CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING,
THE UNIVERSITY OF TEXAS, AUSTIN, TEXAS

The Phase Equilibria and Crystal Chemistry of the Rare Earth Group VI Systems. II. Erbium–Tellurium[1]

BY D. J. HAASE, H. STEINFINK, AND E. J. WEISS

Received September 8, 1964

The phases occurring in the erbium–tellurium system are: the solid solution series ErTe–Er_2Te_3, orthorhombic, Fddd, a = 12.096 Å., b = 8.553 Å., c = 25.659 Å., the lattice constants vary throughout the solid solution series, m.p. 1525–1460°; $ErTe_3$, orthorhombic, Cmc2, a = 4.31 Å., b = 25.45 Å., c = 4.31 Å., peritectic at 575°. A eutectic is observed at approximately 13 atom % tellurium and 1270°. The influence of the ionic ratio on the stability of the structures is discussed.

Introduction

In a continuation of the investigation of the binary phase diagrams of the rare earth–group VI elements the erbium–tellurium system was developed.

Iandelli[2] and Brixner[3] report that ErTe has the NaCl-type structure. Miller, *et al.*,[4] report that Er_2Te_3 exists, although they remark that they were observing two phases. Flahaut, *et al.*,[5] labeled Er_2Te_3 as having a ζ structure. Dismukes, *et al.*,[6] have recently described the structure of Sc_2S_3, which is the structure of the ζ type. The aim of this investigation was to determine the intermediate phases that exist in this system and to characterize their crystal structures.

Experimental

The techniques used to produce the intermediate phases and the methods of interpretation are the same as developed and used in the erbium–selenium system.[7] Tellurium of 99.99% purity was obtained from the American Smelting and Refining Co.

Results

The condensed phase diagram is shown in Figure 1. The erbium–tellurium system has two eutectic points, one peritectic composition, and an extended solid solution region. The known eutectic point occurs at 13 atom % tellurium and 1270°. From phase equilibria principles an undefined eutectic is believed to exist very near the tellurium-rich end of the phase diagram. The liquidus line was not investigated in detail in this region, and no other intermediate phases of higher tellurium composition than the 1:3 exist. A peritectic point was determined for the composition $ErTe_3$ at 575°. The decomposition temperature is dependent on the pressure above the sample and the reported value applies to samples which are sealed in evacuated quartz tubes.

$ErTe_3$.—The composition $ErTe_3$ [*Anal.* Calcd. for $ErTe_3$: Er, 30.6; Te, 69.4. Found: Er, 31.5; Te, 69.4] is gold-colored, incongruently melting at 575°, and is isostructural with similar phases in other lanthanide systems.[8–10] The peritectic point was determined from quenched specimens which were sealed in quartz capillary tubes. Single crystal X-ray diagrams showed that the diffraction symmetry was mmm and the orthorhombic unit cell has the constants: a = 4.31 Å., b = 24.45 Å., and c = 4.31 Å. Systematic absences of hkl for $h + k$ odd and $h0l$ for l odd indicate the space group Cmcm, Cmc2, or C2cm. There are four molecules per unit cell based on a measured density of 7.25 g./cm.^{3}.

ErTe–Er_2Te_3.—The compound ErTe has previously been reported as an ordered face-centered cubic, NaCl-type structure, a = 6.02 Å.[2,3] The Er_2Te_3 composition was reported as having a slightly deformed cubic structure.[5] This investigation shows that ErTe and Er_2Te_3 are the terminal compositions of a continuous solid solution region. Single crystal X-ray data indicate that the crystalline structure of this solid solution series is isostructural with that of the Er_2Se_3–Er_3Se_4 solid solution series and has therefore the Sc_2S_3 structure. The lattice constants are observed to vary slightly in this system and are reported in Table I for the various compositions. The lattice constants were obtained by the Debye–Scherrer film technique in the back-reflection region. The film was indexed on a cubic subcell, and lattice constants were determined by least squares. The cubic subcell lattice constant was converted to the orthorhombic cell constants by the relationships: $a = 2a_0$, $b = \sqrt{2}a_0$, $c = 3\sqrt{2}a_0$.

The melting points for the solid solution series range continuously from 1525° for the 1:1 composition to 1460° for the 2:3 composition. The Er_2Te_3 composition has a slightly greenish appearance and varies to a slightly bluish appearance in the region of the 3:4 composition. The higher Er compositions of the series have a metallic black appearance.

Discussion

The 16-fold cation sites which are vacant in the Er_2Te_3 composition are filled statistically as one progressively adds Er up to the composition 1:1. The two columns in Table I labeled vacancies refer to the number of vacancies observed experimentally and the number cal-

---

[1] This work is being sponsored by a grant from the U. S. Air Force Office of Scientific Research.

[2] A. Iandelli, "Rare Earth Research," The Macmillan Company, New York, N. Y., 1961, p. 135.

[3] L. H. Brixner, *J. Inorg. Nucl. Chem.*, **15**, 199 (1960).

[4] J. F. Miller, L. K. Matson, and R. C. Himes, Proceedings of the Third Rare Earth Conference, 1963.

[5] J. Flahaut, L. Domange, M. Guittard, M. Pardo, and M. Patrie, *Compt. rend.*, **257**, 1530 (1963).

[6] J. P. Dismukes and J. G. White, *Inorg. Chem.*, **3**, 1220 (1964).

[7] D. J. Haase, H. Steinfink, and E. J. Weiss, *ibid.*, **4**, 538 (1965).

[8] T. H. Ramsey, Doctoral Dissertation, The University of Texas, 1964.

[9] W. Lin, Master's Thesis, The University of Texas, 1964.

[10] F. L. Carter, "Metallurgy of Semiconductor Materials," Interscience Publishers, New York, N. Y., 1961, p. 260.

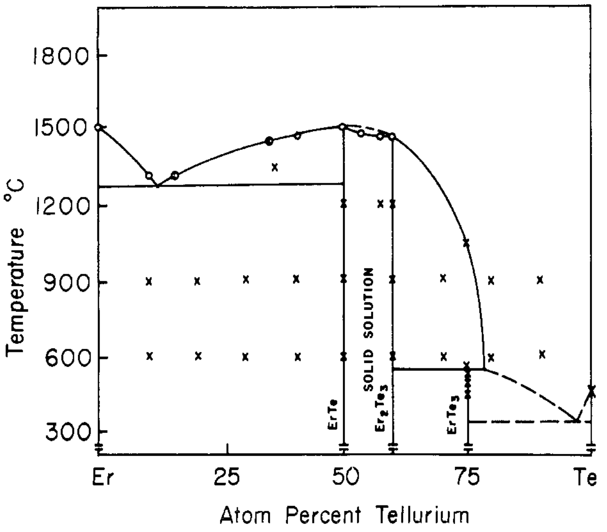

Figure 1.—The condensed phase diagram, Er–Te: crosses represent quench data; open circles are observed melting points. The dashed lines indicate uncertain phase boundaries.

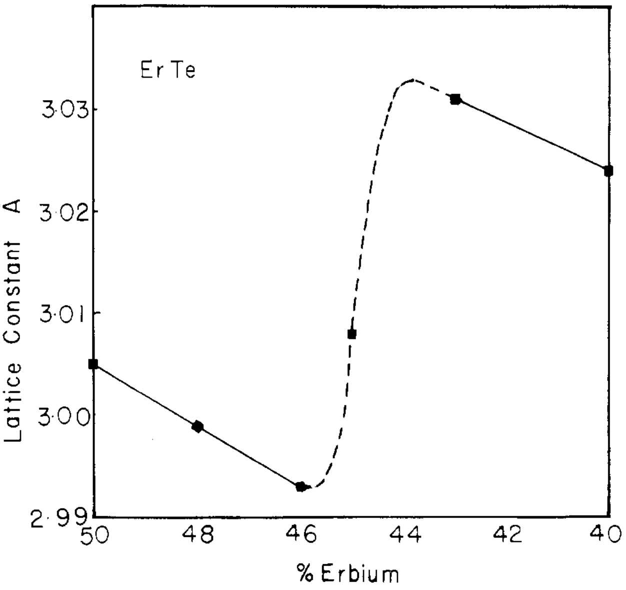

Figure 2.—Pseudocubic cell constant, a_0, as a function of Er concentration for the solid solution region ErTe–Er_2Te_3.

culated from the structure for that particular composition.

The "cubic" cell constant plotted as a function of composition, Figure 2, indicates that a change in bond character takes place as the concentration of Er increases. The function is linear over two regions from 40% erbium to less than 45% erbium and from slightly larger than 45% erbium to 50% erbium. In the neighborhood of 45% erbium, a transition zone is observed. In this region, the bonding changes from predominantly ionic for the 2:3–3:4 composition to a predominantly covalent, metallic type for the ErTe region. In each region, the lattice constant varies linearly as expected for a solid solution series.

The structure of the $ErTe_3$ compound is postulated, based on single crystal 0*k*0 data.

Atom	*x*	*y*	*z*
Er	0	0.050	0
Te(I)	0	0.450	0
Te(II)	0	0.179	0
Te(III)	0	0.312	0

The refinement of this structure from three-dimensional data is now in progress.

It is of great interest to consider the variations of the crystal structures and the extent of solid solubility which occur in these compositions. Flahaut, *et al.*,[5] discussed the stability on the basis of the ratio of the metalloid S, Se, and Te ionic radius to the rare earth

Table I

Erbium Telluride Solid Solution Data

Chemical compn.[a]	Obsd. density, g./cm.[3]	*a*, Å.	*b*, Å.	*c*, Å.	Vacancies Theory	Vacancies Exptl.
$Er_{0.50}Te_{0.50}$	8.6	12.020	8.499	25.497	0	0
$Er_{0.48}Te_{0.52}$	8.1	11.996	8.482	25.446	3.7	3.7
$Er_{0.46}Te_{0.54}$	7.7	11.972	8.465	25.395	7.1	7.2
$Er_{0.45}Te_{0.55}$	7.6	12.048	8.519	25.557	8.8	8.8
$Er_{0.43}Te_{0.57}$	7.3	12.124	8.573	25.719	12.0	11.0
$Er_{0.40}Te_{0.60}$	7.1	12.096	8.553	25.659	16.0	16.0

[a] Actual determined values.

Table II

Diffraction Data[a]

d	*hkl*	Rel. intensity, %
	Er_2Te_3	
6.80	1 1 1	18
5.53	2 0 2	3
4.14	1 1 5	5
3.63	3 1 1	9
3.50	2 2 0	10
3.252	1 1 7	9
3.035	4 0 0	100
2.855	1 3 1	14
2.777	1 3 5	9
2.561	3 1 7	12
2.336	5 1 1 (2 0 10)	9
2.220	1 1 11	11
2.149	0 4 0	80
1.753	4 0 12	32
1.518	0 4 12	21
1.357	5 5 5	32
1.239	4 6 6	30
	$ErTe_3$	
6.32	0 0 4	40
3.150	0 0 8	90
3.057	0 1 6	10
2.842	1 1 3	100
2.590	1 1 5	70
2.318	1 1 7	12
2.139	2 0 2	50
1.829	1 1 11	20
1.802	1 2 5	10
1.769	1 0 13	25
1.323	3 1 5	15
1.226	3 1 9	8
1.216	0 1 20	10
1.194	3 2 1 (2 3 0)	15

[a] All X-ray diffraction patterns were obtained with Cu Kα, Ni-filtered radiation and were recorded on a diffractometer.

ionic radius. They found that the Sc_2S_3 type structure, which they labeled ζ, was stable for ratios above 2.10 and the Th_3P_4 structure existed for ratios below 1.95, with a transition structure in the ratio range 1.95 to 2.10. The Th_3P_4 structure is stable for the sulfides of La to Gd and for the selenides of La to Sm and the Sc_2S_3 structure is stable for Sc_2S_3 and for the selenides of Y, Er, Yb, Lu, and Sc. These limits of stability, based on radius ratios, are calculated using the ionic radii of 1.82 and 1.93 Å. for sulfur and selenium, respectively. This analysis will not hold for the tellurides based on the Te^{-2} ionic radius of 2.12 Å., however a corrected radius of 2.03 Å. for the ion will fit the above conclusions. Thus the stability of the structure to be expected in the 2:3 compositions is strongly dependent on the ratio of rare earth to metalloid ionic radius and appears to have distinct limits.

The Th_3P_4 structure is ordered with the 12 rare earth and 16 metalloid crystallographic sites filled at the 3:4 composition and becomes progressively more disordered toward the 2:3 composition as the rare earth concentration decreases. The disorder in the Th_3P_4 structure is a result of the statistical occupancy of the 12 rare earth sites by vacancies. The limits of stability of the structure are due to the ionic character of the 2:3 composition and the complete filling of all the rare earth sites at the 3:4 composition. The basic skeleton of the Th_3P_4 structure is the tellurium network, as the rare earth sites are statistically variable with the composition. The erbium solid solution structure, however, has as its basic skeleton the 2:3 composition of the erbium and metalloids. Richer erbium concentrations are obtained by the statistical filling of vacant sites which are crystallographically different from the erbium sites of the 2:3 composition. We believe that the limits of solubility observed for solid solutions having the Sc_2S_3-type structure are due to slight distortions of the idealized framework.[7] The strong X-ray diffraction lines obtained from the solid solution compositions in this system are sharp even in the back-reflection region and can be indexed unequivocally on a cubic subcell. It is therefore possible to add erbium statistically to the 16 vacancies of the 2:3 skeleton without distorting it, and the structure is stable over the composition Er_2Te_3 to the composition ErTe.

It is reported that Dy_2Te_3 and Y_2Te_3 have the Sc_2S_3 structure and an undistorted cubic subcell.[5] From the above discussion it is therefore expected that these systems should also exhibit a solid solution range from the 2:3 to 1:1 compositions. The tellurides Dy, Y, and Er have radius ratios of 2.28 or larger. The Sc_2S_3 structure and the extended solid solubility range are also expected for the tellurides of Yb, Lu, and Sc, as well as for the Sc–Se system, because their radius ratios also exceed 2.28.

CONTRIBUTION NO. 325 FROM THE DEPARTMENT OF CHEMISTRY,
TUFTS UNIVERSITY, MEDFORD, MASSACHUSETTS

Systems of Lithium Hydride with Alkaline Earth and Rare Earth Hydrides

BY CHARLES E. MESSER AND IRA S. LEVY[1]

Received October 5, 1964

Solid–liquid equilibrium has been investigated by thermal analysis of systems of lithium hydride with the dihydrides of strontium, barium, europium, ytterbium, scandium, lanthanum, cerium, and samarium. The compound $LiSrH_3$, with congruent melting point 745°, was found. Eutectic temperatures and compositions found, in mole % MH_2, were: SrH_2 644.6°, 11.2%; BaH_2 670.8°, 5.0%; EuH_2 664.1°, 6.8%; YbH_2 668.7°, 6.8%. The dihydrides of the other rare earth metals, and also $LaH_{2.5}$, did not affect the freezing point of LiH within experimental error. The soluble hydrides are the saline ones; the insoluble ones have metallic conduction electrons which contribute an interaction unfavorable to solubility in the saline molten LiH. The apparatus is described, and the purity and melting point of the lithium hydride are discussed.

Introduction

Earlier investigations in this laboratory, by the method of thermal analysis, on systems of LiH with Li metal,[2] LiF[3], CaH_2,[4] and Li_2O[4] showed behavior closely resembling that to be expected from the ionic nature of LiH and its physical similarity to LiF. X-Ray crystallographic determinations of the probable inverse perovskite structures of $LiBaH_3$,[5] $LiSrH_3$,[5] and $LiEuH_3$[6] further substantiated the crystallographic similarity between LiH and LiF. No novel phases were found in the LiH–CaH_2 and LiH–YbH_2 systems.

However, it was also found that TiH_2[4] and ZrH_2,[4] which are considerably metallic in nature, failed to

---

[1] From a dissertation submitted by Ira S. Levy in partial fulfillment of requirements for the degree of Doctor of Philosophy in Chemistry, Tufts University, Oct. 1963.

[2] C. E. Messer, E. B. Damon, P. C. Maybury, J. Mellor, and R. A. Seales, *J. Phys. Chem.*, **62**, 220 (1958).

[3] C. E. Messer and J. Mellor, *ibid.*, **64**, 503 (1960).

[4] C. E. Messer, J. Mellor, J. A. Krol, and I. S. Levy, *J. Chem. Eng. Data*, **6**, 328 (1961).

[5] C. E. Messer, J. C. Eastman, R. G. Mers, and A. J. Maeland, *Inorg. Chem.*, **3**, 776 (1964).

[6] C. E. Messer and K. I. Hardcastle, *ibid.*, **3**, 1327 (1964).