Structural Transition of Gd_2O_3:Eu Induced by High Pressure *

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The structural transition of bulk and nano-size Gd_2O_3:Eu are studied by high pressure energy disperse x-ray diffraction (XRD) and high pressure photoluminescence. Our results show that in spite of different size of Gd_2O_3 particles, the cubic structure turns into a possible hexagonal one above 13.4 GPa. When the pressure is released, the sample reverses to the monoclinic structure. No cubic structure presents in the released samples. That is to say, the compression and relaxation of the sample leads to the cubic Gd_2O_3:Eu then turns into the monoclinic one.

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Gd_2O_3 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_2O_3 makes it a useful material in optics, e.g. antireflection coatings.[6] When doped with rare-earth ions (Eu^{3+},Tb^{3+}),[7−9] gadolinium oxide presents good luminescent properties. Gadolinium oxide optical thin films for ultraviolet laser[10] and x-ray imaging systems[11,12] have recently been reported. In recent years, researchers have found that cubic Gd_2O_3 can also effectively passivate the GaAs surface.[13] Crystalline Gd_2O_3 exists in cubic, monoclinic, or hexagonal phases. Most of the applications of Gd_2O_3 are based on its cubic structure. However, monoclinic[14] and hexagonal structure[15] can also form in the process of the fabrications.[16] Thus it is important to realize the structural transitions between the cubic, monoclinic and hexagonal structures. In this communication, high pressure structural transitions of Gd_2O_3 are studied by high pressure XRD and photoluminescence (PL).

Our experimental procedures were as follows. We prepared the $Gd(NO_3)_3$ solution by mixing 0.3625 g Gd_2O_3 (99.999%) and 0.0035 g Eu_2O_3 (99.999%) with 50 ml distilled water and adding appropriate HNO_3 to the mixture with proper stirring to form a clear solution. The solution was diluted to 100 ml by adding more distilled water. An additional 10 ml NaOH solution (0.6 M) was added into the solution. After being stirred for about 30 min, white precipitations, i.e. $Gd(OH)_3$, were separated out by centrifugation. They were washed by hot distilled water and were separated out by centrifugation again. After the precipitations are dried in air, they are heated to 1073 K and last for two hours. Pure nanosized cubic Gd_2O_3 (about 30 nm) are obtained.[16] Then we fabricate bulk cubic Gd_2O_3 by heating the above precipitation to 1273 K and last for two hours.

The experiment of high pressure is performed in Beijing. Energy-dispersive XRD and diamond anvil cavity (DAC) equipment are used to investigate the structural transitions of Gd_2O_3 under high pressure. The details of experimental equipment and method are reported in Ref. [17]. In our experiment, the diameter of anvil surface is 500 μm; the gasket is T301 iron plate, which is pressed at 10 GPa in advance; and the sample cavity is a Φ200 μm hole. The pressure of this cavity is marked by ruby. We obtain the energy-dispersive XRD spectrums under the x-ray radiation with the spot across size of 80 μm. The energy peak E and space distance d obey the energy-dispersive formula,

$$E \cdot d = 6.1993/\sin\theta\,(\mathrm{keV}\cdot\text{Å}),$$

where θ represents Bragg angle and $\theta = 8.27^\circ$ is taken.

Under the excitation of 488 nm, high pressure PL spectra of our samples are also obtained on the same DAC equipment with the pressure mark of ruby. The first sample we studied is bulk cubic Gd_2O_3. High pressure XRD spectra of bulk Gd_2O_3 are shown in Fig. 1. At the ambient pressure, the diffraction peaks present a cubic structure with lattice constant of 10.81 Å. The results of index are marked at the bottom of the graph. With the increasing pressure, the

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strong (222) peak clearly changes its intensity. When the pressure reaches 10.97 GPa, we can find that the peaks of cubic structure completely disappear. Three new strong peaks can be seen clearly. This indicates that a structural transition takes place. These three new peaks are broad due to the fact that the new phase is not well crystallized at the high pressure. The broad shape and small number of peaks make it hard to determine an unambiguous high pressure structure. However, considering the cubic Y_2O_3 turns into hexagonal structure at the high pressure,[18] we guess that the high pressure phase of Gd_2O_3 is also a hexagonal one. Based on these scanty peaks, we test many lattices and find that the (002), (102) and (110) diffractions of a possible hexagonal structure agree well with them up to the highest pressure of 33.70 GPa. The detailed data are shown in Table 1. Although the lattice of this possible hexagonal structure is not well refined for the above reasons, our results show that this possible hexagonal structure is the stable structural phase of Gd_2O_3 in the range between 10.97 to 33.70 GPa. In other words, the XRD spectrum of the bulk cubic Gd_2O_3 shows a structural transition from cubic to a possible hexagonal.

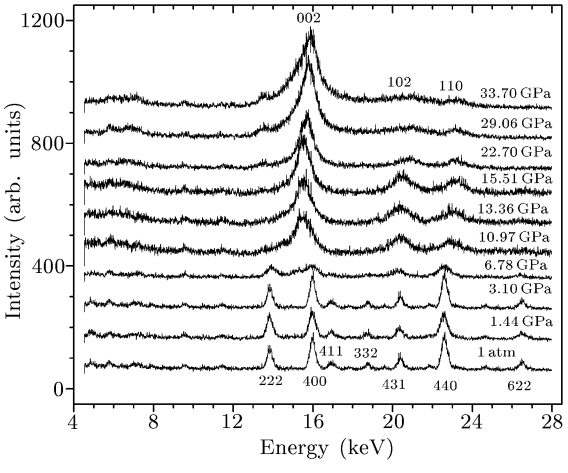


Fig. 1. High pressure XRD spectrum of bulk cubic Gd_2O_3.

Table 1. Detailed structure data of high pressure hexagonal Gd_2O_3.

Pressure (GPa)	d_{002}(Å)	d_{102}(Å)	d_{110}(Å)	a (Å)	c (Å)	V (Å^3)
6.78	2.816	2.123	1.908			
10.97	2.781	2.114	1.882	3.763	5.562	136.4
13.36	2.779	2.112	1.875	3.750	5.558	135.4
15.51	2.775	2.102	1.862	3.724	5.550	133.3
22.70	2.750	2.092	1.862	3.724	5.319	132.1
29.06	2.737	2.077	1.862	3.724	5.474	131.5
33.70	2.731	2.096	1.862	3.724	5.462	131.2

To know the effect of the size on the high pressure structural transition of Gd_2O_3, we also study the high pressure behaviour of nanosized pure cubic Gd_2O_3. High pressure XRD spectra of nanosized cubic Gd_2O_3 are shown in Fig. 2. At ambient pressure, the diffraction peaks show a cubic structure with lattice constant of 10.81 Å. The index results are marked at the bottom of the graph. We can find that, when the pressure reaches 14.07 GPa, the structure of Gd_2O_3 also transfers into the possible hexagonal one. Compared with the spectra of bulk Gd_2O_3, the (002) peak in the one of nanosized Gd_2O_3 has an additional strong shoulder. This shoulder covers 28–32 keV, which is in the range of peaks belonging to monoclinic Gd_2O_3.[16] Up to 32.32 GPa, which is the highest pressure in this experiment, the shoulder always exists and its height is almost the same as the (002) peak. This shows that a quite amount of monoclinic Gd_2O_3 exits in the nanosized sample under high pressure. This is different from the bulk sample. When the pressure is released, the spectrum presents a very broad peak, which may be a summation of diffraction peaks of monoclinic structure which is not well crystallized. In summary, this interesting phenomenon can be described as follows: at the released pressure, the high pressure hexagonal structure transits to the monoclinic structure which does not exist in the original sample.

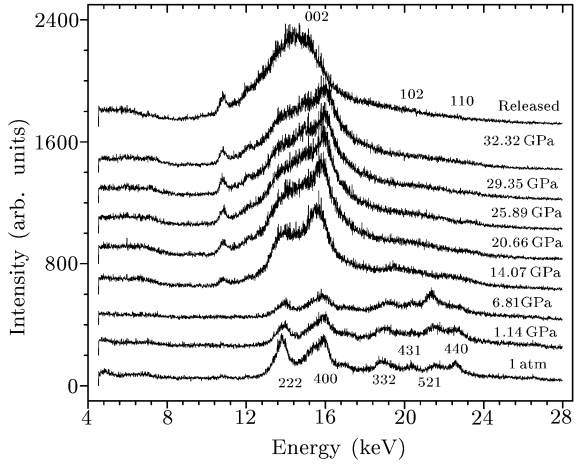


Fig. 2. High pressure XRD spectrum of nanosized cubic Gd_2O_3.

To confirm the above structural transitions of Gd_2O_3, we study the high pressure PL spectrum of Gd_2O_3:Eu nanoparticles. Figure 3 shows the high pressure PL spectrum of pure cubic Gd_2O_3:Eu nanoparticles. At pressure 1 atm, it shows a characteristic $4f-4f$ emission of Eu^{3+} in cubic Gd_2O_3 host. The strong peak at 610 nm is from the $5D_0 \rightarrow 7F_2$ transition of Eu^{3+} at the C_2 site. With the increasing pressure, its position and intensity change. In the range from 1 atm to 8.8 GPa, the position of this peak has a small red shift of 0.44 nm, and the intensity of this peak decreases slightly with the increasing

pressure. However, when the pressure is greater than 12.9 GPa, the intensity of the peak at 610 nm is almost zero and a broad peak at 630 nm emerges and starts to increase its intensity. This indicates that a structural transition takes place. From the XRD result of nanosized cubic Gd_2O_3 structural transition induced by high pressure, we know that the possible hexagonal is the dominant structure above this pressure. Thus we believe that the peak near 630 nm is from Eu^{3+} in the possible hexagonal host. This peak always has a high shoulder, which becomes ignorable only at the highest pressure of 26.8 GPa. When the pressure is released, two peaks at 613.5 nm and 620.7 nm can be clearly seen. They belong to the $5D_0 - 7F_2$ transition of Eu^{3+} in a monoclinic host.[16] This indicates that when the pressure is released, the high pressure hexagonal Gd_2O_3 transits to the monoclinic structure. This also clarifies the fact that in the course of increasing and releasing pressure, the shoulder of the peak near 630 nm is the emission peak of Eu^{3+} in monoclinic host. Thus, the result of high-pressure PL shows that the sample at high pressure is a mixture of the possible hexagonal and monoclinic structure. This is consistent with the high pressure XRD result of the nanosized cubic Gd_2O_3.

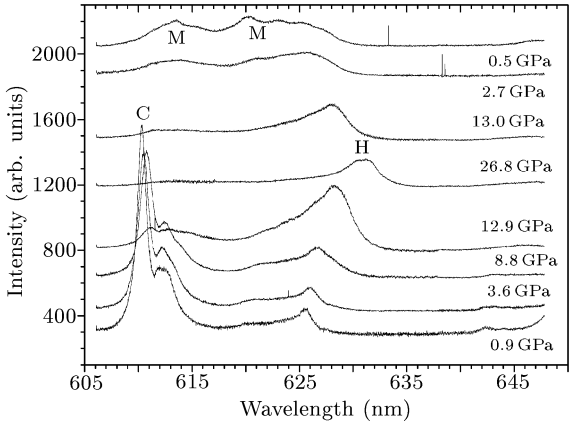


Fig. 3. High pressure PL spectrum of pure cubic Gd_2O_3:Eu nanoparticles.

In conclusion, we have studied the structural transitions of bulk and nanosized cubic Gd_2O_3:Eu by high pressure energy disperse XRD and PL. Our results show that in spite of different size of Gd_2O_3 particles, cubic structure turns into a possible hexagonal structure above 10.97 GPa. For the nanosized sample, besides the hexagonal structure, a small portion of monoclinic structure can present up to the highest pressure of 36.2 GPa. When the pressure is released, the possible hexagonal structure transits to the monoclinic structure. The structural transition from cubic to other structure is irreversible. The structural transition of Gd_2O_3 may be helpful to reveal the reason that monoclinic Gd_2O_3 formed in the process of fabricating cubic Gd_2O_3. Specially, for the nanosized sample, in which the surface tension may bring an additional pressure to the crystal during the fabrication process containing a heat treatment, which is companied with the large alteration of the surface tension. These indicate that for improving the property based on cubic Gd_2O_3 it is important to keep an eye on the pressure effect in the process of fabrication.

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