the spectrochemical series,[20] replacement of one of these ligands by the other is not influenced particularly by the magnitude of the crystal field stabilization energy, which is $12Dq$ for chromium(III) and 0 for high spin iron(III). (Thiocyanate ion is also adjacent to water in the spectrochemical series, being on the opposite side of water from fluoride.) Fluoride ion is adjacent to water also in the nephelauxetic series,[21] which seems related to the complex-forming tendencies of ligands.[22]

[20] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958, p. 44.

[21] C. E. Schaffer and C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **8**, 143 (1958).

[22] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., New York, N. Y., 1962, p. 222.

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

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Received September 8, 1964

The phases occurring in the erbium–selenium system are: ErSe, f.c.c., $a = 5.662$ Å., m.p. 1630°; the solid solution series, Er_2Se_3–Er_3Se_4, orthorhombic, Fddd, $a = 11.38$ Å., $b = 8.09$ Å., $c = 24.20$ Å., m.p. 1400–1440°; α-$ErSe_2$, orthorhombic, Cmma, $a = 16.22$ Å., $b = 15.80$ Å., $c = 11.88$ Å., transition to β-$ErSe_2$ at 890°; β-$ErSe_2$, orthorhombic, Immm, $a = 4.061$ Å., $b = 5.571$ Å., $c = 13.16$ Å., peritectic at 1010°. Two eutectics were observed at approximately 3 atom % selenium and 1310° and approximately 55.5 atom % selenium and 1370°.

Introduction

The phase equilibrium relations in the binary system erbium–selenium were investigated as part of a program of research on compounds formed between rare earth and group VI elements.

Iandelli[2] has reported that ErSe is face-centered cubic; Muir[3] in his investigations of rare earth chalcogenides prepared a material which had a composition corresponding to $ErSe_{1.49}$, but it was not a single phase specimen. Miller, *et al.*,[4] report a phase Er_2Se_3 on which they made physical measurements, but no crystal data are given. The aim of this investigation is to study the binary phase diagram systematically and to characterize the intermediate phases which exist in this system.

Experimental

Elemental erbium (Lindsay, 99.9% purity) in the form of millings or ingots and selenium (American Smelting and Refining Co., 99.99% purity) in exactly weighed portions were prereacted in evacuated 9-mm. o.d. Vycor tubes at 600° for 48 hr. The reaction temperature of the prereaction cycle was limited to less than 700° because at temperatures in excess of 700° the erbium reacted with Vycor. The prereacted material having compositions greater than 40 mole % erbium was then sealed in tantalum tubes in an argon environment and the sealed tantalum tubes were heated in a vacuum induction furnace to temperatures of approximately 1800°. The surface of the tantalum tubing which had been in contact with the molten material showed no evidence of having been attacked during the reaction period. The material thus obtained was equilibrated and quenched at various temperatures. The samples containing less than 40 mole % erbium reacted completely in the Vycor tubing and did not require further reaction in tantalum at the high temperature. These two techniques were sufficient to produce all of the phases present in the systems.

The melting points of the congruent melting phases and the liquidus lines were determined by cycling small portions of the samples in an argon-filled resistance furnace in which a V-formed tantalum strip constituted the heating element. The samples were observed with a focused optical pyrometer. The pyrometer was calibrated against the melting point of platinum and also against an NBS standard Pt—Pt-10% Rh thermocouple. No emissivity corrections were made and the temperatures in Figure 1 are considered accurate to ±25°, although the precision of the measurements is ±5°. At the end of the cycling process, the samples were investigated by powder X-ray diffraction analysis and in all cases the patterns were identical with those obtained from the samples before they had been exposed to this treatment. The temperature of the incongruent melting phase was obtained by quenching compositions from various temperatures and determining the phases present by X-ray diffraction techniques and microscopic examination. The chemical composition of the specimens was determined by a chelometric titration of erbium, and selenium was determined by the sodium thiosulfate procedure. The densities of the materials were determined by the displacement method using acetone as the submersing liquid.

Results

The condensed phase diagram is shown in Figure 1. The solid lines represent that portion of the diagram which could be located accurately and the dashed lines represent those areas which are uncertain. The system has three eutectic points and one continuous solid solution region. The known eutectic points appear at approximately 3 atom % selenium and 1310° and at approximately 55.5 atom % selenium and 1370°, and an

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[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] H. M. Muir, "Rare Earth Chalcogenides—Final Report," Research Chemical Division of Nuclear Corporation of America, June 1961.

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

TABLE I

CRYSTALLOGRAPHIC AND PHYSICAL DATA FOR INTERMEDIATE PHASES IN THE Er–Se SYSTEM

	M.p., °C.	Space group	Unit cell dimensions, Å.	No. of molecules in unit cell	Density (calcd.)	Density (measd.)
ErSe	1630 ± 25	Fm3m	a = 5.662	4	9.06	9.0
Er_3Se_4	1440 ± 25		a = 11.38	12	7.33	7.3
		Fddd	b = 8.09			
Er_2Se_3	1400 ± 25		c = 24.20	16	6.92	6.9
α-$ErSe_2$	890 ± 10[a]	Cmma	a = 16.22	44	7.80	7.7
			b = 15.80			
			c = 11.88			
β-$ErSe_2$	1010 ± 10	Immm	a = 4.061	4	7.35	
			b = 5.571			
			c = 13.16			

[a] Phase transition.

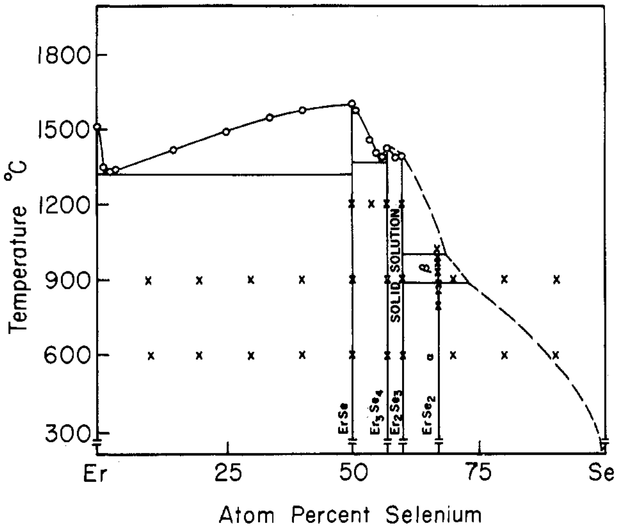

Figure 1.—The condensed phase diagram Er–Se: the dashed lines represent uncertain boundaries; crosses indicate quench data; circles represent melting point observations.

undefined eutectic point is believed to exist very near the selenium-rich end of the phase diagram. A solid solution region exists over the range of composition from Er_2Se_3 to Er_3Se_4. The system exhibits a phase transition at 890° and a peritectic reaction at 1010° for the $ErSe_2$ compound.

ErSe.—The compound with the composition 50 atom % selenium, ErSe, was reported by Iandelli[2] as having the sodium chloride, face-centered cubic structure, a = 5.662 Å. The present investigation confirms this result and the crystal chemical parameters are summarized in Table I. ErSe is a rose-colored material. *Anal.* Calcd. for ErSe: Er, 67.9; Se, 32.1. Found: Er, 67.9; Se, 30.6.

Er_2Se_3–Er_3Se_4.—A solid solution region exists from $42^6/_7$ atom % erbium to 40 atom % erbium. Single crystal X-ray diffraction data display mmm diffraction symmetry. Systematically absent spectra are observed for hkl when the indices are mixed even and odd; $hk0$ when $h + k \neq 4n$, $h0l$ when $h + l \neq 4n$, and $0kl$ when $k + l \neq 4n$ The crystal chemical parameters are shown in Table I. The terminal composition Er_2Se_3 has a melting point of 1400° and has a greenish appearance. *Anal.* Calcd. for Er_2Se_3: Er, 58.6; Se, 41.4. Found: Er, 58.5; Se, 41.5. Finely divided particles of Er_2Se_3 are yellowish green. The color gradually darkens as the erbium content is increased, and Er_3Se_4 is metallic blue in appearance with finely divided particles being black. *Anal.* Calcd. for Er_3Se_4: Er, 61.6; Se, 38.4. Found: Er, 61.1; Se, 38.4. The crystal structure of this solid solution does not exhibit the thorium phosphide (Th_3P_4) structure as encountered in the analogous compositions in the first part of the lanthanide series, La to Gd,[4] but is isostructural with the recently reported Sc_2S_3[5] structure. The intensities of the Er_2Se_3 diffraction pattern agree very well with the intensities calculated from the parameters of the Sc_2S_3 structure. Within the experimental error of the determination of the lattice constant no variations were observed over the range of solid solution composition.

$ErSe_2$.—Single crystal X-ray diffraction data display mmm diffraction symmetry. The crystal chemical parameters are shown in Table I. The $ErSe_2$ phase displays a transition, α → β, at 890°. The β phase melts incongruently at 1010°. *Anal.* Calcd. for $ErSe_2$: Er, 51.5; Se, 48.5. Found: Er, 51.2; Se, 47.9.

Discussion

The Er_2Se_3 structure is basically a NaCl type, the large orthorhombic unit cell being required by an ordering of the positions where one-third of the cations are missing. In contrast to the La to Gd disordered Th_3P_4-type structure for the 2:3 composition, the erbium selenide is an ordered structure. The unit cell dimensions a, b, and c of the orthorhombic unit cell are approximately 2, $\sqrt{2}$, and $3\sqrt{2}$ multiples of the ErSe unit cell dimension. Therefore the interatomic distances and angles are approximately the same: 2.83 Å. and 90°, respectively.

The Er_2Se_3 unit cell has 32 erbium atoms and 48 selenium atoms. The structure therefore has a 16-fold cation site which is vacant. The filling of these sites statistically produces the solid solution series toward higher concentrations of erbium. The reflection lines show a distinct broadening and in some instances several resolved peaks can be seen. It is concluded that the selenide skeleton is slightly distorted and consequently

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

Table II

Diffraction Data[a]

d, Å.	hkl	Rel. int., %
	ErSe	
3.266	1 1 1	15
2.830	2 0 0	100
1.998	2 2 0	70
1.702	3 1 1	10
1.630	2 2 2	25
1.412	4 0 0	18
1.262	4 2 0	31
1.151	4 2 2	25
	Er_3Se_4–Er_2Se_3 Solid Solution Series	
6.40	1 1 1	20
6.06	0 0 4	7
5.15	2 0 2	8
3.89	1 1 5	11
3.398	3 1 1	10
3.299	2 2 0	8
3.066	1 1 7	7
2.847	4 0 0	100
2.612	1 3 1	6
2.307	1 3 5	3
2.225	2 0 10	4
2.179	5 1 1	5
2.083	1 1 11	8
2.013	0 4 0	55
1.853	3 1 11	8
1.643	4 0 12	50
1.420	0 4 12	10
1.271	5 5 5	19
1.160	0 2 20	20
	$ErSe_2$	
4.09	2 2 2	15
3.587	0 3 2	60
3.217	2 3 2	6
3.005	5 1 1	10
2.855	1 3 1	9
2.815	4 0 4	63
2.732	3 3 3	50
2.664	2 3 4	70
2.533	4 2 4	6
2.321	1 5 1	100
2.253	5 3 3	90
1.989	3 2 7	55
1.963	7 2 3	6
1.792	5 5 3	8
1.735	2 6 4	12
1.609	1 7 3	30
1.517	2 5 8	20
1.493	1 7 5	35
1.408	7 0 9	12
1.292	3 6 9	10
1.259	6 7 6	9
1.204	9 5 7	22

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

it is not possible to add erbium to all 16 crystallographic vacancies. As a vacancy is filled by an erbium atom the three neighboring vacancies are distorted and are no longer able to accept additional erbium atoms. Thus the limit of solubility in the selenide case is one-quarter of the 16 vacancies or the composition Er_3Se_4. Attempts to add further erbium atoms to the three neighboring unfilled vacant interstices result in an unstable structure and rearrangement to two separate phases ErSe and Er_3Se_4 takes place. Single crystal X-ray structure studies are currently in progress to test this hypothesis. The $ErSe_2$ compound also differs in its crystal structure from similar phases in other lanthanide systems.[6] The low temperature α form has a subcell which can be considered either as a tetragonal or as a cubic cell. The tetragonal subcell, a = 3.96 Å. and c = 8.10 Å., space group P4/nmm, is $^1/_{24}$ the volume of the unit cell. The subcell, which must contain the same molecular weight, can be considered to have 1.85 formula units of composition $ErSe_2$ or 2 formula units of $ErSe_{1.7}$. The subcell is isomorphous with the unit cell of the $LaTe_2$[6] type. The larger unit cell of $ErSe_2$ may be a consequence of ordering of vacant sites which does not occur in $LaTe_2$.

The crystalline structure of $ErSe_2$ can best be postulated from the cubic subcell. The cubic subcell a = 4 Å. will be $^1/_2$ the volume of the tetragonal subcell or $^1/_{48}$ the volume of the true unit cell. There are 44 Er atoms and 88 Se atoms per unit cell or 4 out of the 48 Er positions and 8 of the 96 Se positions are empty when the positions of the Er and Se are considered as located on the corners and on the face centers of the cubic subcell, respectively. These cubic subcells are then stacked to satisfy the symmetries demanded by space group Cmma. This leaves a 4-fold ordered vacancy for the cation. This postulated structure yields alternate layers of Se atoms and Er atoms or a layer-type structure, as is expected from the habit of the crystals, which are tabular in appearance.

The verification and refinement of this structure from three-dimensional X-ray data is now in progress. No range of homogeneity has been observed for this phase and the knowledge of the exact crystal structure should show why solid solubility can exist for $LnTe_2$ and $LnSe_2$, where Ln represents elements in the first half of the lanthanide series,[7,8] while the corresponding phases for the heavy lanthanides display very limited solid solubility or none at all.

No additional compounds having a selenium composition greater than 66.7 atom % have been observed. The liquidus line in this region of the phase diagram was not investigated in detail.

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

[7] M. P. Pardo, J. Flahaut, and L. Domange, *Compt. rend.*, **256**, 1793 (1963).

[8] A. Benacerraf, L. Domange, and J. Flahaut, *ibid.*, **248**, 1672 (1959).