

Effect of calcination temperature on the luminescent properties of Tb-doped borosilicate glasses

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The luminescent properties of Tb³⁺ have been studied for borosilicate glasses prepared by a sol-gel method. Gel bodies were formed from solutions consisting of silicon tetraethoxide, triethyl borate, ethanol, water and terbium nitrate, then sintered into a bulk glass. The Tb³⁺ luminescence in glasses mostly shows green light under UV excitation, because the emission line at 545 nm occupies the main part of the energy emitted. The observed luminescence consisted of four main emission lines originating from the ⁵D₄ level. However, a remarkable spectral change has been observed for the Tb³⁺ luminescence in borosilicate glasses after firing at about 800 °C. This spectral change due to heat treatment was found to be large enough to show yellow or red luminescence, suggesting that the crystal field acting on Tb³⁺ is very strong. The spectral energy distribution of Tb³⁺ luminescence in sol-gel derived borosilicate glasses were investigated in relation to the effects of calcination temperature. © 1999 Kluwer Academic Publishers

1. Introduction

Rare-earth (RE) doped materials are becoming more attractive for many applications, such as phosphors, lasers, scintillators, optical amplifiers, optical isolators, memories, and integrated optics [1, 2]. Sol-gel technology has a tremendous potential for fabrication of low-cost integrated optics and optoelectronic devices [3, 4]. A buildup of a single-phase glassy network at room temperature is one of the main advantages of sol-gel processing. Multicomponent sol-gel processing allows the preparation of a large number of materials, including ceramics and glasses doped with organic molecules. Transparent SiO₂, Al₂O₃, TiO₂, etc. matrices prepared by the sol-gel method are considered as excellent hosts for various dopants. Homogeneous borosilicate glasses were successfully obtained by the sol-gel method [5–9].

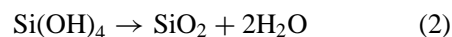
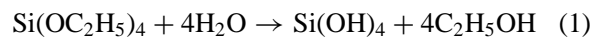
Terbium-activated phosphors are well known as excellent emitters of green light. The luminescence of Tb³⁺ under UV excitation is mainly due to the ⁵D₄ → ⁷F_{*j*} (*j* = 0, . . . , 6) transitions. In addition to these emission lines, a considerable contribution from the higher-level emission ⁵D₃ → ⁷F_{*j*} is often observed in the luminescence. The Tb³⁺ photoluminescence in most oxide glasses consists of four main emission lines around 490 (blue), 545 (green), 580 (yellow) and 620 (red) nm, which correspond to the ⁵D₄ → ⁷F_{*j*} (*j* = 6, . . . , 3) transitions. Since the emission due to the ⁵D₄ → ⁷F₅ transition (≈545 nm) mostly dominates over all other emissions, the Tb³⁺ luminescence usually appears green to the human eye. The color of luminescence is determined by the spectral energy distribution of the emitted light. The luminescence intensity is con-

sidered to be dependent on the host lattice through the crystal field due to the surrounding ions. It is known that the sol-gel derived glasses can easily change in their structures during firing. Therefore, the luminescence properties of Tb³⁺ in sol-gel glasses were expected to be affected by heat treatment.

In this work, remarkable spectral changes in the Tb³⁺ luminescence have been reported for the first time in borosilicate glasses. These spectral changes were found to be so large that the typical green luminescence of Tb³⁺ turned into yellow or red after calcinations at about 800 °C. The spectral change observed in the Tb³⁺-activated borosilicate glasses were studied in terms of the compositional changes using XPS analysis.

2. Experimental

Sol-gel technology is suitable for preparation of amorphous bulk, fibers and films [10, 11]. The initial stage of a sol-gel processing for a simple one-component silica glass is hydrolysis and polymerization of a silicon alkoxide, e.g., silicon tetraethoxide as in the following reactions.



These reactions are enhanced at low pH (≈1) in the formation of a gel body. Alcohol is usually added to facilitate miscibility between water and silicon tetraethoxide. A microporous gel-glass is formed by a complex sequence of polymerization, sol formation, gelation,

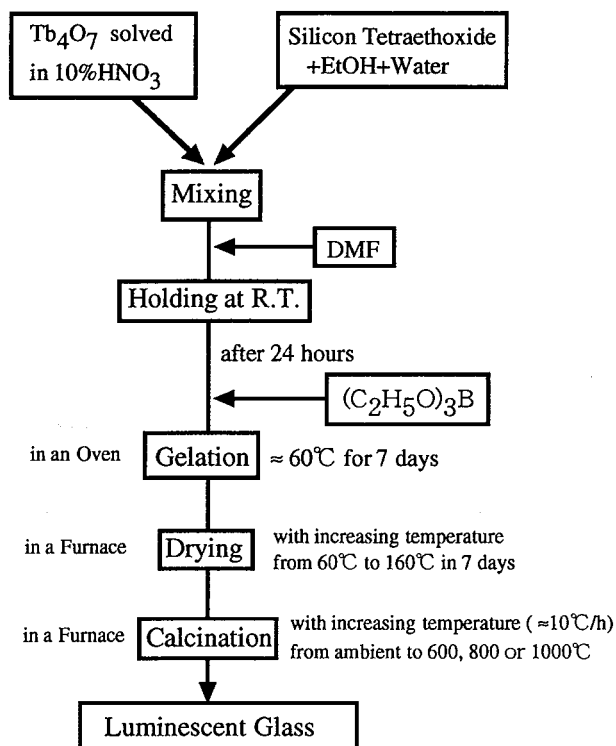


Figure 1 Flow diagram for the synthesis of Tb-doped $\text{SiO}_2\text{-B}_2\text{O}_3$ glasses by a sol-gel method.

and gel drying. The stress produced by the capillary forces associated with the gas-liquid surfaces often cause cracking in the gel body during drying. This gel body will sinter into a dense non-porous glass during firing at about 1000°C .

Preparation of multicomponent glasses from a mixture of alkoxides containing different metals is complicated by the different hydrolysis rates of different alkoxides. Terbium nitrate was chosen because of its solvability in water as a source of Tb^{3+} ions. Silicon tetraethoxide and triethyl borate were used as sources of SiO_2 and B_2O_3 , respectively. Fig. 1 shows the flow diagram for the synthesis of Tb^{3+} -doped $\text{SiO}_2\text{-B}_2\text{O}_3$ glasses by a sol-gel method. Our first composition targeting $83\text{SiO}_2\cdot 17\text{B}_2\text{O}_3\cdot 0.4\text{Tb}_2\text{O}_3$ (mol %) was prepared according to the following scheme: (1) mixing of 0.028 mol of silicon tetraethoxide with 0.03 mol of ethanol (EtOH), Tb nitrate in a minimal amount of water and dimethylformamide (DMF); the total amount of water was 0.6 mol; (2) holding the solution at room temperature for ≈ 24 h; (3) adding 0.012 mol of triethyl borate to the solution; and (4) holding the solution at $\approx 60^\circ\text{C}$ in an oven to form wet gel. After 2-3 days a transparent wet gel was formed. DMF was added as a drying control chemical additive (DCCA) [12] to the solution to avoid the gel cracking by modifying the surface tension of the interstitial liquid and the pore size of the gel. Preliminary partial hydrolysis of silicon tetraethoxide was expected to facilitate the eventual formation of a multication network by compensating its slow hydrolysis rate compared with that of triethyl borate. Silicate glasses doped with Tb^{3+} were also prepared along a procedure similar to that in Fig. 1, however, addition of ethyl borate to the precursor solution was skipped. From the precursor amounts, the silicate sample should have a composition of $99.6\text{SiO}_2\cdot 0.4\text{Tb}_2\text{O}_3$ (mol %).

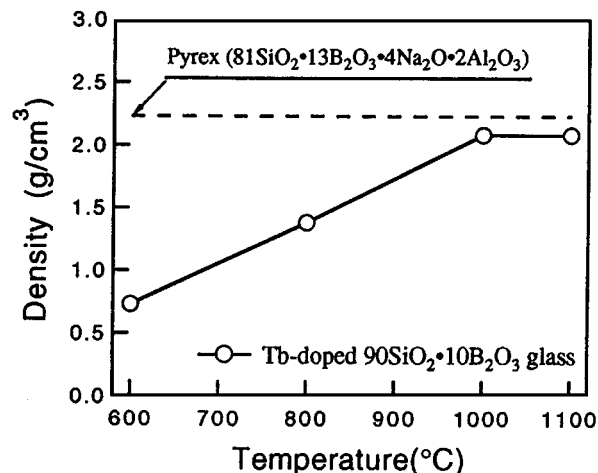


Figure 2 Density of sol-gel derived borosilicate glasses calcined at various temperatures.

The gels were dried and calcined in a furnace in air. The gel body shrank into about one-tenth in its volume of itself during drying and firing. Although DMF was added to the precursor solution, a careful heat treatment in the drying process was necessary to obtain a crack-free dried gel. The gel cracking was still the major problem with the samples at this stage. Firing at 600°C resulted in the formation of a transparent amorphous bulk. It was found that the luminescent and physical properties of the samples depended strongly on the calcination temperature. Fig. 2 shows the density of the sol-gel derived borosilicate samples as a function of the calcination temperature, compared with that of Pyrex at room temperature. An observed saturation in density for the samples calcined above 1000°C suggests that the sol-gel glasses fired lower than 1000°C are still porous in its microstructure. A similar dependence of the density on calcination temperature was observed for all sol-gel samples.

The atomic composition and the chemical state of atoms in the Tb-doped borosilicate luminescent glasses were analyzed by X-ray photoelectron spectroscopy (XPS). The XPS spectra measurements were taken using the monochromated AlK_α line (1486.6 eV) as X-ray source with an input power of 225 W. The pressure in the analysis chamber was maintained below 1×10^{-7} Pa. The binding energy scale was calculated vs. the Au $4f_{7/2}$ peak at 83.8 eV. A charge shift was observed for all samples because of their low electric conductivity and was corrected by the Au $4f_{7/2}$ peak from the small quantity of gold evaporated onto the sample. Signals from Si, B, C, O, and Tb were observed in a XPS spectrum ranging from 100 to 1250 eV for a Tb-doped borosilicate sample. Each XPS peak corresponding to the Si 2p, O 1s, Tb 3d_{5/2} and B 1s core levels of the sample are shown in Fig. 3. The results of the atomic composition and the chemical state obtained from core-level measurement are summarized in Table I.

3. Results and discussion

Fig. 4 shows energy diagram and main luminescence process of Tb^{3+} after the Dieke diagram. The luminescence of Tb^{3+} under UV excitation is mainly from the $^5\text{D}_3$ and $^5\text{D}_4$ levels [13, 14]. The emission

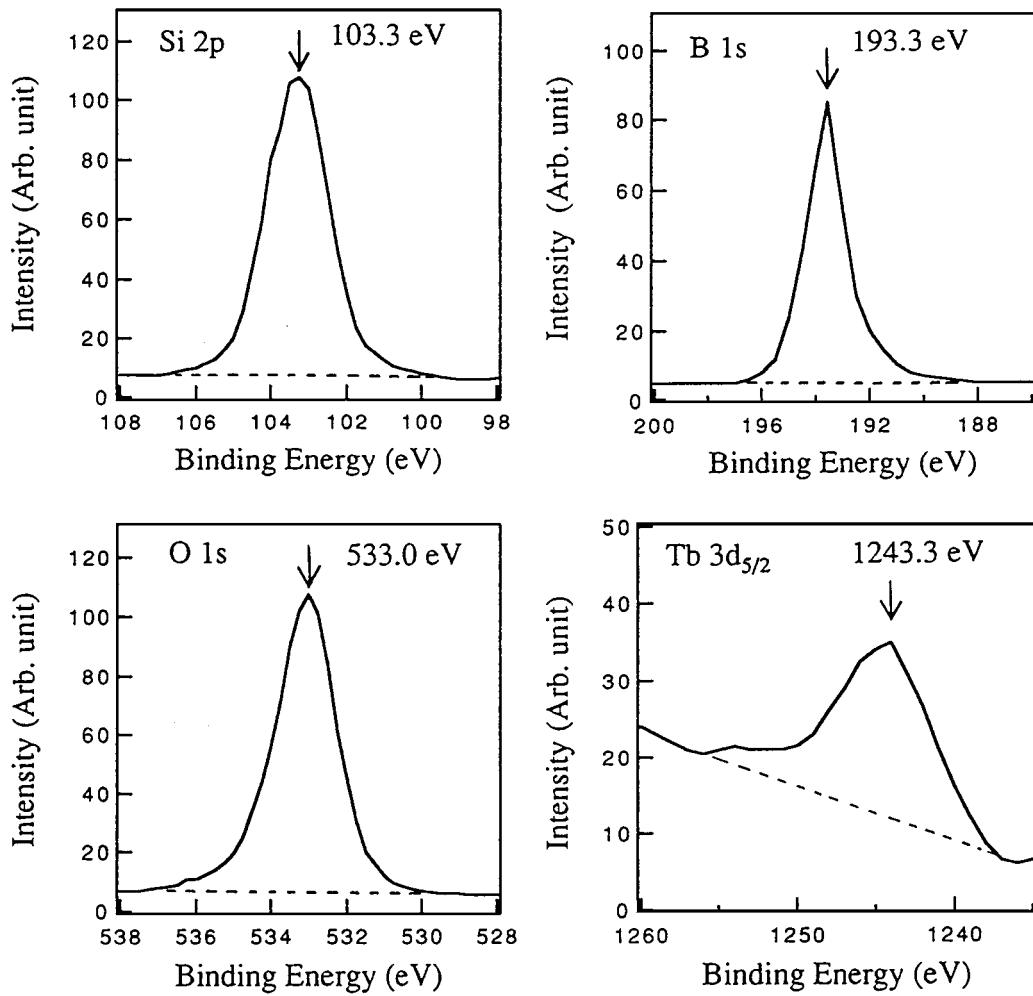


Figure 3 XPS spectra of Si, B, O and Tb in a SiO₂-B₂O₃:Tb sample.

TABLE I Elements and their oxides determined by the XPS analysis

Element	XPS Peak	XPS Peak Binding Energy (ev)	
		This Work	Reference ¹
Tb	Tb 3d _{5/2}	1243.3 ± 1	Tb ₂ O ₃ 1241.5
Si	Si 2p	103.3 ± 0.2	SiO ₂ 103.5 ± 0.2
B	B 1s	193.3 ± 0.2	B ₂ O ₃ 193.3
O	O 1s	533.0 ± 0.2	B ₂ O ₃ 533.0
			SiO ₂ 533. ± 0.3

¹Handbook of X-ray Photoelectron Spectroscopy, Perkin-Elmer, 1992

due to the $^5D_4 \rightarrow ^7F_5$ transition is usually so strong that almost phosphors activated with Tb³⁺ show green luminescence. The luminescence spectra were measured using a fluorospectrometer at room temperature. Fig. 5 shows the luminescence spectra of Tb³⁺ in 83SiO₂·17B₂O₃ and SiO₂ glass samples calcined at 600 °C for 5 h. Emissions corresponding to the $^5D_4 \rightarrow ^7F_j$ ($j = 6, 5, 4, 3$) transition were observed for these samples doped with 0.4 mol % Tb₂O₃. The emissions from the 5D_3 level were too weak to observe in our samples prepared by the sol-gel method, whereas the luminescence largely from the 5D_3 level was reported for Tb³⁺-doped glasses prepared by a traditional melting method when the concentration of Tb³⁺ is as low as 1 wt % [15]. In our sample with the

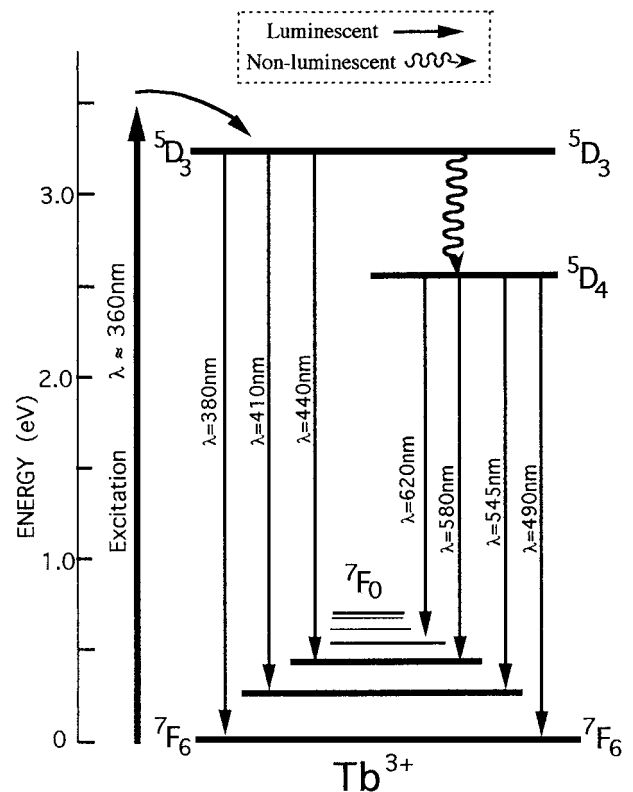


Figure 4 Energy diagram and main luminescence process of Tb³⁺.

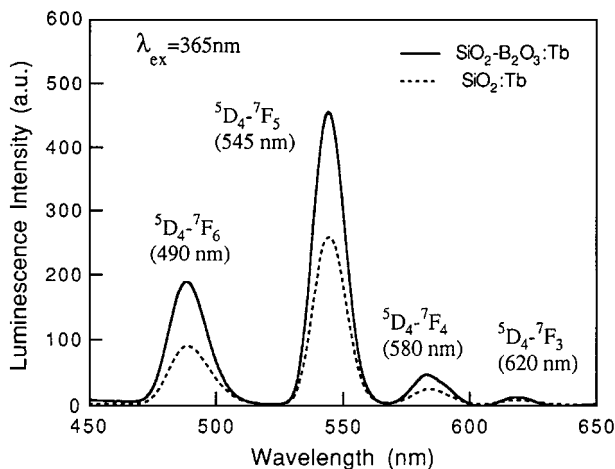


Figure 5 Photoluminescence spectra of Tb^{3+} in $83SiO_2 \cdot 17B_2O_3$ and SiO_2 samples calcined at $600^\circ C$ for 5 h.

composition $83SiO_2 \cdot 17B_2O_3 \cdot 0.4Tb_2O_3$, the concentration of Tb^{3+} is 0.6 wt %. This experimental result on sol-gel glasses suggested that the main part of the excitation energy was emitted as photons from the 5D_4 level. It should be noted, in the first place, that UV irradiation at $\lambda \approx 365$ nm excites the Tb^{3+} ions mostly to the 5D_3 level. Subsequently, the energy relaxation process from the 5D_3 level to the 5D_4 level was considered to be much more dominant than the radiative transitions from the 5D_4 level in sol-gel glasses. Therefore, there must be a sequence of internal relaxation processes from the higher energy level 5D_3 to the main emission level 5D_4 of Tb^{3+} in sol-gel glasses. It was also found that the Tb^{3+} luminescence in SiO_2 - B_2O_3 samples was twice as strong as that in SiO_2 samples. Similarly, the luminescence spectra of Tb^{3+} in borosilicate and silicate samples calcined at $800^\circ C$ for 5 h were measured. As shown in Fig. 6, the Tb^{3+} luminescence in the borosilicate sample was intensified during the calcination at $800^\circ C$, whereas that in the silicate sample remained. Moreover, the luminescent light of the borosilicate sample appeared to be yellow. The color of the radiation is determined by the spectral energy distribution of the emitted light. This luminescence color

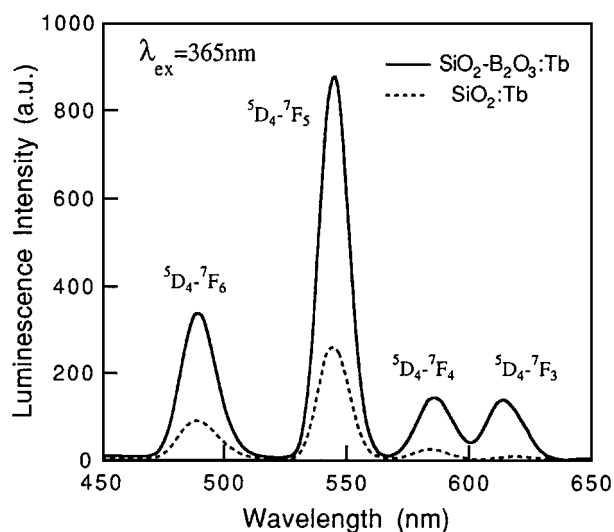


Figure 6 Photoluminescence spectra of Tb^{3+} in $83SiO_2 \cdot 17B_2O_3$ and SiO_2 samples calcined at $800^\circ C$ for 5 h.

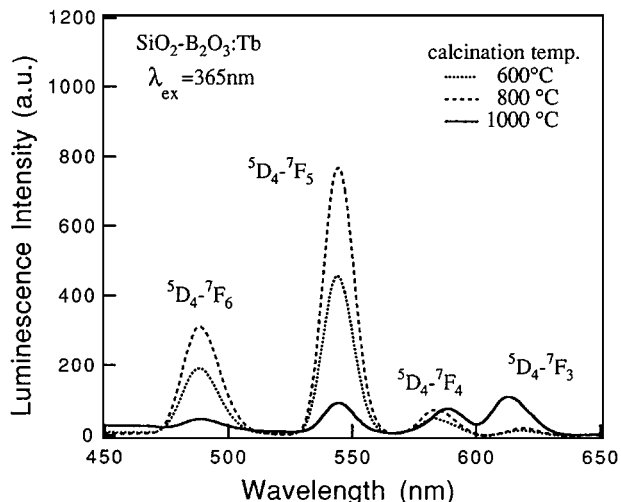


Figure 7 Photoluminescence spectra of Tb^{3+} in $83SiO_2 \cdot 17B_2O_3$ glasses calcined at various temperatures.

change from green to yellow is recognized as a result of an increased intensity of the emissions corresponding to the $^5D_4 \rightarrow ^7F_3$ and $^5D_4 \rightarrow ^7F_4$ transitions, while no considerable color change in luminescence was observed for the Tb^{3+} -doped silicate samples during firing.

To look into this spectral change further, the luminescence color and the relative intensities of main four emission lines of Tb^{3+} were examined for SiO_2 - B_2O_3 samples calcined at $1000^\circ C$. Fig. 7 shows the luminescence spectra of sol-gel borosilicate glasses doped with 0.4 mol % Tb_2O_3 calcined at 600, 800 and $1000^\circ C$ for 5 h. It can be seen from the spectral change in the figure that the emission due to the $^5D_4 \rightarrow ^7F_5$ transition reached its maximum for the sample calcined at $800^\circ C$ and that the emissions due to the $^5D_4 \rightarrow ^7F_3$ and $^5D_4 \rightarrow ^7F_4$ transitions increased with increasing calcination temperature. The color of the Tb^{3+} luminescence was found to be red for the sample calcined at $1000^\circ C$, whereas the intensity was reduced to about one-tenth of that of the sample calcined at $600^\circ C$. Thus the spectral change was large enough to cause a color change of the Tb^{3+} luminescence in sol-gel derived borosilicate glasses. Similar measurements were carried out on Eu^{3+} -activated glasses, however, no noticeable spectral change due to the heat treatment was found in the sol-gel borosilicate samples doped with Eu^{3+} ions.

Since there was no considerable change in the energy distribution of the Tb^{3+} luminescence for the sol-gel silicate samples after firings at various temperatures, boron was suggested to be a key element affecting the spectral change of the Tb^{3+} luminescence in borosilicate glasses. Accordingly, the atomic fractions of Si, B, O, and Tb in the samples with various compositions calcined at 600, 800 and $1000^\circ C$ were examined by using XPS analysis. Fig. 8 shows the dependence of the atomic fraction of the glass samples on the calcination temperature. It was found that boron content was reduced in the samples from $(OC_2H_5)_3B/Si(OC_2H_5)_4 = 0.42$ in precursor solutions, corresponding to a composition of $83SiO_2 \cdot 17B_2O_3 \cdot 0.4Tb_2O_3$, when they were calcined above $800^\circ C$. On the other hand, the atomic fraction changed very little in the samples from $(OC_2H_5)_3B/Si(OC_2H_5)_4 = 0.02$

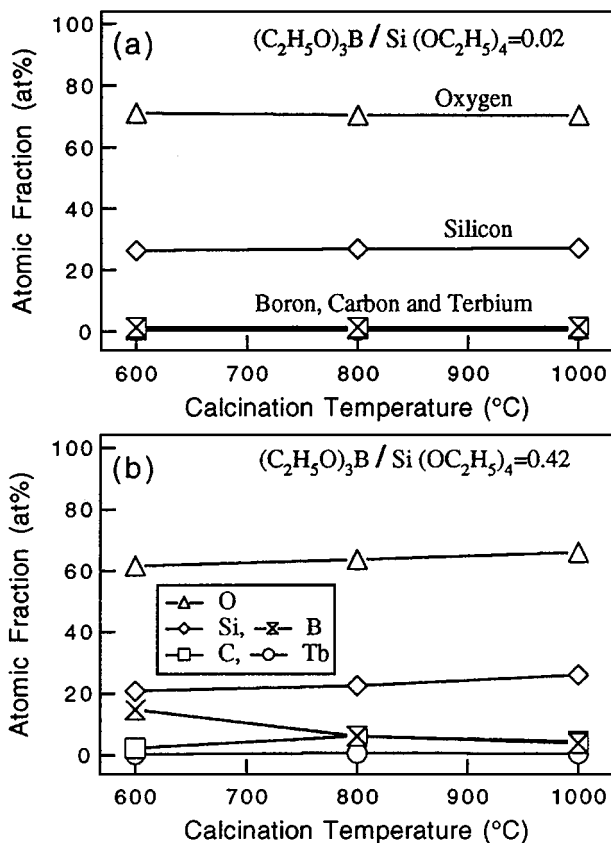


Figure 8 Dependence of the atomic fraction on the calcination temperature: (a) samples from $(OC_2H_5)_3B/Si(OC_2H_5)_4 = 0.02$ and (b) samples from $(OC_2H_5)_3B/Si(OC_2H_5)_4 = 0.42$ in precursor solutions.

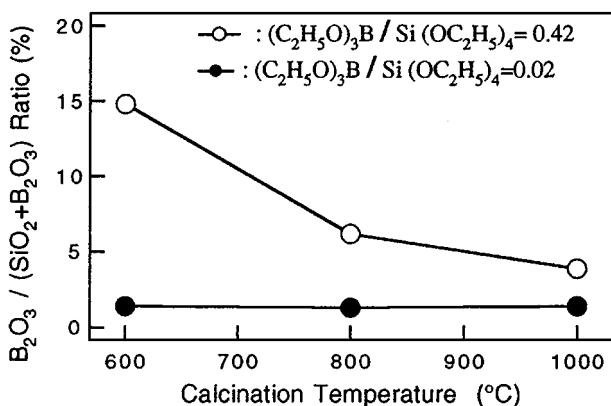


Figure 9 Dependence of the B_2O_3 fraction in the sol-gel $SiO_2-B_2O_3:Tb$ glasses on the calcination temperature.

solutions. These samples containing low concentration of B_2O_3 showed no noticeable color change in the Tb^{3+} luminescence after firings up to 1000 °C. Fig. 9 shows the B_2O_3 fraction determined by the XPS results on the $SiO_2-B_2O_3:Tb$ samples prepared from solutions consisting of silicon tetraethoxide, triethyl borate, EtOH, water and terbium nitrate. This result about the samples prepared from $(OC_2H_5)_3B/Si(OC_2H_5)_4 = 0.42$ in precursor solutions showed that the B_2O_3 fraction decreased from 15% for the sample calcined at 600 °C, to 7% for that calcined at 800 °C, then to 4% for that calcined at 1000 °C. The reduction of B_2O_3 fraction with increasing calcination temperature is considered

as a result of the volatilization of boron species during the heat treatment. Researchers [16–18] reported that the percentage of boron lost during processing increases as the concentration of boron in the precursor solution increases. Incorporation of boron into the glass structure for fired sol-gel derived borosilicate glasses is also suggested from the observation of $Si-O-B$ bonds in infrared spectroscopy [7, 19]. Arai and Terunuma [16] noticed the formation of boric acid and its eventual volatilization in borosilicate glass films fired to low temperatures (≈ 400 °C). Taylor *et al.* [19] reported a highest loss of boron during low temperature (≤ 500 °C) furnace firing and little loss during high-temperature (> 500 °C) firing. The volatilization of boric acid must be enhanced by the slow heating at 10 °C/h from ambient to its firing temperature in our experiment. The reaction of borosilicate glass to form boric acid is considered to be limited by the diffusion of water in the glass. Therefore, the significant boron loss would be brought by the porous characteristics of the glass samples and the slow heating in air.

The boron volatilization during firing will cause rearrangement of the network, phase separation or vacancies in borosilicate glasses. Since borosilicate glasses have a tendency of phase separation [20], firing at low temperatures would have induced silica-rich and boron-rich phases in the borosilicate samples. If such phase separation is the main factor affecting the Tb^{3+} luminescence, emissions coming from $SiO_2:Tb^{3+}$ and $B_2O_3:Tb^{3+}$ regions should be observed for fired borosilicate samples. Then we examined the spectral energy distribution of Tb^{3+} luminescence in B_2O_3 glasses. Fig. 10 shows the luminescence spectrum of Tb^{3+} in a $80B_2O_3 \cdot 20Na_2O_3$ glass prepared by a classical melting method fired at 800 °C. Judging from the energy partitioning into the $^5D_4 \rightarrow ^7F_3$ and $^5D_4 \rightarrow ^7F_4$ transitions, the emission spectrum was found to be similar to that for $SiO_2-B_2O_3:Tb^{3+}$ shown in Fig. 6, however, the Tb^{3+} luminescence in the $80B_2O_3 \cdot 20Na_2O_3$ glass appeared still green. One should note that the luminescence spectrum observed in the $80B_2O_3 \cdot 20Na_2O_3:Tb^{3+}$ glass is much different from that observed in the sol-gel derived $SiO_2-B_2O_3:Tb^{3+}$ sample fired to 1000 °C. Therefore the phase separation

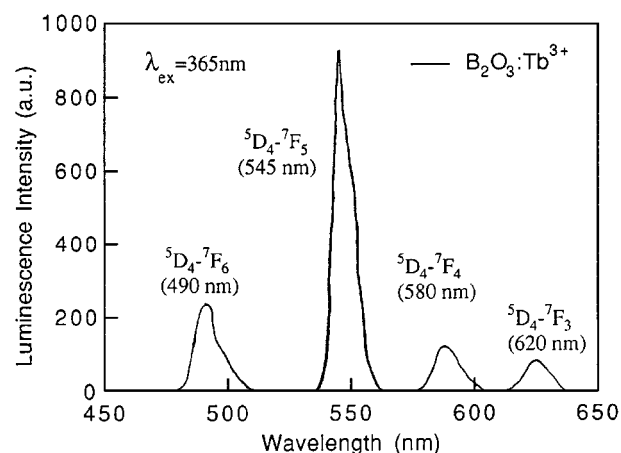


Figure 10 Photoluminescence spectrum of Tb^{3+} in a $80B_2O_3 \cdot 20Na_2O_3$ glass prepared by a classical melting method fired at 800 °C.

in Tb-doped borosilicate glasses cannot account for the significant spectral change in the Tb³⁺ luminescence.

The local environment of a RE ion can be estimated from its optical properties in the host material, because the optical radiation of RE ion is mainly due to the forced electric dipole transition induced by odd parity terms of the crystal field. Luminescent spectra and intensity of RE ions are strongly dependent on the symmetry and strength of crystal field by the surrounding ions. Spectral properties of some trivalent RE ions were satisfactorily explained [21–23] along the Judd-Ofelt [24, 25] approximation based on the crystal field theory. Kuboniwa and Hoshina [26] reported a good agreement between observed luminescence and calculation for Tb³⁺ in some oxides such as YPO₄, YBO₃ and ScBO₃. Their theoretical calculation showed that the ⁵D₄ → ⁷F₅ transition has the largest probability in the ⁵D₄ → ⁷F_{*j*} (*j* = 3, 4, 5, 6) transitions for all these matrices. The largest transition rate at ⁵D₄ → ⁷F₅ is expected for both the electric dipole and magnetic dipole transitions of Tb³⁺ in the metal ion site of the point group having center or no center of symmetry. It was also pointed out that the intensity of ⁵D₄ → ⁷F₃ transition can become comparable to that of ⁵D₄ → ⁷F₅ when the crystal field is very strong, where the Judd-Ofelt approximation may be inadequate. This theoretical prediction agrees well with our finding in Tb-doped borosilicate glasses; the ⁵D₄ → ⁷F₃ transition has intensity comparable to that of ⁵D₄ → ⁷F₅. Thus, the significant spectral change in the Tb³⁺ luminescence is well understood as a result of the strengthened crystal field.

According to the arguments above, the strengthened crystal field acting on Tb³⁺ rather than the phase separation is directly responsible for the change in luminescent properties of Tb-doped borosilicate glasses during firing. The volatilization of boron oxides is expected to modify the crystal field on Tb³⁺ in the borosilicate glasses. The local structure of borosilicate glasses would have adjusted after loss of boron species, although, the adjustment was found to be inadequate to account for the experimental results of the Tb³⁺ luminescence in sol-gel derived borosilicate glasses. Consequently, the defects due to the volatilization of boron oxides from the host glass, where the luminescent Tb³⁺ is embedded, was suggested to be a probable reason causing the remarkable change in luminescence.

4. Conclusions

The strong dependence of the luminescent properties of Tb³⁺ on heat treatment was found in borosilicate glasses prepared by the sol-gel method. The intensity of the Tb³⁺ luminescence increased with the calcination temperature up to 800 °C, but at 1000 °C a sharp decrease was observed in the sol-gel derived borosilicate samples. The color of the Tb³⁺ luminescence in sol-gel borosilicate samples showed a strong dependence on the calcination temperature. The dominant factor determining the luminescence color is the spectral energy distribution, which generally consists of four major emission lines around 490, 545, 580

and 620 nm for the Tb³⁺ luminescence. The spectral changes due to the heat treatments were found to be large enough to show green, yellow and red luminescence for the 83SiO₂·17B₂O₃·0.4Tb₂O₃ glass samples calcined at 600, 800 and 1000 °C, respectively. These spectral changes in the Tb³⁺ luminescence were suggested to be due to the boron loss and the generation of defects in borosilicate glasses. The sol-gel processing and the borosilicate network seemed essential for such large spectral changes in the Tb³⁺ luminescence. The unusual Tb³⁺ luminescence observed in this study corresponded to a case of strong crystal field. The detailed mechanism determining the ⁵D₄ → ⁷F_{*j*} transition rates is to be studied in terms of the crystal field acting on Tb³⁺ ions. The experimental observation of the spectral change shows a possible approach to control the luminescent properties of the RE ions.

References

1. MARVIN J. WEBER, *Ceramic Transactions* **67** (1995) 3.
2. G. BLASSE and B. C. GRABMAIER "Luminescent Materials" (Springer-Verlag, Berlin, 1990) p. 25.
3. Y. DJAOUED, VU HONG PHONG, S. BADILESCU, P. V. ASHRIT, F. E. GIROUARD and VO-VAN TROUNG, *Thin Solid Films* **293** (1984) 108.
4. C. ANDERSON and A. J. BARD, *J. Phys. Chem.* **99** (1995) 9882.
5. M. NOGAMI and Y. MORITA, *J. Non-Cryst. Solids* **48** (1982) 359.
6. B. KUMAR, *Mater. Res. Bull.* **19** (1984) 331.
7. A. D. IRWIN, J. S. HOLMGREN, T. W. WERDA and J. JONAS, *J. Non-Cryst. Solids* **89** (1987) 191.
8. N. TOHGE, A. MATSUDA and T. MINAMI, *J. Amer. Ceram. Soc.* **70** (1987) C-13.
9. N. TOHGE and T. MINAMI, *J. Non-Cryst. Solids* **112** (1989) 432.
10. H. DISLICH, *ibid.* **63** (1984) 237.
11. P. HINTZ and H. DISLICH, *ibid.* **82** (1986) 411.
12. L. L. HENCH, G. ORCEL and J. L. NOGUES, in "Better Ceramics Through Chemistry II," edited by C. J. Brinker, D. R. Ulrich and D. E. Clark (Materials Research Society, Pittsburgh, 1986) p. 35.
13. L. G. VAN UITERT and L. F. JOHNSON, *J. Chem. Phys.* **44** (1966) 3514.
14. E. NAKAZAWA and S. SHIONOYA, *ibid.* **47** (1967) 3211.
15. B. V. SHULGIN, K. N. R. TAILAOR, A. HOAKSEY and R. P. HUNT, *J. Phys. C: Solid State Phys.* **5** (1972) 1716.
16. E. ARAI and Y. TERUNUMA, *J. Electrochem. Soc.* **121** (1974) 676.
17. S. YAMANAKA, J. AKAGI and M. HATTORI, *J. Non-Cryst. Solids* **70** (1985) 279.
18. E. A. TAFT, *J. Electrochem. Soc.* **118** (1971) 1985.
19. D. J. TAYLOR, D. Z. DENT, D. N. BRASKI and B. D. FABES, *J. Mater. Res.* **11** (1996) 1870.
20. W. HALLER, D. H. BLACKBURN, F. E. WAGSTAFF and R. J. CHARLES, *J. Amer. Ceram. Soc.* **53** (1970) 34.
21. J. D. AXE, Jr., *J. Chem. Phys.* **39** (1963) 1154.
22. W. T. CARNALL, P. R. FIELDS and B. G. WYBOURNE, *ibid.* **42** (1965) 3797.
23. W. F. KRUPKE, *Phys. Rev.* **145** (1966) 325.
24. B. R. JUDD, *ibid.* **127** (1962) 750.
25. G. S. OFELT, *J. Chem. Phys.* **37** (1962) 511.
26. S. KUBONIWA and T. HOSHINA, *Jpn. J. Appl. Phys.* **32** (1972) 1059.

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