

Preparation and Site Selective Luminescence of Eu^{3+} in Triclinic GdBO_3 *

Zhang Weiwei^{ac}, Xie Pingbo^c, Zhang Weiping^{bc**},
Zhang Yunsheng^a, Lou Liren^c, Xia Shangda^c

(*a. Structure Research Laboratory, University of Science and
Technology of China, Academia Sinica, Hefei 230026;*

b. State Key Laboratory of Rare Earth Materials Chemistry and Application, Beijing 100081;

c. Department of Physics, University of Science and Technology of China, Hefei 230026)

Abstract Low-temperature phase of GdBO_3 with triclinic form was prepared by Sol-Gel process, while only pseudo-vaterite form could be obtained from the conventional solid state reaction. The triclinic form will change to pseudo-vaterite structure when being heated at higher than 1000°C . Luminescence of the triclinic $\text{GdBO}_3:\text{Eu}$ indicated the existence of two different sites of the cations in the host, which were denoted as A and B in the work. Then site selective luminescence of the sample was investigated. The influences of concentration and temperature on the luminescence properties were reported. For high Eu^{3+} concentration, a very strong interaction took place between the dopants. Emissions from the two sites were both strong and could not be separated. At low temperature and with a low concentration, selective luminescence from the two sites was obtained. Different energy transfer rates of site $\text{A}\rightarrow\text{B}$ and $\text{B}\rightarrow\text{A}$ were also observed.

Key words Sol-Gel technique, Triclinic GdBO_3 , Photoluminescence, Energy transfer, Phase transition

1 Introduction

The rare earth borates have high UV transparency and exceptional damage threshold. Orthoborates activated by some rare earth ions such as Eu^{3+} , Tb^{3+} have efficient visible emission under the excitation of UV or VUV light, making them quite attractive for fluorescent lamps and plasma display panels.

Nevertheless, most of the studies on the rare earth orthoborates have not clearly identified the crystallographic structure. For example, a vaterite form was given for YBO_3 in early work^[1], and revised as a pseudo-vaterite structure with two C_2 sites for Y^{3+} in 1997^[2]. While other authors gave the different symmetry as D_3 and D_{3d} ^[3], three D_3 sites^[4] or a unique C_1 site in a recent report^[5]. However, we haven't found the characteristic luminescence of all these candidate symmetries^[6]. In

* Project supported by the National Natural Science Foundation of China (19874058) and Anhui National Natural Science Foundation (00046106).

** To whom correspondence should be addressed, Email: wpzhang@ustc.edu.cn

Received date: 1999-09-23.

most cases, GdBO_3 and YBO_3 are homeomorphous. However, a triclinic L- GdBO_3 was reported recently by Corbel *et al.* [7]. In this work, we synthesized pure phase L- GdBO_3 by a simple Sol-Gel process, reported their optical properties and phase transition to the known YBO_3 -type GdBO_3 .

2 Experimental

The triclinic GdBO_3 :Eu was prepared by Sol-Gel (SG) process: analytical grade $\text{B}(\text{OC}_4\text{H}_9)_3$ and aqueous solution of the rare earth nitrates were mixed and stirred, ethyl alcohol was dropped into the mixture at the same time till a uniform clear solution was achieved. Warm it in a water-bath at 85°C for a period, the solution was hydrolyzed to sol and then to gel. Pre-heat the gel to get rid of alcohol and free water, then grind it to powder. At last, sinter the powder at a certain temperature to crystallize.

For comparison, a conventional solid-state reaction (SS) was also used: a mixture of the starting materials Y_2O_3 , Eu_2O_3 and H_3BO_3 with a chemical ratio was pre-heated at 500°C for 2h. Grind the powder, and sinter it at 1100°C for 3h.

Both products are white powders.

The crystal structure was analyzed by a MAC Science Co. Ltd. MXP18AHF X-ray diffraction apparatus with $\text{Cu K}\alpha$ radiation. The thermal analysis of phase transition was investigated using a Shimadzu DTA-50 analyzer. DTA measurements were carried out from room temperature to 1100°C at a heating rate of $10^\circ\text{C}/\text{min}$. The Raman spectrum was measured with a Spex-1403 laser Raman spectrometer at room temperature, with an argon ion laser of 514.5nm in the back-scattering configuration used as excitation source. A Hitachi H-850 fluorescence spectrophotometer was used to measure the excitation spectrum in UV-Vis region. The emission was analyzed using a Jobin-Yvon HRD1 monochromator and detected by a Hamamatsu R374 photomultiplier. The excitation light source was R6G dye laser pumped by an argon laser.

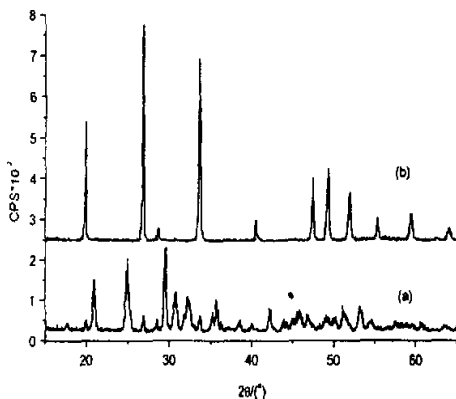


Fig. 1 XRD patterns of GdBO_3

- a. SG prepared triclinic form,
- b. YBO_3 -type by sintering (a) at 1100°C

3 Results and discussion

Crystal phase of the SG sample sintered at 900°C was examined by XRD pattern (Fig. 1 a). A fine crystallization could be obtained even at a low temperature 800°C . No phase transition was observed until 1000°C , confirming that the triclinic form [7] of this SG GdBO_3 is a low-temperature phase. Phase transition to the pseudo-vaterite form [6] occurs near 1046°C . The XRD pattern of such form is shown in Fig. 1b. A direct observation of the phase transition can be achieved from the DTA curve (Fig. 2). However, a pseudo-vaterite structured GdBO_3 could be directly

prepared by the SS reaction. Here lies great difference between our result and reference^[7] where no triclinic GdBO_3 was found during the process of the SS preparation (After pre-heating powder was used for the study). No phase transition from the pseudo-vaterite form to the triclinic one was observed, and results reported by Ren *et al.*^[5] was argued. The ambiguities are still being studied.

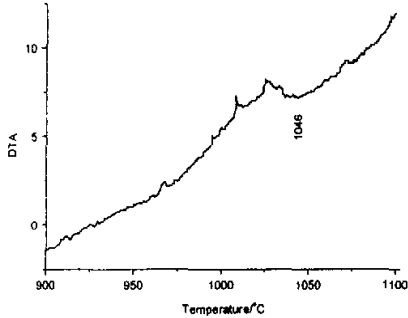


Fig. 2 DTA curve of the SG prepared GdBO_3

Vibration spectra could also give us messages about the crystal structure. In the Raman spectra (Fig. 3), peaks in the range of $240 \sim 1020\text{cm}^{-1}$ were due to the vibration of B, O bonds^[8]. The curves indicate that the form of B, O groups is greatly changed after the phase transition, which is consistent with the reference^[2,7], in which the existence of $[\text{BO}_4]$ and BO_3^{3-} groups in the crystal respectively have been declared.

It should be noted that the SG process of GdBO_3 is much different from that of YBO_3 . We have reported the properties of $\text{YBO}_3:\text{Eu}$ and YBO_3 -type $\text{GdBO}_3:\text{Eu}$ ^[6] when the former-mentioned SG and SS processes were carried out for preparing YBO_3 , both final products had the pseudo-vaterite form.

Luminescent study for Eu^{3+} doped triclinic phase GdBO_3 is important both for application and for structure investigation of the host; $\text{GdBO}_3:\text{Eu}$ is a promising PDP phosphor; the Eu^{3+} is a good structure probe for local symmetry. High luminescent intensity of $\text{GdBO}_3:\text{Eu}$ under an UV excitation was observed (Fig. 4). The strong excitation band centered at about 250 nm is due to the absorption of the charge transfer state of Eu-O. Compared with the SS sample, the CTS absorption peak shifts towards the red about 9 nm. This is consistent with

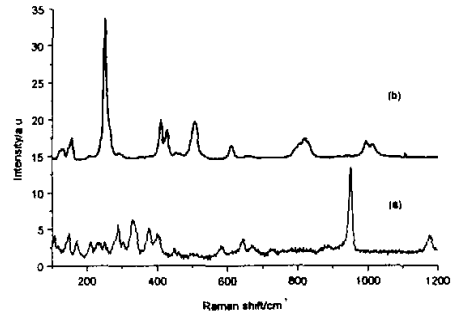


Fig. 3 Raman spectra of GdBO_3

- SG prepared triclinic form,
- YBO_3 -type by sintering (a) at 1100°C

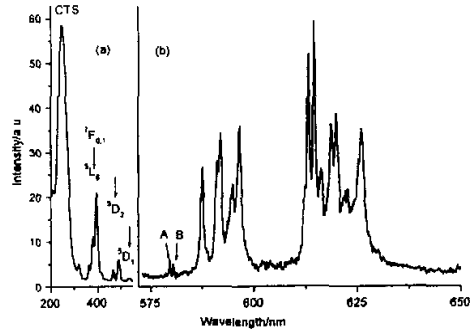


Fig. 4 Fluorescence spectra of triclinic $\text{Gd}_{0.95}\text{BO}_3:\text{Eu}_{0.05}$

at room temperature

- Excitation spectrum monitoring at 620 nm,
- emission spectrum under the excitation of 254 nm.

the reported results : two types of [YO_8] polyhedron with an average Y - O distance 0 . 2 3 7 nm in YBO_3 ^[2], and two [EuO_8] polyhedron with an average Eu - O distance 0 . 2 4 4 nm in triclinic $EuBO_3$ ^[7]. The CTS band position varies as a function of the host lattice. With increasing bond length the band shifts to lower energies^[9]. The other narrow peaks originate in the 4f - 4f absorption of Eu^{3+} , and have been denoted in Fig. 4a.

Under 254nm excitation from a Hg lamp, an efficient emission from the 5D_0 energy level of Eu^{3+} in a SG sample is observed (Fig. 4b). Here an equal excitation into Eu^{3+} occupying different Y^{3+} sites can be assumed since the excitation energy is transferred to the ions from the host material.

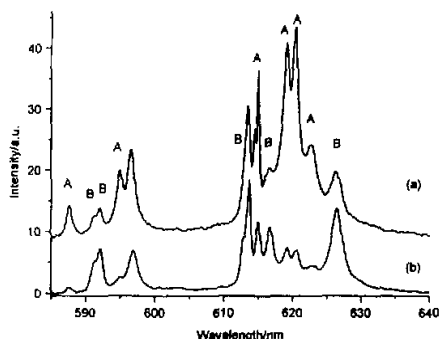


Fig. 5 Emission spectra after exciting into the 5D_0 level of Eu^{3+} at site A (a) and site B (b) at room temperature

In the figure, there are two $^5D_0 \rightarrow ^7F_0$ transition peaks denoted as A and B respectively, A at 579.6nm and B at 580.5nm, indicating there are two sites (also denoted as A and B) for the cations in the host crystal. Considering that the photon energies of $^7F_0 \rightarrow ^5D_0$ and $^5D_0 \rightarrow ^7F_0$ transition are exactly the same, selective excitation into the 5D_0 level of Eu^{3+} at site A and B (Fig. 5) were conducted. Though both patterns are similar to Fig. 4b, their relative intensities show strong dependence on the excitation condition.

For example, the strongest peak is at 620.4nm (a), while (b) peak at 613.6nm takes the first place. Transitions from the two sites here can be identified. See Fig. 5, transitions be-

longing to Eu^{3+} at site A and site B are denoted by symbol A and B respectively. The emission spectra are consistent with the structure analysis^[7], from which we can predict the total number of transition peaks as six $^5D_0 \rightarrow ^7F_1$ and eight $^5D_0 \rightarrow ^7F_2$ (5 and 8 are observed respectively in Fig. 5).

There exists efficient energy transfer between the two sites. And that explains why there is emission of site B(A) when we selectively excite the Eu^{3+} at site A(B). The energy transfer strongly depends on the dopant's concentration and the energy mismatch. Let us first investigate the fluorescence dependence on the concentration of Eu^{3+} .

Higher concentration leads to a shorter distance R of Eu-Eu, which can be estimated by

$$R = \left(\frac{3V}{4\pi x} \right)^{1/3} \quad (1)$$

where V is the cell volume, and x is the doping concentration.

Normally, a dipole-dipole interaction between Eu^{3+} , which has an energy transfer probability proportional to R^{-6} ^[10], is taken into account. When the concentration increases from 5% to 40%, the energy transfer probability increases 63 times. Stronger interaction causes efficient excitation into both sites. For the sample of 40% concentration, we even can't distinguish the two sites (Fig. 6).

For the triclinic sample, the energy mismatch of the 5D_0 level of Eu^{3+} at site A and B is

26cm⁻¹. Spatial transfer between them requires that the phonons make up the mismatch. As the mismatch is considerably large, it is enough to consider a one-phonon-assisted process. The process is affected by temperature, as shown in Fig. 7: with increasing temperature, the intensity of peak

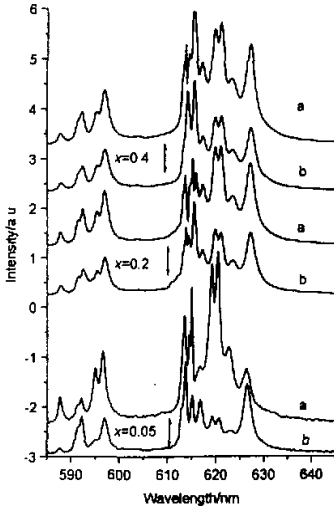


Fig. 6 Concentration dependence of the emission spectra of Cd_{1-x}BO₃:Eu_x at room temperature
a. selectively exciting the Eu³⁺ at site A,
b. selectively exciting the Eu³⁺ at site B.

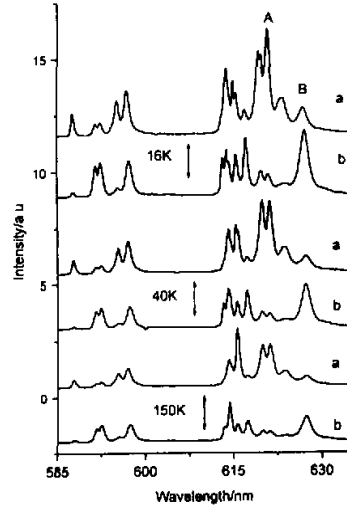


Fig. 7 Temperature dependence of the emission spectra of Gd_{0.95}BO₃:Eu_{0.05}
a: selectively exciting the Eu³⁺ at site A;
b: selectively exciting the Eu³⁺ at site B.

A(B) decreases under selective excitation of site A(B). It means that energy transfer rates of A→B and B→A are both being improved. At higher temperature, the emission spectra, no matter site A or B is excited, are more similar to Fig. 4b. In addition, one can also see a stronger energy transfer of A→B than that of B→A in Fig. 7. The transfer is described as^[11]

$$\omega_{A \rightarrow B} = \frac{J^2 (f-g)^2 |\Delta E_{AB}|}{\pi (h/2\pi)^4 \rho} \left(\sum_i \frac{\alpha_i}{\nu_i^5} \right) [n(|\Delta E_{AB}|) + 1] \quad (2)$$

$$\omega_{B \rightarrow A} = \frac{J^2 (f-g)^2 |\Delta E_{AB}|}{\pi (h/2\pi)^4 \rho} \left(\sum_i \frac{\alpha_i}{\nu_i^5} \right) [n(|\Delta E_{AB}|)] \quad (3)$$

where J is the matrix element of the site-site coupling Hamiltonian, which relies on the doping concentration; f/g is the ground-state/excited-state coupling strength for the ion at the site; ρ is the mass density, α_i is of order unity, and $n|\Delta E_{AB}| = [\exp(|\Delta E_{AB}|/kT) - 1]^{-1}$, which is a function of the temperature and the energy mismatch. Thus, we have

$$\begin{aligned} \frac{\omega_{A \rightarrow B}}{\omega_{B \rightarrow A}} &= \frac{n+1}{n} \\ &= \exp \frac{|\Delta E_{AB}|}{kT} \end{aligned} \quad (4)$$

At 16K, the ratio is about 9.9, while at room temperature (300K), the value is 1.13. Therefore the energy transfer of A→B is dominant at low temperature. While at room temperature, the transfer rates of A→B and B→A are both large and comparable. Consequently, the two emission spectra are getting more similar to each other.

4 Conclusions

We have carried out a survey of the influence of concentration and temperature on the luminescence properties of Eu^{3+} activated triclinic GdBO_3 . The energy transfer between Eu^{3+} in the two sites increases rapidly with concentration and temperature. At high concentration of 40%, we can't even separate the emission from the two sites. At low temperature, because of the directionality of the energy transfer, emissions from two sites are clearly identified and higher transfer rate of A→B than B→A is observed.

References

- [1] Holsa J. *Inorgan. Chem. Acta.*, 1987, **139**: 257
- [2] Chadeyron G, El-Ghozzi M, Mahiou R, Arbus A, Cousseins J C. *J. Solid State Chem.*, 1997, **128**: 261
- [3] Newnham R E, Redman M J, Santoro R P. *J. Am. Ceram. Soc.*, 1963, **46**: 253
- [4] Bradley W F, Graf D L, Roth R S. *Acta Crystallogr.*, 1966, **20**: 283
- [5] Ren M, Lin J H, Dong Y, Yang L Q, Su M Z. *Chem. Mater.*, 1999, **11**: 1576
- [6] Zhang W W, Xie P B, Zhang W P, Yin M, Jing L, Lu S Z, Lou L R, Xia S D. *Chin. J. Inorg. Mater.*, 2001, **16**: 9
- [7] Corbel G, Leblanc M, Antic-Fidancev E, Lemaitre-Blaise M, Krupa J C. *J. Alloys & Compound*, 1999, **287**: 71
- [8] Denning J H, Ross S D. *Spectrochim. Acta.*, 1972, **28A**: 1775
- [9] Hoefdraad H E. *J. Solid State Chem.*, 1975, **15**: 175
- [10] Dexter D L. *J. Chem. Phys.*, 1953, **21**: 836
- [11] Holstein T, Lyo S K, Orbach R; Excitation Transfer in Disordered Systems, in *Laser Spectroscopy of Solids*, Edit by Yen W M and Selzer P M, Topics in Applied Physics, Springer, Berlin, Heiderberg, New York, 1981, Vol. 49: 47

三斜相 $\text{GdBO}_3:\text{Eu}$ 的溶胶-凝胶法制备 及其格位选择激发下的光谱*

张巍巍^{a,c}, 谢平波^c, 张慰萍^{b,c**}, 张运生^a, 楼立人^c, 夏上达^c

(a. 中国科技大学结构与分析开放研究实验室, 合肥 230026)

(b. 稀土化学与应用国家重点实验室, 北京 100081)

(c. 中国科技大学物理系, 合肥 230026)

摘要: 用溶胶-凝胶法合成了具有三斜结构的低温相 GdBO_3 , 并与用常规的固相反应制备的类球方解石结构的样品作了比较。在高于 1000°C 时发生了三斜相向常规相的相变。三斜相 $\text{GdBO}_3:\text{Eu}$ 的荧光光谱表明阳离子在基质晶格中占据了两种格位, 用 A 和 B 来分别标明。选择激发 A、B 格位上 Eu^{3+} , 结果揭示了 GdBO_3 结构上的变化和 Eu^{3+} 之间的能量传递过程。在较高的 Eu^{3+} 掺杂浓度时, 两个格位均有较强的发光; 在低温和低浓度条件下, 得到了可分辨的相应于不同格位的发光, 并观察到了两个格位间不同几率的能量相互传递。

关键词: 溶胶-凝胶法; 三斜相 GdBO_3 ; 选择激发; 能量传递; 相变

中图分类号: O433.5⁺4 **文献标识码:** A

* 国家自然科学基金资助项目(19874058)、安徽省自然科学基金资助项目(00461006)。

** 通讯联系人, Email: wpzhang@ustc.edu.cn