

Structural transition induced by the release of residual stress in the complex of cubic and monoclinic Gd₂O₃:Eu nanoparticles

Shiyong Gao^a, Hongliang Lu^a, Yanguang Nie^a, Haiyong Chen^{a,*}, Dan Xu, Quanqin Dai^a, Jiahua Zhang^{b,*}, Chunxiao Gao^a, Shihai Kan^a, Dongmei Li^a, Guangtian Zou^a

^a State Key Laboratory of Super hard materials, Jilin University, Changchun 130012, PR China

^b Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, PR China

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Abstract

The Photoluminescence (PL) spectra of Gd₂O₃:Eu composed of cubic and monoclinic structure were collected on November 2003 and June 2006, respectively. The results show that a portion of cubic Gd₂O₃ transforms into monoclinic after the sample was left as it is for two years; and the ⁵D₁–⁷F_j emission of Eu³⁺ in cubic host was enhanced in this released complex. Considering the high pressure behavior of Gd₂O₃, we think this structural transition is due to the sample that endures a process of press and release while the residual stress is released slowly.

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1. Introduction

Gd₂O₃ 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]. When doped with rare-earth ions (Eu³⁺, Tb³⁺) [5–7], gadolinium oxide presents good luminescent properties. Its optical thin films for ultraviolet laser [8] and X-ray imaging system [9,10] have recently been reported. In the recent years, the subject of nano-size particles has also been extensively studied and has become a research focus due to its fundamental and technological importance [11,12]. This is particularly true in the case of luminescent materials because of their quantum confinement effect, which leads to novel optoelectronic properties. For example, emission lifetime, luminescence quantum efficiency, and concentration quenching have been found to depend strongly on the particle size in the nanometer range [13–16]. During the fabrication of the

nanosized Gd₂O₃ particles, the complex composed of cubic and monoclinic structure formed [17]. In this letter, we introduce a result that a portion of cubic sample can transform into monoclinic structure after a long-term release of the residual stress.

2. Experimental

Our experimental procedures were as follows. We prepared the Gd(NO₃)₃ solution by mixing 0.3625 g Gd₂O₃ (99.999%) and 0.0035g Eu₂O₃ (99.999%) with 50 ml distilled water and adding appropriate HNO₃ to the mixture with proper stirring to form a clear solution. The solution was diluted to 100 ml by adding more distilled water. Then 3.3 g CTAB was added in it. When the solution became clear, an additional 10 ml NaOH solution (0.6 M) was added into it. 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 were dried in air, they were heated to 1073 K and lasted for 2 h. The products were nanosized Gd₂O₃ (about 30 nm) composed of cubic and monoclinic structure [17]. Then, the PL

* Corresponding authors. Tel.: +86 431 85168340; fax: +86 431 85166089.

E-mail addresses: chenhy@jlu.edu.cn (H. Chen), zjiahua@public.cc.jl.cn (J. Zhang).

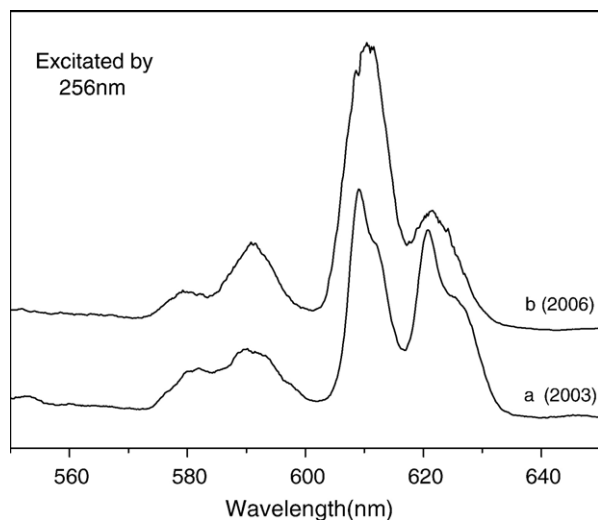


Fig. 1. The emission spectra of the $Gd_2O_3:Eu$ under the excitation of 256 nm.

spectra of this sample were collected in November 2003 and June 2006, respectively.

3. Results and discussion

The emission spectra of $Gd_2O_3:Eu$ composed of cubic and monoclinic structures are shown in Fig. 1. The curve *a* presents the spectrum collected in November 2003 and the curve *b* displays the one collected in June 2006. Under the excitation of 256 nm, they show characteristic 4f–4f emissions of Eu^{3+} in cubic and monoclinic Gd_2O_3 [17]. For the as synthesized sample (in 2003), the strong peak belonging to cubic $Gd_2O_3:Eu$ (610 nm) is clearly stronger than others. The strong peak at 613 nm, which belongs to monoclinic $Gd_2O_3:Eu$, is just like a shoulder of 610 nm emission. This indicates that cubic is the main structure in the sample at the earlier stage. For the sample after two years (in 2006), the emissions of cubic $Gd_2O_3:Eu$ reduced their intensity. Its strongest peak, which is at 610 nm, is covered up by the strong peak at 613 nm, which belongs to monoclinic $Gd_2O_3:Eu$. This indicates that a portion of cubic Gd_2O_3 transforms into monoclinic Gd_2O_3 after a long-term relaxation process.

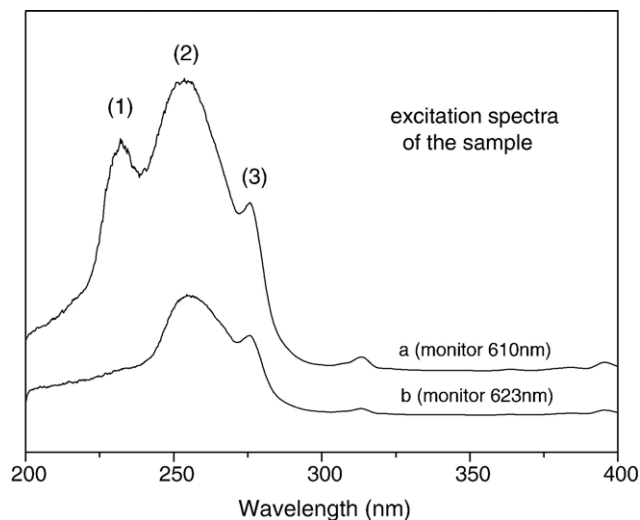


Fig. 2. The excitation spectra of the $Gd_2O_3:Eu$.

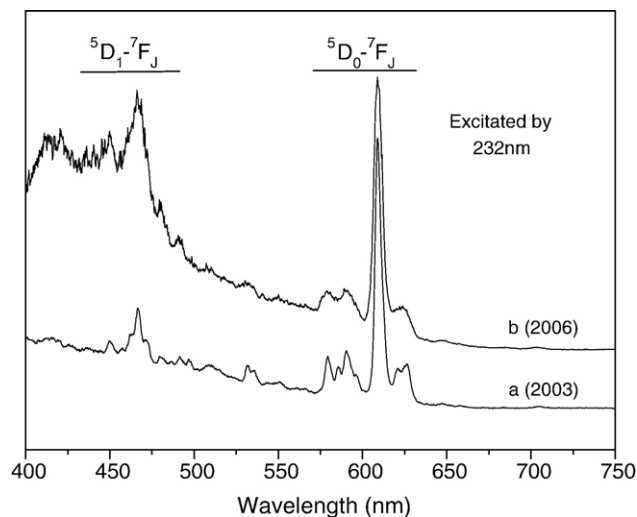


Fig. 3. The emission spectra of the $Gd_2O_3:Eu$ under the excitation of 232 nm.

Fig. 2 is the excitation spectrum of the sample. As shown in curve *a*, which is collected by monitoring the 610 nm emission according to Eu^{3+} in cubic host, we can see three kinds of excitation peaks. They were marked as (1), (2) and (3), where (1) is from the cubic host's absorption (232 nm); (2) is from the charge transfer state (CTS) absorption of $Eu-O$ (256 nm); and (3) is from the absorption of Gd^{3+} ions. For the excitation spectrum of Eu^{3+} in monoclinic host, we choose to monitor the strong peak at 623 nm due to its position that is clearly separate from the peak at 610 nm. As shown in curve *b*, we can only see two kinds of excitation peaks. They are from the CTS absorption of $Eu-O$ (256 nm) and the absorption of Gd^{3+} ions. So, our results show that in spite that the sample is a mixture, the emission from cubic host can be studied by the excitation of 232 nm.

When the sample was excited by 232 nm, according to the cubic host's absorption, cubic Gd_2O_3 host will be excited and monoclinic Gd_2O_3 host will be ineffective, leading to the appearance of mainly the characteristic emission of Eu^{3+} in cubic Gd_2O_3 . As shown in Fig. 3, curve *a* shows the spectrum collected in 2003. It presents normal characteristic emission of Eu^{3+} in cubic host, where the emission of ${}^5D_0-{}^7F_J$ is far stronger than the one of ${}^5D_1-{}^7F_J$. However, for the curve *b*, which shows the spectrum collected in 2006, the intensity of the ${}^5D_1-{}^7F_J$ emission increases and almost reaches to the one of the ${}^5D_0-{}^7F_J$ emission. So, our results show that, after a long-term relaxation process, the released complex enhanced the ${}^5D_1-{}^7F_J$ emission of Eu^{3+} in cubic host. This will be helpful to extend the application of $Gd_2O_3:Eu$ for displaying different color.

We explain the above structural transition as follows. Under high pressure, the structural transition of $Gd_2O_3:Eu$ shows that 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. The compress and relaxation of the sample lead to the cubic $Gd_2O_3:Eu$ turns into monoclinic one [18]. In this experiment, the residual stress is equivalent to a pressure on the nanosized crystallines. After a long-term relaxation, the residual stress is released slowly. This makes the sample endure a press-release process, resulting in a portion of cubic Gd_2O_3 transforms into monoclinic Gd_2O_3 .

4. Conclusion

In conclusion, during the fabrication of the nanosized Gd_2O_3 particles, the complex composed of cubic and monoclinic

structure is formed. The PL spectra of this sample were collected in November 2003 and June 2006, respectively. The results show that a portion of cubic Gd_2O_3 transforms into monoclinic after the sample was left as it is for two years; and the ${}^5\text{D}_1$ – ${}^7\text{F}_J$ emission of Eu^{3+} in cubic host was enhanced in this released complex. This will be helpful to extend the application of $\text{Gd}_2\text{O}_3:\text{Eu}$ for displaying different color. Considering the high pressure behavior of Gd_2O_3 , we think that this structural transition is due to the sample that endures a process of press and release while the residual stress is released slowly.

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References

- [1] G. Bonnet, M. Lachkar, J.P. Larpin, J.C. Colson, *Solid State Ionics* 72 (1994) 344.
- [2] G. Bonnet, M. Lachkar, J.P. Larpin, J.C. Colson, *Thin Solid Films* 261 (1995) 31.
- [3] K.J. Hubbard, D.G. Schlom, *Mater. Res.* 11 (1996) 2757.
- [4] J.P. Coutures, M.H. Rand, *Pure Appl. Chem.* 61 (1989) 1461.
- [5] E. Zych, *Opt. Mater.* 16 (2001) 445.
- [6] C.J. Summers, *IDW'96 Proceedings*, vol. 2, November 18–20, 1996, p. 13.
- [7] Aron Vecht, *Extended Abstracts of Second International Conference on the Science and Technology of Display Phosphors*, San Diego, CA November 18–20, 1996, p. 247.
- [8] N.K. Sahoo, S. Thakur, M. Senthilkumar, D. Bhattacharyya, N.C. Das, *Thin Solid Films* 440 (2003) 155.
- [9] A. García-Murillo, C. Le Luyer, C. Garapon, C. Dujardin, E. Bernstein, C. Pedrini, J. Mugnier, *Opt. Mater.* 19 (2002) 161.
- [10] A. García-Murillo, C. Le Luyer, C. Dujardin, C. Pedrini, J. Mugnier, *Opt. Mater.* 16 (2001) 39.
- [11] R.W. Siegel, E. Hu, D.M. Cox, H. Goronkin, L. Jelinski, C.C. Koch, M.C. Roco, D.T. Shaw, *WTEC Panel Report on Nanostructure Science and Technology*, International Technology Research Institute, 1998.
- [12] R.P. Andres, R.S. Averback, W.L. Brown, L.E. Brus, W.A. Goddard, A. Kaldor, S.G. Louie, M. Moscovits, P.S. Peercy, S.J. Riley, R.W. Siegel, F. Spaepen, Y. Wang, *J. Mater. Res.* 4 (1989) 704.
- [13] S. Sun, C.B. Murray, *J. Appl. Phys.* 85 (1999) 4325.
- [14] C. Suryanarayana, *Int. Mater. Rev.* 40 (1995) 41.
- [15] F.E. Kruis, H. Fissan, A. Peled, *J. Aerosol. Sci.* 29 (1998) 511.
- [16] T. Hase, T. Kano, E. Nakazawa, H. Yamamoto, *Adv. Electron. Electron. Phys.* 79 (1990) 271.
- [17] H.Y. Chen, J.H. Zhang, X.J. Wang, S.Y. Gao, M.Z. Zhang, Y.M. Ma, Q.Q. Dai, D.M. Li, S.H. Kan, G.T. Zou, *J. Colloid Interface Sci.* 297 (2006) 130.
- [18] H.Y. Chen, C.Y. He, C.X. Gao, J.H. Zhang, S.Y. Gao, H.L. Lu, Y.G. Nie, S.H. Kan, D.M. Li, G.T. Zou, *Chin. Phys. Lett.* 24 (2007) 158.