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High-Pressure Synthesis of Rare Earth–Tritin Compounds[1]

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New rare earth–tritin compounds of face-centered cubic structure ($AuCu_3$ type) were prepared for Tb, Dy, Ho, Er, and Y. Pressures to 85 kbars concurrent with temperatures to 1400° were employed in the studies. Analogous compounds were not found for the Lu–Sn and Sc–Sn systems.

Introduction

The rare earth–tritin compound series has been studied since 1933. The compound series is isostructural (only one crystal structure known) but incomplete. Previous workers have prepared the rare earth–tritin compounds of La, Ce, Pr, Nd, Sm, Eu, Gd, and Yb,[3–7] but only negative results are listed for the heavier rare earth elements.[7,8]

It has been demonstrated[9] that application of pressure and temperature will sometimes allow formation of unknown rare earth compounds. It is suggested that size differences, due to the lanthanide contraction, may be the primary cause of instability of the crystal structure of some intermetallic compounds containing heavy rare earth elements. High pressure is capable of changing relative atomic sizes and has been used in this study to allow the formation of some heavy rare earth–tritin compounds. Once formed, the compounds remain metastable on return to room conditions.

Experimental Section

All of the rare earth metals used for this study were 99.5% pure (ingot form) and were obtained from Alfa Inorganics, Beverly, Mass., or Research Chemicals, Phoenix, Ariz. The tin metal was 99.999% pure (shot form) and was obtained from Alfa Inorganics.

The pressures and temperatures required for this research were achieved using a tetrahedral-anvil apparatus with tie bars.[10,11] For pressures up to 70 kbars in conjunction with temperatures up to 1500° the tetrahedral-anvil apparatus was fitted with tungsten carbide anvils having triangular faces 19.1 mm on each edge. For pressures from 70 to 90 kbars in conjunction with temperatures up to 1500° the tetrahedral-anvil apparatus was equipped with tungsten carbide anvils having triangular faces 12.7 mm on each edge.

Pressure and temperature calibration data for the tetrahedral-anvil apparatus were collected during the course of this study. Temperature calibration data were obtained by placing a thermocouple in the geometric center of the tetrahedron and measuring the sample temperature as a function of power input to the graphite heater. The coefficient of variance of the thermocouple data never exceeded ±8%, and the thermocouple readings were not corrected for pressure effects. Room-temperature–pressure calibration data were obtained by using the transition points for Ce (7.3 kbars), Hg (12.8 kbars), Bi(I,II) (25.5 ± 0.06 kbars), Tl(II,III) (36.7 ± 0.3 kbars), Yb(I,II) (38.2 kilobars), Ba(I,II) (55.0 ± 2 kbars), and Bi(III,V) (77.0 ± 3 kbars). The coefficient of variance of the pressure transition data never exceeded ±10%, and the pressure calibration data were not corrected for temperature effects.

A tetrahedral sample assembly consisted of a pyrophyllite tetrahedron to transmit pressure to the sample, two molybdenum tabs to conduct current to the heater, a graphite heater tube and end caps to provide resistive heating, a boron nitride tube and end caps inside the graphite heater to inhibit formulation of rare earth carbides, and the sample mixture packed inside the boron nitride liner assembly. A tetrahedral sample assembly is illustrated in Figure 1, and the dimensions of the sample assembly components are listed in Table I.

The rare earth metals and the tin metal were filed and then sieved using nylon screens. The −100 mesh by +200 mesh portion was used in the synthesis mixes. The components for the starting mixtures, composed of 0.1 g of rare earth plus the appropriate amount of tin, were weighed to within 0.0001 g and then mixed by hand for 5 min using a spatula.

A tetrahedron for a synthesis run was constructed in the following manner. First, the exterior of the tetrahedron was coated with a slurry of rouge in methanol, and the coated tetrahedron was baked for at least 1 hr at a temperature of 110°. Next the tetrahedron was removed from the oven and the rare earth–tin mixture was tamped into a boron nitride liner using a metal rod.

The completed tetrahedron was placed in the tetrahedral-anvil apparatus and held at pressure and temperature for times ranging from 3 to 30 min (see Results and Discussion for information concerning the effect of time on reaction product purity). After removal from the tetrahedral-anvil apparatus, the tetrahedron was broken open with a hammer and the sample pellet was removed. The sample pellet was crushed between two polished tungsten carbide surfaces, and a portion was placed in a 0.05-cm glass capillary. The capillary containing the crushed sample was immediately mounted on a Debye–Scherrer camera of radius 143 mm and an X-ray diffraction pattern was recorded on film. The X-irradiation was supplied by a nickel-filtered copper tube ($\lambda_{K\alpha}$ 1.5418 Å). The tritin compounds synthesized were indexed by comparing them to the $PrSn_3$ indexing given by Rossi.[5] Lattice parameters were calculated by the least-squares method.

Results and Discussion

The systems $RE–Sn_3$ were studied for RE = Tb, Dy, Ho, Er, Tm, Lu, Y, and Sc. A reaction product diagram was constructed for each system studied by making runs at various pressures and temperatures. The reaction product diagrams represent the products obtained by quenching from the pressure–temperature point indicated. The pressure–temperature points on the reaction product diagrams are accurate to ±8% on the temperature scale and ±10% on the pressure scale.

Terbium (Figure 2), Dysprosium (Figure 3), Holmium (Figure 4), Erbium (Figure 5), and Yttrium (Figure 6).—Each of the above rare earth–tritin compounds was synthesized after a minimum temperature and pressure were concurrently reached or

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[3] A. Rossi, *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Natur., Rend.*, **17**, 839 (1933).

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TABLE I
DIMENSIONS OF TETRAHEDRAL SAMPLE ASSEMBLY COMPONENTS

	Dimension, mm	
	Larger anvil	smaller anvil
Tetrahedron edge	25.4	17.15
Tetrahedron slot width	6.35	4.75
Tetrahedron slot depth	5.84	3.68
Molybdenum tab length	11.47	7.62
Molybdendum tab width	6.10	4.32
Molybdenum tab thickness	0.13	0.13
Graphite cylinder o.d.	3.18	3.18
Graphite cylinder i.d.	2.18	2.18
Graphite cylinder length	3.81	3.56
Graphite cap o.d.	3.18	3.18
Graphite cap thickness	1.27	0.64
Boron nitride cylinder o.d.	2.16	2.16
Boron nitride cylinder i.d.	1.40	1.40
Boron nitride cylinder length	2.79	2.79
Boron nitride cap o.d.	2.16	2.16
Boron nitride cap thickness	0.51	0.38

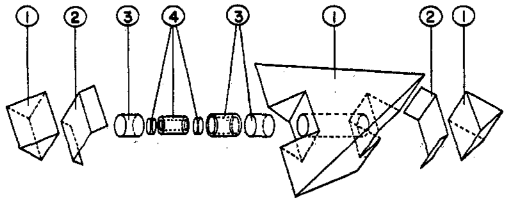

Figure 1.—Tetrahedral sample assembly: 1, pyrophyllite tetrahedron; 2, molybdenum tabs; 3, graphite heater assembly; 4, boron nitride liner assembly.

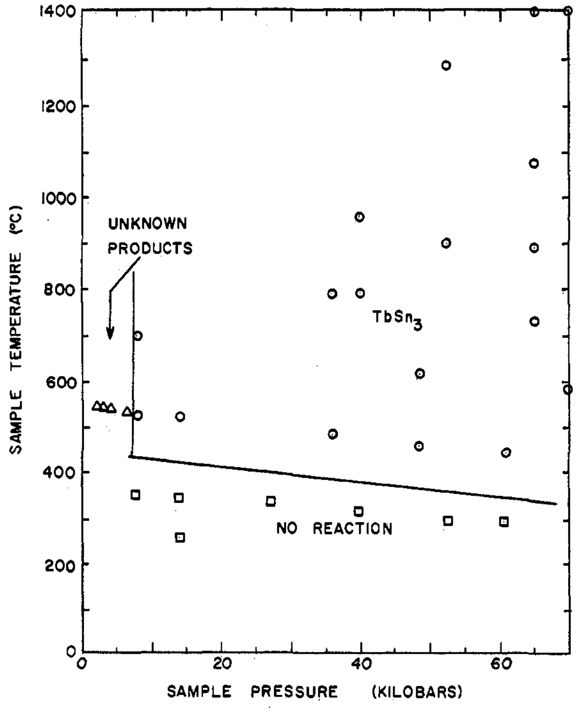

Figure 2.—Tb–3Sn reaction product diagram.

exceeded. Below the minimum temperature no reaction was observed. Below the minimum pressure unidentified reaction products were observed. The unidentified reaction products gave complex and often nonreproducible X-ray patterns which could not be indexed. The amount of material obtained from a run (0.03 g) was too small to allow chemical analysis of the material.

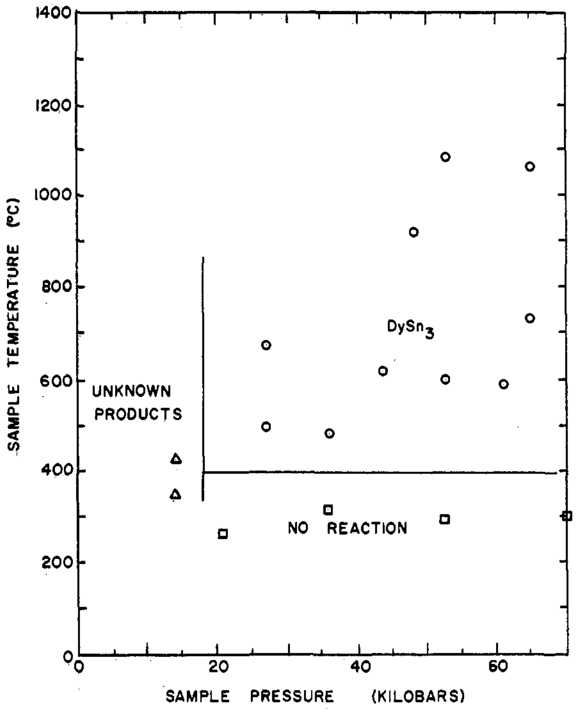

Figure 3.—Dy–3Sn reaction product diagram.

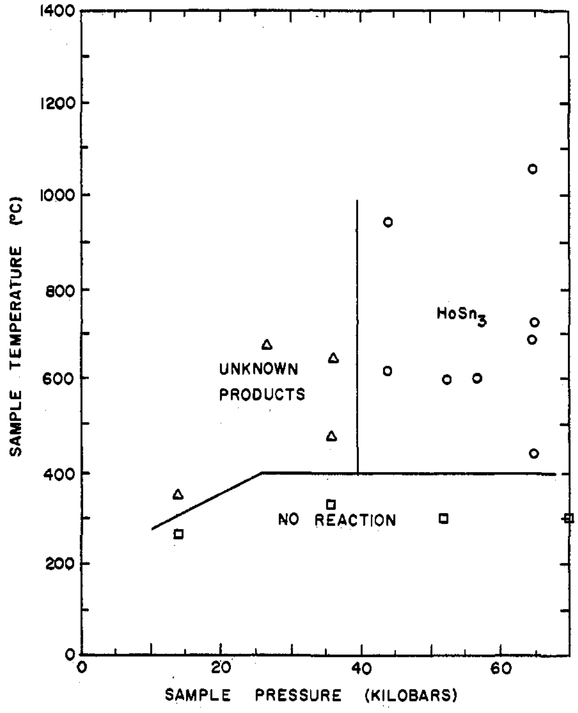

Figure 4.—Ho–3Sn reaction product diagram.

Thulium.—The compound $TmSn_3$ was not synthesized. Runs made at pressures from 14 to 87 kbars concurrent with temperatures from 325 to 1100° produced an unknown reaction product. At pressures of 14–87 kbars and temperatures lower than 300° no reaction was detected.

Lutetium.—The compound $LuSn_3$ was not synthesized. Runs at pressures of 14–87 kbars concurrent with temperatures of 325–1100° produced an unknown reaction product. At pressures of 14–87 kbars and temperatures lower than 300° no reaction was detected.

TABLE II

X-RAY DIFFRACTION DATA FOR RARE EARTH–TRITIN COMPOUNDS

	$TbSn_3$				$DySn_3$				$HoSn_3$				$ErSn_3$				YSn_3			
hkl	I_{obsd}	I_{calcd}	d_{obsd}	d_{calcd}	I_{obsd}	I_{calcd}	d_{obsd}	d_{calcd}	I_{obsd}	I_{calcd}	d_{obsd}	d_{calcd}	I_{obsd}	I_{calcd}	d_{obsd}	d_{calcd}	I_{obsd}	I_{calcd}	d_{obsd}	d_{calcd}
111	30	17	2.671	2.691	30	19	2.687	2.690	35	15	2.675	2.687	30	13	2.671	2.683	100	22	2.682	2.694
200	20	12	2.320	2.331	20	12	2.328	2.330	20	10	2.322	2.327	25	9	2.313	2.324	40	14	2.328	2.333
220	25	14	1.644	1.648	25	16	1.637	1.647	25	13	1.641	1.645	20	11	1.638	1.643	50	17	1.649	1.650
311	30	21	1.402	1.405	25	23	1.405	1.405	30	20	1.401	1.403	25	17	1.399	1.401	60	26	1.406	1.407
222	10	7	1.342	1.346	10	7	1.344	1.345	10	6	1.340	1.343	10	5	1.338	1.342	10	8	1.343	1.347
400	5	4	1.163	1.165	5	4	1.165	1.165	5	3	1.163	1.163	5	3	1.163	1.162	5	5	1.171	1.167
331	20	14	1.068	1.069	25	15	1.068	1.069	25	12	1.067	1.068	20	11	1.065	1.066	15	17	1.069	1.071
420	20	14	1.041	1.042	25	15	1.040	1.042	25	12	1.039	1.041	20	11	1.040	1.039	20	17	1.041	1.043
422	20	14	0.951	0.951	25	15	0.950	0.951	20	12	0.949	0.950	20	11	0.984	0.949	15	17	0.953	0.953
511, 333	25	21	0.896	0.897	25	23	0.896	0.895	25	19	0.895	0.896	30	17	0.895	0.894	20	26	0.899	0.898
440	15	12	0.824	0.824	5	13	0.824	0.824	10	11	0.823	0.823	10	9	0.822	0.822	5	14	0.825	0.825
531	80	90	0.789	0.788	80	91	0.788	0.788	80	79	0.787	0.787	90	72	0.786	0.786	15	100	0.789	0.789
442, 600	100	100	0.778	0.777	100	100	0.777	0.777	100	100	0.776	0.776	100	100	0.774	0.775	...	100	...	0.778

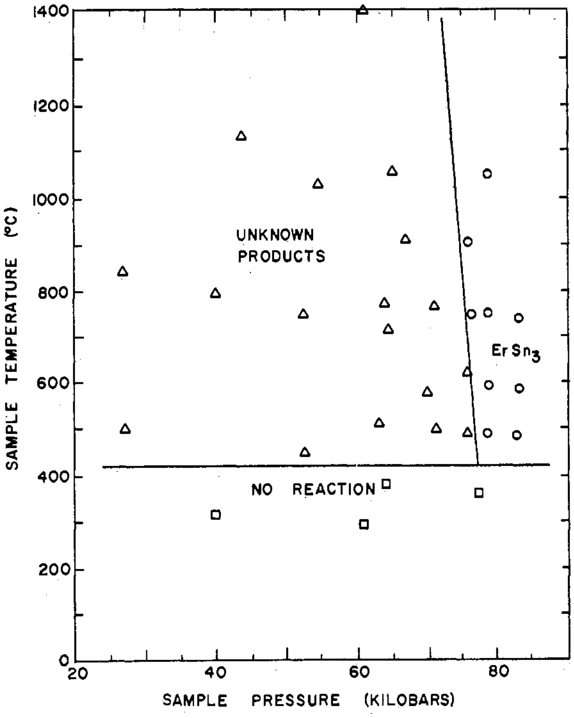

Figure 5.—Er–3Sn reaction product diagram.

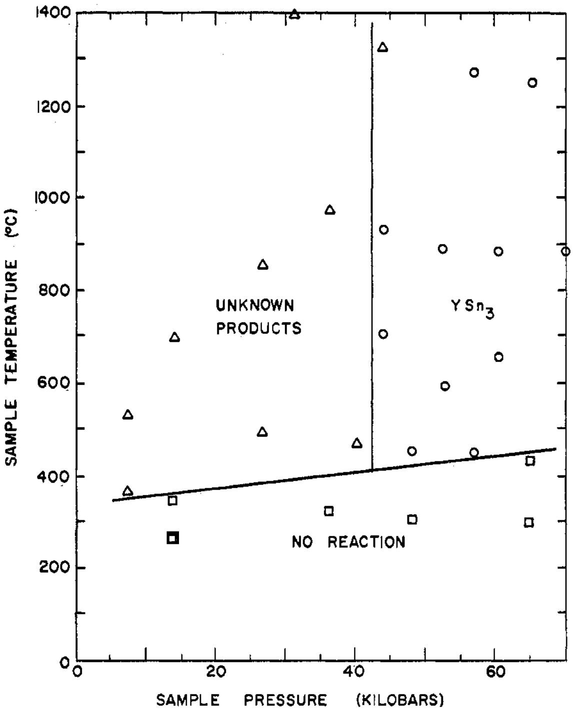

Figure 6.—Y–3Sn reaction product diagram.

Scandium.—The compound $ScSn_3$ was not synthesized. At pressures from 14 to 87 kbars concurrent with temperatures of 265–1300° an unidentified reaction product was observed.

The rare earth–tritin compounds were indexed by comparing them to the $PrSn_3$ indexing given by Rossi[5] ($AuCu_3$ type face-centered cubic with space group *Fm*3*m*). The *d* values, intensities (observed values were measured visually and calculated values were obtained from a Fortran computer program[12]), and Miller indicies for the compounds synthesized during this study are listed in Table II. The cell parameters of the compounds, calculated by the method of least squares, are listed in Table III.

Many of the (RE)Sn_3 synthesis runs made in the rare earth–tritin stable regions (see Figures 2–6) produced a reaction product which contained free β-tin. This behavior has been noted for other rare earth–tritin systems.[7,13] The time of the synthesis runs was increased in an attempt to increase reaction product purity, but for a given pressure and temperature heating times of 0.5–240 min produced reaction products of equivalent purity. Data shown in Figures 2–6 are for heating times of 3–30 min.

TABLE III

LATTICE PARAMETERS OF THE SYNTHESIZED RARE EARTH–TRITIN COMPOUNDS

Compound	a_0, Å	X-Ray density, g/cm³
$TbSn_3$	4.661 ± 0.002	8.45
$DySn_3$	4.659 ± 0.001	8.51
$HoSn_3$	4.653 ± 0.001	8.59
$ErSn_3$	4.648 ± 0.002	8.65
YSn_3	4.666 ± 0.002	7.27

When a rare earth–tritin compound was synthesized in a relatively pure form, the material was dark, shiny, and easily fractured into many small crystals. Some of the unidentified reaction products also exhibited these properties, so X-ray analysis was used to classify all of the reaction products obtained.

The reactivities of $TbSn_3$, $DySn_3$, and $HoSn_3$ were determined by placing the compounds in various solvents. When the compounds were placed in H_2O, concentrated or dilute HCl, concentrated or dilute H_2SO_4, concentrated or dilute HNO_3, or concentrated

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(12) D. K. Smith, "A Fortran Program for Calculating X-Ray Powder Diffraction Patterns," Report UCRL 7196, Ernest O. Lawrence Radiation Laboratory, Livermore, Calif., 1963.

(13) F. Borsa, R. G. Barnes, and R. A. Reese, *Phys. Status Solidi*, **19**, 359 (1967).

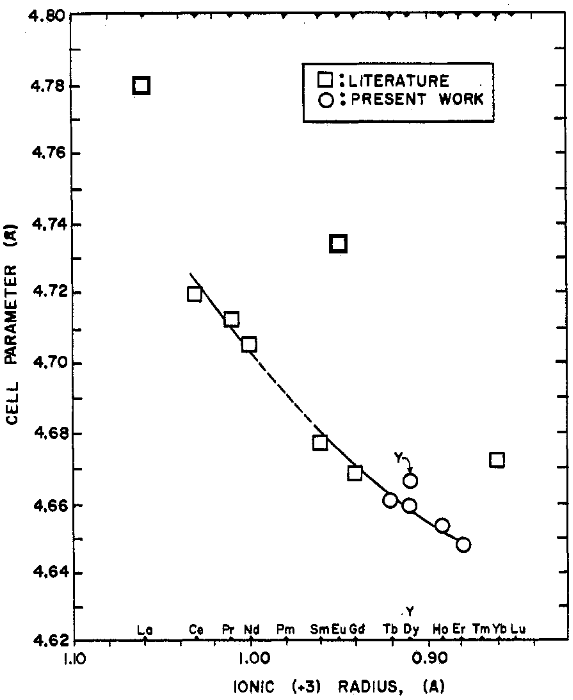

Figure 7.—Cell parameters of (RE)Sn_3 compounds as a function of the ionic (3+) radii of the rare earth elements. The literature cell parameter values were obtained from the references listed in the Introduction of this paper.

NH_4OH, vigorous bubbling transpired and X-ray diffraction patterns of the soaked reaction products showed reversion to metallic tin. The final form of the rare earths was not established. When the same compounds were placed in acetone or methanol, no bubbling occurred, but X-ray diffraction patterns of the soaked materials again indicated reversion to metallic tin. $ErSn_3$ and YSn_3 were not tested for reactivity because the compounds were never obtained in a pure form.

All of the rare earth–tritin compounds synthesized during this study decomposed to metallic tin within 2 weeks on exposure to the atmosphere. Decomposition of other rare earth–tritin compounds has been noted by Borsa, Barnes, and Reese.[13]

As shown in Figure 7, there is a strong correlation between the cell parameters of the rare earth–tritin compounds and the ionic (3+) radii of the rare earth elements. The curve is quite smooth except for Eu and Yb which differ from the other rare earths because of their divalency,[14] La which has no 4f electrons, and Y which is not a true rare earth. A plot of lattice parameters of the rare earth–tritin compounds as a function of the metallic radii of the rare earth elements shows no trends, an observation noted by Iandelli and Palenzona[15] for some rare earth–monometal systems.

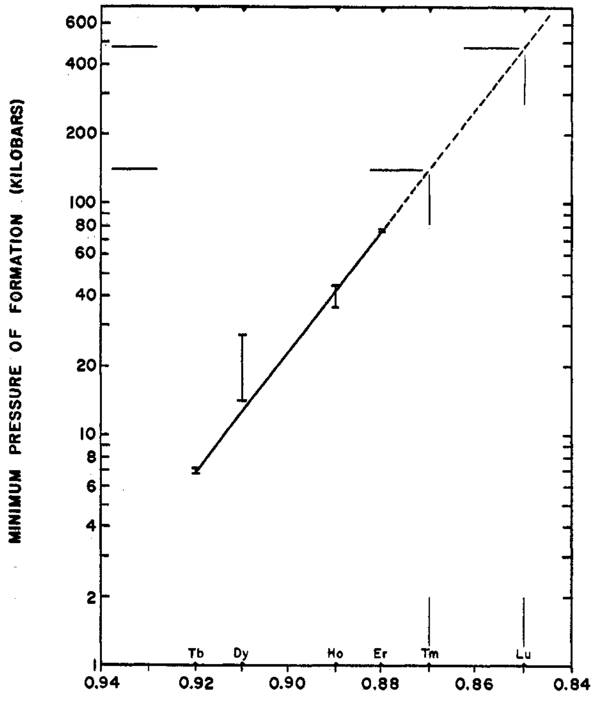

Figure 8.—Minimum pressure of formation as a function of the ionic (3+) radii of the rare earth elements.

An interesting trend was observed concerning the relationship between the minimum pressures of formation of the rare earth–tritin compounds and the ionic (3+) radii of the rare earth elements (see Figure 8). The curve of Figure 8 has been extrapolated to give estimates of the minimum pressures of formation for $TmSn_3$ and $LuSn_3$, and the values obtained are 140 kbars for Tm and 480 kbars for Lu. Using the information shown in Figures 2–6, a minimum temperature of formation of 500° is suggested.

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