Colorless Transparent Fluorescence Material at the VUV Excitation: The Leached Sintered Glass with Impregnation of Tb^{3+} Ions

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First sample of VUV-excited intensely luminescent glass is successfully prepared using the leached sintered glass with impregnation of Tb^{3+} ions which is colorless, transparent and gives intense emission $^5D_4 \rightarrow {}^7F_5$ at 543 nm under the 160 nm VUV excitation.

Recently, the vacuum ultraviolet (VUV, $\lambda < 200$ nm) luminescent materials attract much interest because of the application in new Hg-free fluorescent lamps and plasma display panels (PDPs). Environmental considerations necessitate the researches of Hg-free fluorescent lamps that can be made by replacing Hg with a noble gas, such as Xe, as the discharge medium. A Hg discharge used in fluorescent lamps generates ultraviolet light (UV, mainly with the wavelength $\lambda = 254$ nm), while a Xe discharge emits VUV light with $\lambda = 172$ nm. VUV radiation is also utilized by PDPs where the plasma of xenon and neon is used as light source to excite phosphors deposited on special glass screens. With the goal of exploring efficient VUV-excited luminescent materials, the luminescent properties of rare earth ions in different hosts have been intensively investigated in recent years.[1–5] Oxide glass is an attractive host matrix for emission ions because it has excellent optical and mechanical properties, is very stable in chemistry, and can be easily manufactured. However, as far as VUV-excited luminescent materials are concerned, glasses are hardly used as hosts because of the strong absorption of the glass matrix in the VUV wavelength region. Particularly, the leached sintered glasses with impregnation of rare earth ions have been not reported as VUV-excited intensely luminescent material.

The preparation of Tb^{3+}-impregnated glasses is as follows: firstly the leached porous, nonsintered glass is prepared in a similar way to the process used in manufacturing Vycor glass, then the porous glass is immersed into the solutions of $TbCl_3$, finally the Tb^{3+} ion-impregnated glass is sintered to a compact glass. The details of preparation are described as below. Glass with the composition $7.7Na_2O\cdot4.0CaO\cdot2.7Al_2O_3\cdot0.6CeO_2\cdot33.3B_2O_3\cdot51.7SiO_2$ (wt %) was produced by two-step melting method. The mixed ingredients without H_3BO_3 were melted at 1550 °C for 3 h in a platinum crucible. The glass was broken down and ball-milled into small and even fragments. The required amount of H_3BO_3 was added and remelted at 1400 °C for 3–4 h. After that the glass was poured out and hand-pressed with a brozone plate. Phase separation of alkali borate and silicate was performed at 590 °C for 40 h. The obtained glass was cut into samples having a dimension of 10 × 10 × 1 mm and subsequently polished on both sides. The glass samples were leached in hot (90 °C) 1 M HNO_3 for 16–24 h. After washing with distilled water and drying, leached porous glass was obtained. Adsorption of Tb^{3+} ions was performed by immersing the porous glass into the solutions of $TbCl_3$ (0.05–1 M) for 1 h. At last, the Tb^{3+}-adsorbed glass samples were sintered at 1100 °C in air or reducing atmosphere (CO). The final products (the leached sintered glasses with impregnation of Tb^{3+} ions) are compact, colorless and transparent. Photoluminescence emission spectra were recorded in a home-made spectrophotometer under N_2 flow. The D_2 lamp peak at 160 nm was used for the VUV excitation.

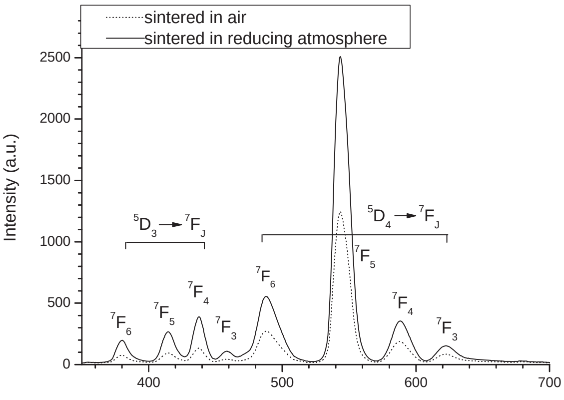

Figure 1. Emission spectra ($\lambda_{exc} = 160$ nm) of the Tb^{3+}-impregnated glasses when sintered in air and reducing atmosphere. 0.1 M solution of $TbCl_3$ is used.

Figure 1 illustrates the emission ($\lambda_{exc} = 160$ nm) spectra of the Tb^{3+}-impregnated glass samples when sintered in air and reducing atmosphere. The VUV-excited emission features of Tb^{3+} are clearly identified by the emissions of both samples mainly resulting from the transitions of $^5D_3$ and $^5D_4$ to ^7F_j. The emission bands located at 379, 414, 437, 460, 488, 543, 588, and 622 nm belong to the $^5D_3 \rightarrow {}^7F_j$, $^5D_4 \rightarrow {}^7F_j$ (j = 6, 5, 4, and 3) transitions, respectively. The observed low-energy $^5D_4 \rightarrow {}^7F_j$ transitions are in accord with those of Tb^{3+}-doped $BaBPO_5$ ($\lambda_{exc} = 172$ nm).[6] Under the VUV excitation at 160 nm, the Tb^{3+} ions ($4f^8$) would be excited to higher spin-allowed $4f^75d^1$ levels and subsequently relax to the $^5D_3$,$^5D_4$ excited states. As a consequence, emission bands of $^5D_3$,$^5D_4 \rightarrow {}^7F_j$ were observed in the range of 350 to 700 nm. Among them, the predominant one is $^5D_4 \rightarrow {}^7F_5$ transition peaking at 543 nm. The FWHM (full width at half maximum) of this emission peak is about 14 nm and the peak intensity is several times higher than other peaks; hence, the glass emits near pure green light. In the case of reducing treatment, a significant enhancement of PL intensity was observed. And the $^5D_4 \rightarrow {}^7F_5$ emission intensity is measured about 1/2 of that of the commercial phosphor $LaPO_4$:Ce,Tb under the same excitation. On the basis of the analysis of photoluminescence emission spectra of blank samples (without impregnation of Tb^{3+}), we obtained that traces of cerium were retained inside the silicate framework and more Ce^{3+} ions were produced by the reduction of Ce^{4+} during the reducing treatment. Thus, it was concluded that the increase of Ce^{3+} ions was mainly responsible for the enhancement of $^5D_3,^5D_4 \rightarrow {}^7F_j$ transitions from Tb^{3+} owing to energy-transfer channel. Ce^{3+} ions maybe act as a sensitiser as well as an activator.

For the Tb^{3+}-impregnated glasses, both samples show high optical transmittance (>85%) at wavelengths longer than 350 nm. Below 220 nm, the optical transmission decreases to almost zero because of the absorption by Ce^{3+}, Ce^{4+}, and Tb^{3+} (Figure 2, inset). Furthermore, we investigated the influence of concentration of $TbCl_3$ solutions that were used to immerse the leached porous glass samples. Figure 2 shows the emission spectra ($\lambda_{exc} = 160$ nm) of glass samples prepared from $TbCl_3$ solutions of different concentration. The emission intensity of $^5D_3,^5D_4$ to ^7F_j transitions were observed to increase with the solution concentration of $TbCl_3$ in the region below 0.1 M then turn to gradually decrease above 0.1 M owing to concentration quenching. Though the intensity of Tb emissions changed with the concentration of $TbCl_3$ solutions, the spectral energy distribution of Tb^{3+} emissions was hardly affected. Normalized PL emission intensity of the $^5D_4 \rightarrow {}^7F_5$ transition was plotted in Figure 3 against the concentration of $TbCl_3$ solutions. We also measured emission spectra (not shown) under UV excitation ($\lambda_{exc} = 231$ nm). An interesting fact was observed that the spectral energy distribution of Tb emissions strongly depended on the concentration of $TbCl_3$ solutions. With an increase of $TbCl_3$ concentration in the region below 0.1 M, the emission intensity of $^5D_3 \rightarrow {}^7F_j$ transitions decreases whereas the emission intensity of $^5D_4 \rightarrow {}^7F_j$ transitions increases. The observation that the high-energy level ($^5D_3 \rightarrow {}^7F_j$) emissions are quenched in favor of the lower-energy level emissions ($^5D_4 \rightarrow {}^7F_j$) is attributed to the cross-relaxation process between Tb^{3+} ions.[7–9] Above 0.1 M, all $^5D_3,^5D_4 \rightarrow {}^7F_j$ emissions gradually decrease in the intensity because of the concentration quenching in agreement with the results obtained under the VUV excitation. It has been known that the cross-relaxation process maybe occur as the follow: $Tb^{3+}(^5D_3) + Tb^{3+}(^7F_6) \rightarrow Tb^{3+}(^5D_4) + Tb^{3+}(^7F_0)$, where excitation from the $^7F_0$ to the $^7F_6$ level promotes the nonradiative drain from the $^5D_3$ to the $^5D_4$ level of a neighboring Tb^{3+} ion. The occurrence of this process depends on the interaction between two adjacent Tb^{3+} ions. In the case of VUV excitation, the phenomenon of cross-relaxation was not observed. Different excitation mechanisms are taken into account. The 231 nm UV light will directly excite Tb^{3+}, and result in the transitions from the lower energy level of the $4f^8$ configuration to the energy levels of the $4f^75d^1$ configuration of the Tb^{3+}. Subsequently the $^5D_3,^5D_4 \rightarrow {}^7F_5$ emissions are measured. In this case, absorption and emission processes involve only the Tb^{3+} (or/and Ce^{3+}) ions. However, when the Tb-impregnated glasses are excited at the wavelength of 160 nm, the excitation is absorbed first by the host and then transferred to Tb^{3+} ions, leading to an indirect excitation of Tb^{3+}. As to the VUV luminescence excitation mechanism, the details are still unclear for the Tb^{3+}-impregnated glasses because of its complexity.[1]

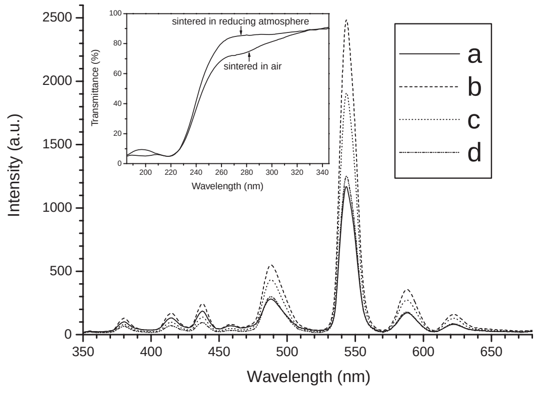

Figure 2. Emission spectra ($\lambda_{exc} = 160$ nm) of glass samples prepared from 0.05 M (a), 0.15 M (b), 0.5 M (c), and 1 M (d) of $TbCl_3$ solution. All samples were sintered in reducing atmosphere. The inset figure is the optical transmission spectra of the Tb^{3+}-impregnated glasses prepared from 0.1 M $TbCl_3$ solution.

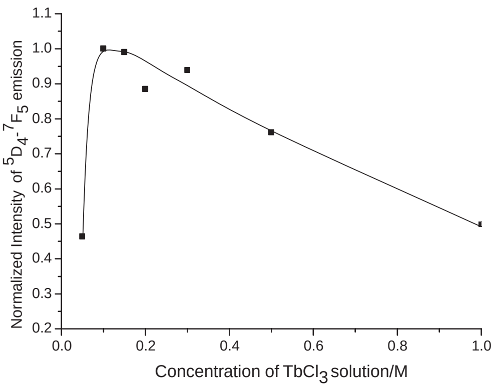

Figure 3. Normalized intensity of $^5D_4 \rightarrow {}^7F_5$ emission ($\lambda_{exc} = 160$ nm) vs concentration of $TbCl_3$ solution (M) for the Tb^{3+}-impregnated glasses when sintered in reducing atmosphere.

It was found that the leached sintered glass with impregnation of Tb^{3+} ions was an intense green emitter. To our knowledge, this is the first sample of the rare earth ion impregnated glasses which intensely emit at the VUV excitation. This work is very useful for application of the rare earth ions impregnated glasses in the VUV wavelength region.

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