

## The structural transition of $\text{Gd}_2\text{O}_3$ nanoparticles induced by high pressure

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2007 J. Phys.: Condens. Matter 19 425229

(<http://iopscience.iop.org/0953-8984/19/42/425229>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 159.226.165.151

The article was downloaded on 05/09/2012 at 07:03

Please note that [terms and conditions apply](#).

## The structural transition of Gd<sub>2</sub>O<sub>3</sub> nanoparticles induced by high pressure

Haiyong Chen<sup>1</sup>, Chunyuan He<sup>1</sup>, Chunxiao Gao<sup>1</sup>, Yanmei Ma<sup>1</sup>,  
Jiahua Zhang<sup>2</sup>, Xiaojun Wang<sup>2</sup>, Shiyong Gao<sup>1</sup>, Dongmei Li<sup>1</sup>,  
Shihai Kan<sup>1</sup> and Guangtian Zou<sup>1</sup>

<sup>1</sup> State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, People's Republic of China

<sup>2</sup> Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, People's Republic of China

Received 3 August 2007

Published 18 September 2007

Online at [stacks.iop.org/JPhysCM/19/425229](http://stacks.iop.org/JPhysCM/19/425229)

### Abstract

The structural transition of nanosize Gd<sub>2</sub>O<sub>3</sub> is studied using high pressure energy dispersive x-ray diffraction and high pressure photoluminescence. The original structure of the nanosized sample shows a mixture of cubic and monoclinic structure. Our results show that the cubic and most of the monoclinic structure turns into hexagonal structure above 10.35 GPa. But a small proportion of monoclinic structure can be present up to the highest pressure, 36.2 GPa. When the pressure is released, the hexagonal structure partly reverts to monoclinic structure, so the sample shows a mixture of hexagonal and monoclinic structure. The structural transition from monoclinic to hexagonal structure is reversible.

Gd<sub>2</sub>O<sub>3</sub> is a versatile material with high application potential in various fields of technology. It is of interest as protective and corrosion resistive coatings [1, 2] due to thermal stability and refractory properties [3, 4]. The high refractive index [5] of Gd<sub>2</sub>O<sub>3</sub> makes it a useful material in optics, e.g. in antireflection coatings [6]. Gadolinium oxide presents good luminescence properties when doped with rare-earth ions (Eu<sup>3+</sup>, Tb<sup>3+</sup>) [7–9]. Gadolinium oxide optical thin films for ultraviolet and deep ultraviolet lasing [10] and europium-doped Gd<sub>2</sub>O<sub>3</sub> waveguiding for x-ray imaging systems [11, 12] have recently been reported. In addition, Gd<sub>2</sub>O<sub>3</sub> can effectively passivate the GaAs surface [13]. Crystalline Gd<sub>2</sub>O<sub>3</sub> exists in cubic, monoclinic, and hexagonal phases. Most of the applications of Gd<sub>2</sub>O<sub>3</sub> are based on the cubic structure. But monoclinic [14] and hexagonal structure [15] can form in the process of the fabrications. So it is important to study the stability of cubic, monoclinic and hexagonal structure. In this paper, high pressure structural transitions of nanosized Gd<sub>2</sub>O<sub>3</sub> are studied using high pressure XRD and PL.

Our experimental procedures were as follows. We prepared the  $\text{Gd}(\text{NO}_3)_3$  solution by mixing 0.3625 g  $\text{Gd}_2\text{O}_3$  (99.999%) and 0.0035 g  $\text{Eu}_2\text{O}_3$  (99.999%) with 50 ml distilled water and adding an appropriate amount of  $\text{HNO}_3$  to the mixture with suitable stirring to form a clear solution. The solution was diluted to 100 ml by adding more distilled water. Then 3.3 g of CTAB was subsequently added at 337 K. After the clear solution cooled down to room temperature, an additional 10 ml of NaOH solution (0.006 M) was added into the solution. After stirring for about 30 min, white precipitations, i.e.,  $\text{Gd}(\text{OH})_3$ , were separated out by centrifugation. They were washed with hot distilled water and were separated out by centrifugation again. The precipitations are dried in air. Then they are heated to 1073 K and last for 2 h. Unlike bulk  $\text{Gd}_2\text{O}_3\text{:Eu}$ , which has a stable cubic structure when the temperature is below 1573 K, the nanosized  $\text{Gd}_2\text{O}_3\text{:Eu}$  (about 30 nm) is a mixture of cubic and monoclinic structures in roughly equivalent quantities after the heat treatment at 1073 K [16].

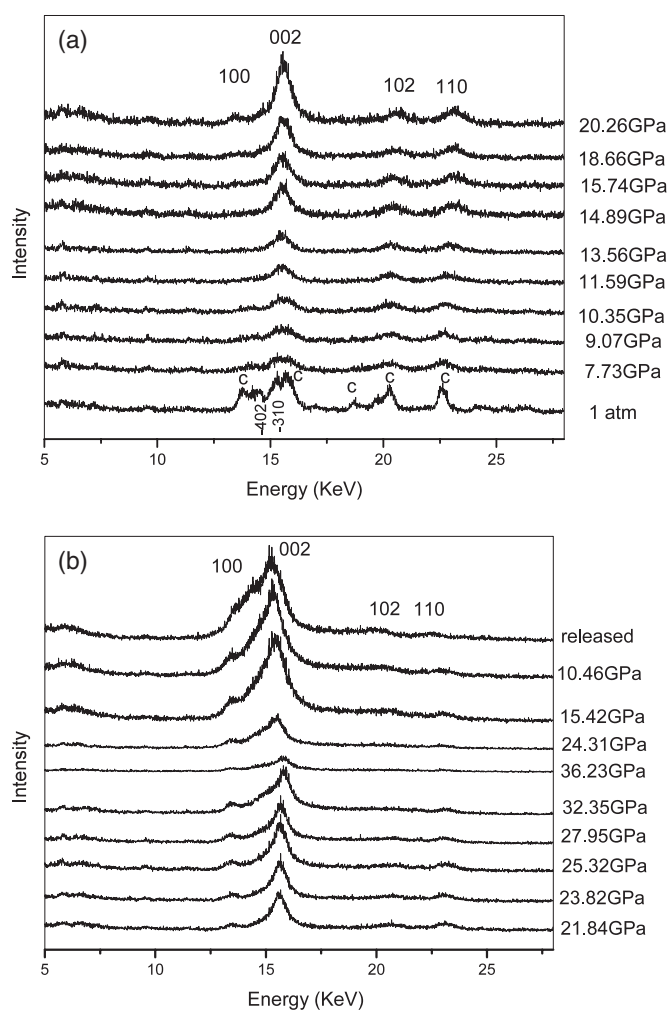
Energy dispersive x-ray diffraction patterns were recorded on Line 3W1A of the Institute of High Energy Physics, CAS, in Beijing. The system was described in detail elsewhere [17]. In our experiment, the diamond anvil cell (DAC) equipment was used to investigate the behavior of  $\text{Gd}_2\text{O}_3$  under high pressure. The diameter of the anvil culet is 500  $\mu\text{m}$ , the gasket is T301 stainless steel which was pressurized to 10 GPa in advance, and the sample cavity is a  $\varnothing 200 \mu\text{m}$  hole. The x-ray spot size is 80  $\mu\text{m}$  across. Ruby works as the pressure marker. The space distance  $d$  and energy peak  $E$  obey the energy dispersive formula:

$$Ed = 6.1993 / \sin \theta (\text{keV } \text{\AA})$$

$\theta$  in the formula represents the Bragg angle. And in our research,  $\theta = 8.27^\circ$ .

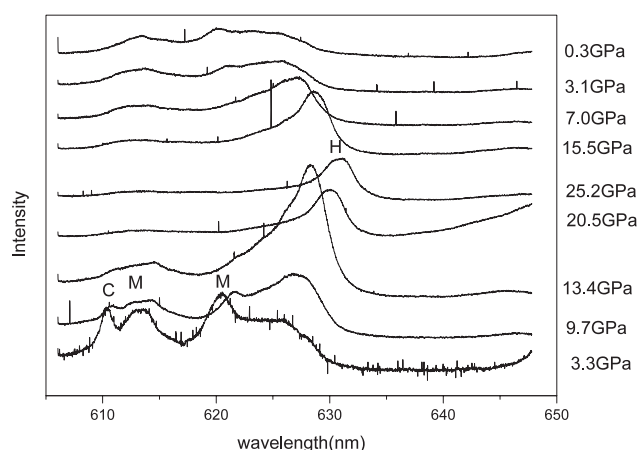
The high pressure behavior of the mixture composed of nanosized cubic and monoclinic  $\text{Gd}_2\text{O}_3$  is studied. The high pressure XRD spectrum of the mixture is shown in figures 1(a) and (b). At ambient pressure, the diffraction peaks can be identified as those of a cubic structure with the lattice constant of 10.81  $\text{\AA}$  and a monoclinic structure with  $a = 14.09 \text{\AA}$ ,  $b = 3.576 \text{\AA}$ ,  $c = 8.769 \text{\AA}$ ,  $\beta = 100.08$ . According to the XRD results for the sample which was presented in the reference [16], two peaks of monoclinic structure are marked at the bottom of graph and the peaks of cubic structure are marked with letter c. When the pressure increases to 7.73 GPa, the intensity of the diffraction peaks attributable to cubic structure is about zero and at the same time the intensity of the diffraction peaks attributable to monoclinic structure decreases rapidly. The three strong peaks present can be identified as relating to 002, 102 and 110 for the hexagonal structure. The data at the pressures above 11.59 GPa are shown in table 1. We can see that the peaks agree well with the hexagonal structure. This indicates that the hexagonal structure is a stable phase at pressure above 11.59 GPa. At 32.35 GPa, which is the highest pressure in this experiment, the (101) peak at 32.2 keV shows an asymmetric shape. Its shoulder covers 28–32 keV which is in the range of peaks attributable to monoclinic structure. We think that a small amount of monoclinic structure may exist at 32.35 GPa. When the pressure is released, the peaks for hexagonal structure are still present and the shoulder of the peak at 32.2 keV becomes very clear. This indicates that when the pressure is released, hexagonal structure partly reverts to monoclinic structure. The released sample shows a mixture of hexagonal and monoclinic structure.

To confirm the structural transition from monoclinic to hexagonal, the PL behavior of the mixture composed of cubic and monoclinic structures under high pressure is also studied. Figure 2 is the high pressure PL spectrum of cubic and monoclinic  $\text{Gd}_2\text{O}_3\text{:Eu}$  nanoparticles under the excitation of 488 nm with ruby as the pressure marker. At 3.3 GPa pressure, it shows characteristic 4f–4f emissions of  $\text{Eu}^{3+}$  in cubic and monoclinic  $\text{Gd}_2\text{O}_3$ . The strong peak at 610 nm is from the  $5D_0 \rightarrow 7F_2$  transition of  $\text{Eu}^{3+}$  in a cubic host and the peaks at 613.67 and 620.56 nm are from the  $5D_0 \rightarrow 7F_2$  transition of  $\text{Eu}^{3+}$  in a monoclinic host. Below



**Figure 1.** (a) High pressure XRD spectrum of the mixture of nanosized cubic and monoclinic  $Gd_2O_3$  for the range of 1 atm–20.26 GPa. (b) High pressure XRD spectrum of the mixture of nanosized cubic and monoclinic  $Gd_2O_3$  for the range with 21.84 GPa released.

13.5 GPa, the intensities of the peaks at 610, 614 and 623 nm decrease simultaneously with the increase of the pressure. At 13.5 GPa, the intensity of the peak at 610 nm is almost zero while peaks at 614.57 and 621.95 nm are still present. This indicates that the cubic structure has completely turned into hexagonal structure but a small amount of monoclinic structure has not yet turned into hexagonal structure. At the same time, an asymmetric peak at 630 nm increases in intensity. Comparing with the result from the high pressure XRD, we consider this emission peak to be from  $Eu^{3+}$  in a hexagonal host. During the course of releasing pressure, the peaks for monoclinic structure are present again. When the pressure is released, two peaks at 613.38 and 620.16 nm can be seen clearly. This shows that some hexagonal structure has reverted to monoclinic structure. After compression at high pressure, the sample became a mixture of monoclinic and hexagonal structure. This is consistent with the result from the high pressure XRD spectrum of the mixture of nanosized cubic and monoclinic  $Gd_2O_3$ .



**Figure 2.** High pressure PL spectrum of a mixture composed of cubic and monoclinic  $\text{Gd}_2\text{O}_3$  for the range of 0.3–25.2 GPa.

**Table 1.** The peak positions of the hexagonal  $\text{Gd}_2\text{O}_3$  at different pressures.

Pressure (GPa)	002	102	110	$a$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )
11.59	2.779	2.122	1.886	3.772	5.558	137.0
13.56	2.784	2.119	1.880	3.760	5.568	136.3
14.89	2.775	2.110	1.865	3.731	5.550	133.8
15.74	2.774	2.109	1.865	3.731	5.548	133.8
18.66	2.769	2.103	1.872	3.744	5.538	134.5
20.26	2.767	2.095	1.866	3.732	5.534	133.5
21.84	2.764	2.092	1.866	3.732	5.528	133.5
23.82	2.760	2.100	1.869	3.737	5.520	133.5
25.32	2.759	2.102	1.867	3.734	5.518	133.3
27.95	2.757	2.111	1.871	3.742	5.514	133.7
36.23	2.725	2.111	1.865	3.730	5.450	133.6

In conclusion, the structural transition of nanosized  $\text{Gd}_2\text{O}_3$  was studied using high pressure energy dispersive XRD and PL. The original structure of the sample is a mixture of cubic and monoclinic. Our results show that the cubic and most of the monoclinic structure turns into hexagonal structure above 10.35 GPa. The hexagonal form is a stable phase above 10.35 GPa, but a small proportion of monoclinic structure can be present up to the highest pressure, 36.2 GPa. When the pressure is released, a proportion of the hexagonal structure can revert to monoclinic structure, so the sample shows a mixture of hexagonal and monoclinic structure. The structural transition from monoclinic to hexagonal is reversible. The result of the structural transition of  $\text{Gd}_2\text{O}_3$  may be helpful for revealing why monoclinic  $\text{Gd}_2\text{O}_3$  formed in the process of fabricating cubic  $\text{Gd}_2\text{O}_3$ , in particular for the nanosized sample, in which the surface tension may produce an additional pressure on the crystallites during the fabrication process, including a heat treatment, which is accompanied with a large alteration of the surface tension. So, for improving properties based on  $\text{Gd}_2\text{O}_3$  it is important to consider the tendency of turning into hexagonal structure and the possibility of monoclinic and hexagonal structures forming in the process of fabrication.

## Acknowledgments

This work was supported by the National Basic Research Program of China (Nos 2006CB601104, 2005CB724400), the Young Teacher Foundation of Jilin University, the Doctoral Foundation Research Project of the Ministry of Education (No 20030183027) and the National Natural Science Foundation of China (No 10374034).

## References

- [1] Bonnet G, Lachkar M, Larpin J P and Colson J C 1994 *Solid State Ion.* **72** 344
- [2] Bonnet G, Lachkar M, Larpin J P and Colson J C 1995 *Thin Solid Films* **261** 31
- [3] Hubbard K J and Schlom D G 1996 *Mater. Res.* **11** 2757
- [4] Coutures J P and Rand M H 1989 *Pure Appl. Chem.* **61** 1461
- [5] *Gmelin Handbuch der Anorganischen Chemie* 1974 8th edn, Syst. no. 39, Teil C1 (Berlin: Springer) p 151
- [6] Heitmann W 1973 *Appl. Opt.* **12** 394
- [7] Zych E 2001 *Opt. Mater.* **16** 445
- [8] Summers C J 1996 *IDW'96 Proc. (Nov. 1996)* vol 2, p 13
- [9] Vecht A 1996 *Extended Abstracts of 2nd Int. Conf. on the Science and Technology of Display Phosphors (San Diego, CA, Nov. 1996)* p 247
- [10] Sahoo N K, Thakur S, Senthilkumar M, Bhattacharyya D and Das N C 2003 *Thin Solid Films* **440** 155
- [11] García-Murillo A, Le Luyer C, Garapon C, Dujardin C, Bernstein E, Pedrini C and Mugnier J 2002 *Opt. Mater.* **19** 161
- [12] García-Murillo A, Le Luyer C, Dujardin C, Pedrini C and Mugnier J 2001 *Opt. Mater.* **16** 39
- [13] Hong M, Kwo J, Kortan A R, Mannaerts J P and Sergent A M 1999 *Science* **283** 1897
- [14] Sun L, Liao C and Yan C 2003 *J. Solid State Chem.* **171** 304
- [15] Flückiger T, Erbudak M, Hensch A, Weisskopf Y, Hong M and Kortan A R 2002 *Surf. Interface Anal.* **34** 441
- [16] Chen H *et al* 2006 *J. Colloid Interface Sci.* **297** 130
- [17] Liu J *et al* 2000 *Chin. J. High Pressure Phys.* **14** 247