Quenchable High Pressure Phases of $DyYbS_3$

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High Pressure Phases, Crystal Structures

Two quenchable high pressure modifications of $DyYbS_3$ are isotypic with U_2S_3 and Ce_2S_3 (Defect-Th_3P_4 type).

In connection with our work on the crystal chemistry at high pressure or rare earth sesquisulfides Ln_2S_3 [1] and $LnLn'S_3$ [2] we investigated the high pressure behaviour of $DyYbS_3$. Two new modifications of this compound could be retained after treatment at high pressures and temperatures.

$DyYbS_3$ was prepared by heating for 150 hours at 1000 °C a finely ground 1:1 mixture of Dy_2S_3 and Yb_2S_3, which had been prepressed into a pellet to insure intimate contact. The pellet was contained in an evacuated sealed quartz ampoule which had been flushed with Ar prior to evacuation. Dy_2S_3 and Yb_2S_3 were prepared by reacting the elements (Dy, Yb 99,9% Rasmus Hamburg; S Merck) at 1150 °C for 80 hours, in evacuated quartz ampoules. The $DyYbS_3$ obtained should be D-type** according to Carré *et al.*[3], but exact characterization was difficult as no diffraction data was presented by Carré *et al.* However, comparison with pure Tm_2S_3 which also had the D-type structure, confirmed that $DyYbS_3$ has the D-type structure. Slight traces of unreacted Dy_2S_3 and Yb_2S_3 were found to be present, however, these unreacted traces disappeared after treatment at high pressures and temperatures.

Table I. Guinier powder data for $DyYbS_3$ after treatment at 10 kbar, 1500 °C (Defect-Th_3P_4 structure).

d_{obs} [Å]	d_{calc} [Å]	*hkl*	I (peak heights)
3,3770	3,3747	211	100
2,9224	2,9226	220	6
2,6148	2,6141	310	86
2,2093	2,2093	321	51
2,0674	2,0666	400	3
1,8487	1,8484	420	26
1,7627	1,7624	332	17
1,6875	1,6874	422	6
1,6212	1,6212	431	30
1,5092	1,5092	521	6
1,4614	1,4613	440	3
1,3409	1,3410	611	30
1,3070	1,3070	620	6
1,2756	1,2755	541	10
1,2187	1,2188	631	5
1,1931	1,1932	444	6
1,1464	1,1463	640	6
1,1250	1,1249	633	17
	1,1249	721	
1,1045	1,1046	642	3
1,0497	1,0498	651	4

Table II. Guinier powder data for $DyYbS_3$ after treatment at 40 kbar, 1500 °C (U_2S_3-type structure).

d_{obs} [Å]	d_{calc} [Å]	*hkl*	I (peak heights)
5,270	5,268	200	8
5,179	5,185	002	4
3,695	3,695	202	100
3,597	3,594	011	46
3,401	3,402	111	39
3,327	3,326	301	50
3,284	3,284	103	46
3,101	3,099	210	23
2,969	2,969	211	shoulder
2,959	2,958	112	58
2,660	2,660	212	35
2,636	2,634	400	27
2,593	2,593	004	14
2,568	2,567	013	27
2,511	2,512	311	27
2,495	2,494	113	54
2,348	2,348	402	12
2,327	2,326	204	12
2,316	2,316	312	37
2,300	2,307	213	shoulder
2,173	2,171	410	6
2,125	2,125	411	25
2,105	2,104	114	31
2,066	2,065	501	14
2,035	2,035	105	8
2,002	2,002	412	23
1,989	1,988	214	19
1,916	1,916	020	23
1,832	1,832	314	17
1,799	1,799	503	25
1,786	1,786	305	27
1,739	1,739	512	10
1,728	1,728	006	6
1,702	1,701	222	14
1,660	1,660	321	15
1,655	1,655	123	17
1,623	1,619	315	10
1,573	1,576	016	8
1,526	1,526	612	8
1,512	1,512	323	6
1,336	1,337	217	4
1,311	1,312	523	8
1,306	1,306	325	14
1,232	1,232	606	10
	1,232	132	
1,113	1,113	911	6

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** Original notation[3] changed by Sleight and Prewitt[4].

Pressure was generated in a Belt device[1]. The samples were contained in BN capsules with no evidence of contamination. Pressure and temperature were read from previously determined calibration curves and are thought to be accurate to ± 2 kbar and ± 75 °C respectively. In all cases pressure and temperature were maintained for 1 hour before quenching to ambient.

The products were examined using a Huber Guinier Camera (film and counter methods) and monochromatized $CuK_{\alpha 1}$ ($\lambda = 1{,}5405$ Å) radiation.

Upon quenching to ambient from 10 kbar, 1500 °C the product was found to have the defect-Th_3P_4 type structure (space group $I\bar{4}3d$). The diffraction data obtained is listed in Table I and could be well indexed using a cubic unit cell with $a = 8.266(4)$ Å. Previously[4] the exact composition of this phase has been questioned, and it has been suggested that it is only obtained when slight decomposition occurs moving the composition to a slightly S-lean value. This is supported in our present work by the detectable presence of H_2S after quenching to ambient. This has also been reported for $GdYbS_3$ [2], which also has the Th_3P_4-type structure after quenching from 10 kbar, 1500 °C.

Upon quenching from 25 kbar, 1500 °C and 40 kbar, 1500 °C the same new modification was obtained. The product quenched from 25 kbar, 1500 °C contained faint traces of the Th_3P_4-type phase. The new modification could be indexed using an orthorhombic cell with $a = 10.535(16)$ Å, $b = 3.832(6)$ Å and $c = 10.370(16)$ Å. The systematic absences confirmed the space group to be Pnma, and combined with the observed intensities this phase must have the U_2S_3-type structure. The diffraction data is listed in Table II. This phase is isostructural with that found for $GdYbS_3$ after treatment at 40 kbar, 1500 °C[2], and certain rare earth sesquisulfides[1].

The relative effect of the different sized rare earth cations has been discussed for $GdYbS_3$ [2]. It is important to note that in the present case the average cationic radius is 0.883 (Templeton radii[5]), which has moved the size relationship into a region where only the U_2S_3-type structure is preferred at high pressure.

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