diffraction pattern is obtained which can be well indexed using a cubic cell with $a = 8{,}310(2)$ Å. The diffraction lines are extremely sharp indicating a well crystallized product. The faint traces of Gd_2S_3 and Yb_2S_3 which were present in the starting product, had vanished. The higher reaction temperature probably facilitated complete reaction of the starting products. The diffraction data is presented in Table I. The observed peaks and their intensities strongly suggest that the space group is T^6_d–$I\bar{4}3d$, and that this phase has the defect-Th_3P_4 (C-Type) structure. The defect-Th_3P_4 structure type also occurs for the related Ln_2S_3 compounds, but the exact composition is still the subject of some discussion[3,1]. It would appear that a partial decomposition is necessary, and this is supported in our present work by the presence of H_2S after experiments at 10 kbar, 1500 °C. No trace of free S can be found in the diffraction patterns, but this is expected as it would probably be amorphous.

Table I. Guinier Powder Data $GdYbS_3$ after treatment at 10 kbar, 1500 °C. (Defect Th_3P_4-type structure.)

d_{obs} [Å]	d_{calc} [Å]	hkl	I (peak heights)
3.3928	3.3925	211	100
2.9382	2.9380	220	3
2.6289	2.6278	310	95
2.2216	2.2209	321	60
2.0778	2.0775	400	4
1.8586	1.8582	420	30
1.7717	1.7717	332	22
1.6962	1.6963	422	14
1.6297	1.6297	431	33
1.5172	1.5172	521	5
1.4693	1.4690	440	2
1.3479	1.3481	611	27
1.3140	1.3139	620	7
1.2822	1.2823	541	10
1.2252	1.2252	631	3
1.1994	1.1994	444	5
1.1525	1.1524	640	6
1.1308	1.1308	721	19
	1.1308	633	
1.1103	1.1105	642	3
1.0553	1.0553	651	4

After treatment at 25 kbar, 1500 °C only slight traces of the defect-Th_3P_4 phase can be found, but the bulk of the material appears as a new phase. The Guinier pattern can be indexed using an orthorhombic cell with $a = 7.279(4)$ Å, $b = 15.119(6)$ Å and $c = 3.875(3)$ Å (Table II). Unit cell dimensions, systematic absences and intensity data strongly suggest that this phase has the A-type (Gd_2S_3) structure. The composition of this phase is almost surely $GdYbS_3$ and this would suggest that the defect-Th_3P_4 phase found at lower pressures does indeed represent a decomposition process which

Table II. Guinier Powder Data for $GdYbS_3$ after treatment at 25 kbar, 1500 °C. (A-type structure.)

d_{obs} [Å]	d_{calc} [Å]	hkl	I (peak heights)
4.147	4.143	130	5
3.781	3.779	040	11
3.758	3.755	011	7
3.640	3.639	200	16
3.539	3.538	210	19
3.337	3.354	140	shoulder
3.329	3.337	111	100
3.282	3.279	220	shoulder
3.073	3.073	031	23
2.793	2.792	150	14
2.654	2.653	201	shoulder on Th_3P_4-peak
2.536	2.536	141	11
2.503	2.503	221	32
2.384	2.384	051	12
2.348	2.348	231	12
2.326	2.326	250	11
2.3101	2.3100	320	7
2.2652	2.2656	151	11
2.1864	2.1858	330	9
2.1735	2.1715	241	5
2.0779	2.0715	260	4
2.0703	2.0705	170	4
2.0379	2.0377	311	9
2.0283	2.0288	161	5
1.9933	1.9942	251	7
1.9840	1.9843	321	7
1.9382	1.9382	002	14
1.9040	1.9040	331	5
1.8888	1.8897	080	7
1.8715	1.8775	022	7
1.8277	1.8270	261	12
1.8064	1.8064	410	9
	1.8064	341	
1.7471	1.7476	360	11
1.7255	1.7246	042	2
1.7104	1.7107	202	5
1.7000	1.7004	351	12
1.6963	1.6968	212	19
1.6779	1.6782	142	12
1.6680	1.6684	222	7
1.6365	1.6367	190	5
1.5927	1.5932	361	7
1.5588	1.5590	450	7
1.5412	1.5413	091	4
1.4849	1.4848	322	7
1.4501	1.4502	332	7
1.4293	1.4293	520	7
1.4187	1.4192	291	11
1.3306	1.3303	182	4
1.3061	1.3066	422	11
1.2981	1.2979	362	7
1.2679	1.2678	113	4
1.2599	1.2598	0 12 0	7
	1.2517	442	5
1.2512	1.2516	033	

does not occur fully at 25 kbar, 1500 °C because of the higher pressure. As would be expected from the small amount of the Th_3P_4 phase present, very faint traces of H_2S could be detected after the experiment.

After treatment at 40 kbar, 1500 °C all traces of the C- and A-type phases are removed, and are replaced by the diffraction peaks of a third phase. These peaks can be indexed using an orthorhombic cell with $a = 10.603(5)$ Å, $b = 3.869(3)$ Å and $c = 10.385(5)$ Å (Table III). Systematic absences are consistent with the space group Pnma, and the intensity data suggest that this phase has the U_2S_3 structure. This structure was also found for certain Ln_2S_3 compounds[1].

Table III. Guinier Data for $GdYbS_3$ after treatment at 40 kbar, 1500 °C. (U_2S_3-type structure.)

d_{obs} [Å]	d_{calc} [Å]	hkl	I (peak heights)
5.309	5.301	200	13
5.197	5.192	002	10
3.710	3.710	202	100
3.625	3.625	011	63
3.432	3.430	111	43
3.348	3.346	301	87
3.292	3.291	103	60
3.126	3.125	210	33
2.994	2.993	211	shoulder
2.979	2.978	112	63
2.678	2.678	212	40
2.653	2.651	400	33
2.595	2.596	004	shoulder
2.579	2.580	013	33
2.533	2.531	311	27
2.506	2.507	113	77
2.361	2.361	402	20
2.331	2.332	312	47
2.186	2.187	410	17
2.140	2.140	411	30
2.112	2.113	114	37
2.081	2.084	313	13
2.039	2.038	105	17
2.018	2.015	412	27
1.997	1.997	214	13
1.935	1.934	020	40
1.872	1.872	121	10
1.840	1.840	314	20
1.808	1.808	503	27
1.805	1.803	115	shoulder
1.790	1.790	221	33
1.766	1.767	600	7
1.752	1.751	512	13
1.729	1.730	215	13
1.715	1.715	222	20
1.674	1.675	321	20
1.668	1.668	123	23
1.622	1.625	315	7
1.486	1.484	505	10
1.339	1.339	424	10
1.314	1.314	325	13
1.305	1.306	713	10

Discussion

The present results show a close relationship with those obtained for the simple Ln_2S_3 compounds[1]. The highest pressures used in the present study produced the Ln_2S_3–III (U_2S_3) structure type which was found to be the most dense form for the smaller rare earths. Previously[3] the A-type was found to be the most dense form for the larger rare earths. The U_2S_3 structure type is marginally more dense than the A-type structure. However, the size of the cation was found to be the deciding factor and no transformation from the A-type structure to the U_2S_3-structure has been observed.

In the present study both structure types occur, with the U_2S_3-structure being favoured at higher pressures as would be expected. This is certainly due to the size differences between the Gd and Yb. At high pressures Gd_2S_3 retains the A-type structure to 70 kbar whereas Yb_2S_3 adopts the U_2S_3-structure at 20 kbar. These contrasting features obviously result in both structure types appearing for $GdYbS_3$.

The two structure types have approximately the same spacefilling requirements, and the coordination number of the cation is equal in both cases. The coordination of the cation in the U_2S_3-structure is particularly interesting and is described in detail in ref. 1. A comparison of the unit cell volumes for the Ln_2S_3 compounds is presented in Table IV,

Table IV. Unit cell volumes for Ln_2S_3 and $LnLn'S_3$ compounds.

Structure type	Compound		$\bar{r}_{Cation}$ [Å]	Unit cell volume [Å^3]	Ref.
U_2S_3-Type ($Z = 4$)	Lu_2S_3	HP	0.848	405.3	1
	Yb_2S_3	HP	0.858	408.1	1
	Tm_2S_3	HP	0.869	412.8	1
	Er_2S_3	HP	0.881	417.6	1
	Ho_2S_3	HP	0.894	422.6	1
	$GdYbS_3$	HP	0.898	425.9	This work
Gd_2S_3-Type (A-Type) ($Z = 4$)	$GdYbS_3$	HP	0.898	426.5	This work
	Dy_2S_3	NP	0.908	427.2	3
	Tb_2S_3	NP	0.923	433.1	3
	Gd_2S_3	NP	0.938	440.7	3
	Sm_2S_3	NP	0.964	451.1	3
	Nd_2S_3	NP	0.995	465.3	3
	Pr_2S_3	NP	1.013	473.1	3
	Ce_2S_3	NP	1.034	483.0	3
	La_2S_3	NP	1.061	498.4	3

HP = High Pressure Phase; NP = Normal Pressure Phase.