova and O. I. Rachmatov

The Institute of Chemistry of Tajik Academy of Science, Aini St. 299/2, 734063 Dushanbe, Tajikistan

Reprint requests to Prof. M. N. A.;
Fax: 992372210404; E-mail: dali@ac.tajik.net

Paper presented at the NATO Advanced Study Institute, May 4–14, 2001 (Kas, Turkey)

Z. Naturforsch. **57a,** 98–100 (2002);
received December 28, 2001

The phase diagrams of Er-Sb and Er-Bi have been obtained. Erbium forms three compounds with antimony as well as bismuth. The antimonides and bismuthides Er_5Sb_3 (1640 °C), Er_5Bi_3 (1427 °C), $ErSb_2$ (650 °C) and $ErBi_2$ (595 °C) are formed by peritectic reactions. ErSb (2040 °C) and ErBi (1860 °C) melt congruently.

Key words: Rare Earth Elements; Phase Diagram.

Antimonides and bismutides are compounds of Sb and Bi with more electropositive elements. We present phase diagrams of the systems Er-Sb and Er-Bi.

1. Introduction

The system Er-Sb has been investigated by calorimetry [1]. In system occur three compounds: Er_5Sb_3, ErSb and $ErSb_2$.

In [2] on the system Er-Sb serious mistakes in printing have been done. Data on ErSb, which crystallizes in the NaCl-tube cubic structure, were presented in [3].

Two compounds between erbium and bismuth were previously reported: Er_5Bi_3 has orthorhombic structure of the Y_5Bi_3 type, and ErBi has cubic NaCl-type structure [3–5].

2. Experimental

A) Materials

Erbium was distillated. Its major impurities are given in Table 1. Antimony and bismuth of high-purity were used.

Table 1. Impurities in erbium.

Impurity	Impurity other RE	Fe	Ca	Cu
weight %	0.08	0.01	0.008	0.01

B) Preparation of Alloys

Erbium-antimony and erbium-bismuth alloys were obtained by low temperature reaction of the elements placed in evacuated quartz tubes at 600 °C (Er-Sb) and at 500 °C (Er-Bi) for 5–7 days.

The homogenization of alloys containing up to 50 at.%Sb took place in sealed Mo crucibles, immediately before the thermal analysis, by heating the crucible with the specimen to a temperature several times higher than the melting temperature with successive slow cooling. The homogenization of the alloys containing more than 50 at.%Sb (or 50 at.%Bi) was carried out by annealing at 600 °C (Er-Sb) and at 500 °C (Er-Bi) for a long time.

C) Examination of the Alloys

1. Thermal analysis. A high temperature differential thermal analysis was used for the DTA measurements, which were made in very pure helium (99,985 vol.%He). The heating and cooling rates were both 30 °C/min, using a high temperature sensor with string W/W-20%Re thermocouples.

The thermocouple was calibrated at the melting points of the following superpure metals and oxides: tin, 231,8 °C; lead, 327 °C, zinc, 419,5 °C; aluminum, 660,0 °C; silver, 960 °C; cooper, 1083 °C; nickel, 1453 °C; iron, 1539 °C; platinum, 1769°C; vanadium, 1950 °C; Al_2O_3, 2042 °C; Sm_2O_3, 2325 °C; Y_2O_3, 2410 °C. The temperature was accurate to within ±1% of the measured value.

2. X-ray method. The X-ray analysis was carried out with Cu Kα radiation.

3. Microscopic analysis. Microstructures were studied with a Neofot-30 type microscope.

3. Results and Discussion

The results of thermal, metallographic, and X-ray methods were used to construct the phase diagrams shown in Figs. 1 and 3.

A) The Er-Sb System

The solubility of antimony in erbium is bigger than 1 at.%. A eutectic event does not occur on the DTA curve of the sample with a content of 1 at.%Sb. Hence, the antimony solubility in erbium is bigger than 1 at%.

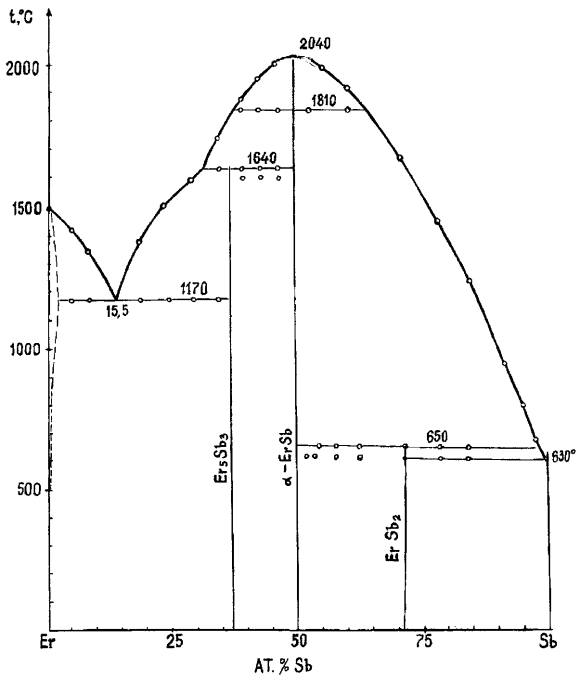

Fig. 1. The phase diagram of Er-Sb

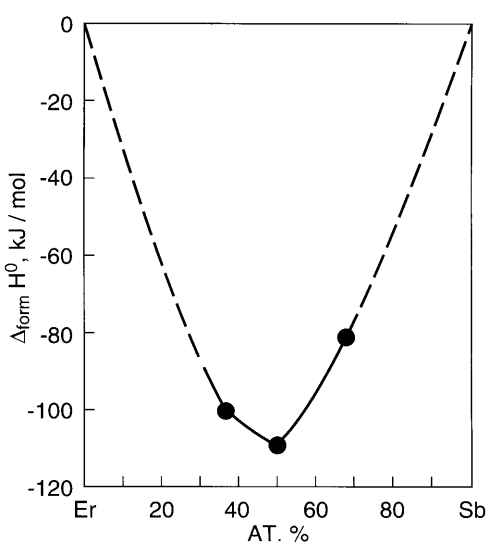

Fig. 2. The Er-Sb system by calorimetry [1]

Er_5Sb_3 is formed by a peritectic reaction at 1640 °C. The monoantimonide ErSb melts congruently at 2040 °C and is the most refractory phase in the system. The antimonide $ErSb_2$ melts incongruently at 650 °. The eutectic e_1 between the erbium solid solution and Er_5Sb_3 at 1170 °C has the composition 15,5 at.%Sb. The eutectic e_2 at 620 °C has the composition of approximately 99,4 at.%Sb.

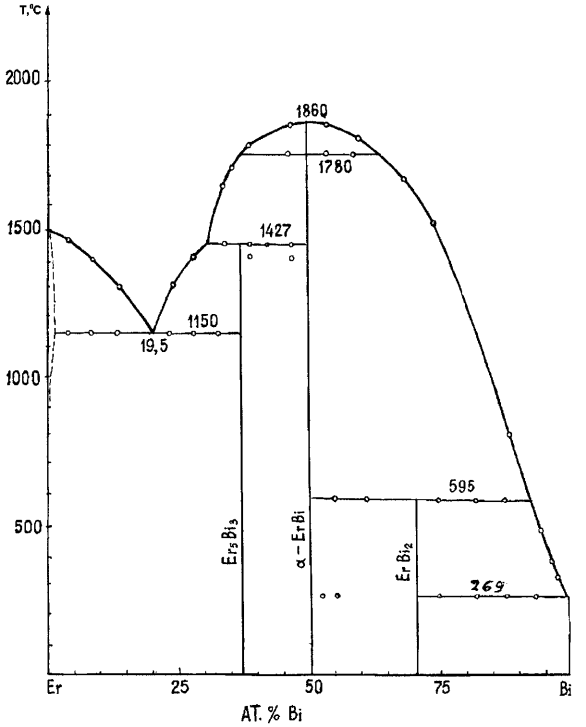

Fig. 3. The phase diagram of Er-Bi

B) The Phase Diagram of the Er-Bi System

In the system of Er-Bi are tree compounds: Er_5Bi_3, ErBi and $ErBi_2$. The bismuth solubility in erbium is less than 1 at.% Bi. A eutectic event occurs on the DTA curve of a sample with a content of 1 at.%Bi. This is also confirmed by microstructure analysis data. The most Er-rich phase is Er_5Bi_3, which forms by a peritectic reaction at 1427 °C. The highest melting point in the system has ErBi, which melts congruently at 1860 °. $ErBi_2$ melts incongruently at 595 °C.

The eutectic e_1 between the erbium solid solution and Er_5Bi_3 at 1150 °C corresponds to 19.5 at.%Bi, and the eutectic e_2 at 269 °C to 99.7 at.%Bi.

C) Polymorphic Transformation in Er-Sb and Er-Bi Systems

In DTA curves of the alloys containing ErSb and ErBi the melting events of these phases are always preceded

by sharp events at 1810 °C and 1780 °, respectively. On cooling, these events are reproduced with a slight supercooling. The diffraction pattern of ErSb and ErBi plotted at temperatures a little below 1810 °C and 1780 °, respectively, seem to have additional reflections. These reflections do not refer either to any of the phases or to the pure components or their oxides. Thus the existence of polymorphic transformations in ErSb and ErBi at 1810 °C and 1780 °, respectively, is established from the DTA and X-ray data.

D) In the vicinity of the temperatures of incongruent melting of Er_5Sb_3 and Er_5Bi_3 occurs a reversible termo effect. These effects were also observed for Tm_5Sb_3, Lu_5Sb_3, and Tb_5Bi_3.

Perhaps these compounds have polymorphic transformations. We did not obtain pure compounds.

The phase diagram of Er-Sb agrees with the Er-Sb calorimetry (Fig. 2).

The crystallographic data of the compounds are given in Table 2.

Table 2. Crystallographic data of the phases of the Er-Sb, Er-Bi systems.

Compound	Crystal system	Structure	Lattice parameters, nm *a*	*b*	*c*	Ref.
Er_5Sb_3	Orthorhom.	Yb_5Sb_3	1.1632	0.8585	0.7900	our
			1.1662	0.9136	0.8007	[1]
ErSb	Cubic	NaCl	0.611	–	–	our
			0.6107	–	–	[3]
Er_5Bi_3	Orthorhom.	Y_5Bi_3	0.810	0.9338	1.179	our
			0.8093	0.9340	1.181	[2]
ErBi	Cubic	NaCl	0.611	–	–	our
			0.6206	–	=	[3]

[1] G. Cacciamani, G. Borzone, N. Parodi, and R. Ferro, Z. Metallkd. **87,** 562 (1996).
[2] M. N. Abdusalyamova and O. I. Rachmatov, J. Alloy and Comp. 299, L1–L3.
[3] A. Iandelli, in Rare Earth Research, E. V. Kleber, Ed., MacMillan C, New York 1961, 135.
[4] K. Yoshihara, J. B. Taylor, L. D. Calvert, and J. G. Despault, J. Less. Common. Met. **41,** 329 (1975).
[5] K. A. Gschneider, Jr. and F. W. Calderwood, Bulletin of Alloy Phase Diagrams **10,** 4a, 453 (1989).
[6] Yu. A. Krakovetsky-Kocherhinsky, aut. svid. N 231863, January 30 (1964).