

# Synthesis and Crystal Structure of a New Oxysulfide $\text{Gd}_{6+x}\text{Ti}_{4-x}\text{S}_{10-y}\text{O}_{6+y}$ (where $x \sim 0.04$ and $y \sim 0.27$ )

Vincent Meignen, Alain Meerschaut, Laurent Cario, and Alain Lafond

Institut des Matériaux Jean Rouxel, UMR 6502 CNRS-Université de Nantes, Laboratoire de Chimie des Solides, 2, rue de la Houssinière, BP 32229 44322 Nantes cedex 03, France

Reprint requests to Prof. Dr. A. Meerschaut. Fax: (33) 240 37 39 95.

E-mail: Alain.Meerschaut@cnrs-imn.fr

Z. Naturforsch. **59b**, 963 – 968 (2004); received June 16, 2004

*Dedicated to Professor Kurt O. Klepp on the occasion of his 60<sup>th</sup> birthday*

A new phase in the quaternary system Gd/Ti/S/O was obtained from a mixture of  $\text{Gd}_2\text{O}_3$ ,  $\text{Gd}_2\text{S}_3$ ,  $\text{TiO}_2$ ,  $\text{TiS}_2$  and Ti by a solid state reaction at 1323 K in a sealed fused-silica tube. The structure of  $\text{Gd}_{6+x}\text{Ti}_{4-x}\text{S}_{10-y}\text{O}_{6+y}$  (where  $x \sim 0.04$ , and  $y \sim 0.27$ ), was solved by single-crystal X-ray diffraction, with  $R_{(\text{obs})} = 2.69\%$  for 2391 reflections ( $I > 3\sigma(I)$ ) and 155 variables. This compound crystallizes with four formula units in the orthorhombic space group  $Pnma$ , and the lattice constants (Å):  $a = 13.991(1)$ ,  $b = 3.7124(2)$ ,  $c = 34.029(3)$  Å. The structure is built up from the stacking of ribbons of five Gd-polyhedra alternating with ribbons of five Ti- and Gd/Ti-polyhedra along the *a*-axis. This is the first example of a rare earth (RE) and titanium oxysulfide compound that shows mixed RE/Ti sites together with pure RE- and Ti-sites.  $\text{Gd}_{6+x}\text{Ti}_{4-x}\text{S}_{10-y}\text{O}_{6+y}$  is a mixed-valent titanium oxysulfide in which half of the Ti cations are  $\text{Ti}^{3+}$  and half are  $\text{Ti}^{4+}$ .

*Key words:* Oxysulfide, Gadolinium, Mixed-Valent Titanium, Crystal Structure