

Quenchable High Pressure Phases of GdYbS_3

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High Pressure Phases, Crystal Structures

Three new modifications of GdYbS_3 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 Th_3P_4 -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 U_2S_3 -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 Ln_2S_3 are discussed.

Introduction

The crystal chemistry of the rare earth sesquisulfides with formula Ln_2S_3 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 $\text{LnLn}'\text{S}_3$. 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 GdYbS_3 are investigated and related to the quenchable phases obtained for the rare earth sesquisulfides.

Experimental

Gd_2S_3 and Yb_2S_3 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. GdYbS_3 was then prepared by grinding a 1:1 mixture of Gd_2S_3 and Yb_2S_3 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 Gd_2S_3 and Yb_2S_3 present, with the bulk of the material single phase. GdYbS_3 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 $\text{CuK}_{\alpha 1}$ ($\lambda = 1,5405$) radiation.

Results

Three new quenchable phases were found for GdYbS_3 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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