

Quenchable High Pressure Phases of GdYbS₃

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High Pressure Phases, Crystal Structures

Three new modifications of GdYbS₃ can be retained metastably, after quenching from high pressure and temperature. The Guinier powder data is presented and indexed. The three modifications include a cubic defect Th₃P₄-type phase with $a = 8.310(2)$ Å, an orthorhombic A-type phase with $a = 7.279(4)$ Å, $b = 15.119(6)$ Å and $c = 3.875(3)$ Å, and an orthorhombic U₂S₃-type phase with $a = 10.603(5)$ Å, $b = 3.869(3)$ Å and $c = 10.385(5)$ Å. Structural relationships between the present group of structures and the structures of the rare earth sulfides with formula Ln₂S₃ are discussed.

Introduction

The crystal chemistry of the rare earth sesquisulfides with formula Ln₂S₃ has been investigated by a number of workers. Recently RANGE and LEEB¹ published the structures of quenched high pressure phases for certain rare earth sesquisulfides. In their paper the relevant literature is reviewed.

To obtain more information on the influence of cationic size on the transformations present, we extended the investigations to include mixed rare earth sulfides with the general formula LnLn'S₃. The crystal chemistry of these compounds at atmospheric pressure has been reported by CARRÉ *et. al.*².

In the present paper the quenchable high pressure phases of GdYbS₃ are investigated and related to the quenchable phases obtained for the rare earth sesquisulfides.

Experimental

Gd₂S₃ and Yb₂S₃ were prepared by heating stoichiometric quantities of the elements (Gd, Yb 99,9% Rasmus Hamburg; S, Merck) in evacuated quartz ampoules for 80 hours at 1150 °C. The com-

pounds were found to be well crystallized and single phase using diffraction techniques. GdYbS₃ was then prepared by grinding a 1:1 mixture of Gd₂S₃ and Yb₂S₃ very finely, then pressing the mixture into a tablet, and heating the tablet in an Ar flushed, evacuated sealed quartz ampoule for 150 hours at 1000 °C. X-ray analysis of the product showed only slight traces of Gd₂S₃ and Yb₂S₃ present, with the bulk of the material single phase. GdYbS₃ was reported to be F-type² but exact characterization was difficult due to the lack of diffraction data in ref. 2. From the present results the F-type characterization seems doubtful with a D-type structure being more probable.

Pressure was generated in a Belt device. The experimental procedure has been described previously¹. Pressure and temperature were read from previously determined calibration curves, and are thought to be accurate to ± 4 kbar and ± 75 °C respectively. The samples were contained in BN capsules with no evidence of reaction. In all cases pressure was increased and maintained until constant, when the temperature was increased slowly to the desired value. The pressure-temperature conditions 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 _{α 1} ($\lambda = 1,5405$) radiation.

Results

Three new quenchable phases were found for GdYbS₃ after treatment at 10, 25, 40 kbar and 1500 °C respectively.

At 10 kbar, 800 °C only the normal atmospheric starting phase is present upon quenching. However, after quenching from 10 kbar, 1500 °C a simple

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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 Gd₂S₃ and Yb₂S₃ 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 T⁶_a-I43d, and that this phase has the defect-Th₃P₄ (C-Type) structure. The defect-Th₃P₄ structure type also occurs for the related Ln₂S₃ compounds, but the exact composition is still the subject of some discussion^{9,1}. It would appear that a partial decomposition is necessary, and this is supported in our present work by the presence of H₂S 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 GdYbS₃ after treatment at 10 kbar, 1500 °C. (Defect Th₃P₄-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-Th₃P₄ 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

(Gd₂S₃) structure. The composition of this phase is almost surely GdYbS₃ and this would suggest that the defect-Th₃P₄ phase found at lower pressures does indeed represent a decomposition process which

Table II. Guinier Powder Data for GdYbS₃ 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 ₃ P ₄ -peak | |
| | 2.536 | 141 | 11 | |
| | 2.503 | 221 | 32 | |
| | 2.384 | 051 | 12 | |
| | 2.348 | 231 | 12 | |
| | 2.326 | 250 | 11 | |
| | 2.3101 | 320 | 7 | |
| | 2.2652 | 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 Th₃P₄ phase present, very faint traces of H₂S 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 U₂S₃ structure. This structure was also found for certain Ln₂S₃ compounds¹.

Table III. Guinier Data for GdYbS₃ after treatment at 40 kbar, 1500 °C. (U₂S₃-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 Ln₂S₃ compounds¹. The highest pressures used in the present study produced the Ln₂S₃-III (U₂S₃) structure type which was found to be the most dense form for the smaller rare earths. Previously³ the A-type was found to be the most dense form for the larger rare earths. The U₂S₃ 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 U₂S₃-structure has been observed.

In the present study both structure types occur, with the U₂S₃-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 Gd₂S₃ retains the A-type structure to 70 kbar whereas Yb₂S₃ adopts the U₂S₃-structure at 20 kbar. These contrasting features obviously result in both structure types appearing for GdYbS₃.

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 U₂S₃-structure is particularly interesting and is described in detail in ref. 1. A comparison of the unit cell volumes for the Ln₂S₃ compounds is presented in Table IV,

Table IV. Unit cell volumes for Ln₂S₃ and LnLn'S₃ compounds.

| Structure type | Compound | \bar{r}_{Cation} [Å] | Unit cell volume [Å ³] | Ref. |
|---|-----------------------------------|-------------------------------|------------------------------------|-----------|
| U ₂ S ₃ -Type (Z = 4) | Lu ₂ S ₃ HP | 0.848 | 405.3 | 1 |
| | Yb ₂ S ₃ HP | 0.858 | 408.1 | 1 |
| | Tm ₂ S ₃ HP | 0.869 | 412.8 | 1 |
| | Er ₂ S ₃ HP | 0.881 | 417.6 | 1 |
| | Ho ₂ S ₃ HP | 0.894 | 422.6 | 1 |
| | GdYbS ₃ HP | 0.898 | 425.9 | This work |
| Gd ₂ S ₃ -Type (A-Type) (Z = 4) | GdYbS ₃ HP | 0.898 | 426.5 | This work |
| | Dy ₂ S ₃ NP | 0.908 | 427.2 | 3 |
| | Tb ₂ S ₃ NP | 0.923 | 433.1 | 3 |
| | Gd ₂ S ₃ NP | 0.938 | 440.7 | 3 |
| | Sm ₂ S ₃ NP | 0.964 | 451.1 | 3 |
| | Nd ₂ S ₃ NP | 0.995 | 465.3 | 3 |
| | Pr ₂ S ₃ NP | 1.013 | 473.1 | 3 |
| | Ce ₂ S ₃ NP | 1.034 | 483.0 | 3 |
| La ₂ S ₃ NP | 1.061 | 498.4 | 3 | |

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

illustrating that the present unit cell volume of the A-type is probably the smallest unit cell volume possible for this structure type, whereas that of the U₂S₃ phase, is one of the largest of its type. However, the U₂S₃ phase is probably more compressible at higher pressures. These factors indicate that for the present compound GdYbS₃, we have a critical relationship between the sizes of the Gd and Yb which makes it possible to obtain both structure types for the same compound. The average radius of the cations Gd and Yb is 0.898 Å, which lies between the cationic radii of Ho and Y⁴. Preliminary

experimental results on the compounds Ho₂S₃ and Y₂S₃ at low pressures and high temperatures indicate that the A-type structure may also occur for these compounds.

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