Orange Emission of TbF_3-Containing Fluoride Oxide Glass

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A new fluoride oxide glass containing TbF_3 was prepared in the composition of $xTbF_3{\cdot}20BaF_2{\cdot}10AlF_3{\cdot}(70-x)GeO_2$ ($x = 10-40$). The temperature of melt was 1200 °C. The glass transition temperatures were 600–800 °C, depending on composition. Fluorescence spectra of the glasses were changed with Tb^{3+} concentration. The color of emission light changed from green to orange for $x = 10$-30 and from orange to green for $x = 30-40$.

Rare earth-containing glasses have been intensively studied because of their unique optical and magnetic properties.[1–6] There are a number of reports on the fluorescence and absorption spectra of Tb^{3+} in various host materials such as salts, glasses and crystals.[7–10] Tb^{3+}-containing materials usually give intense fluorescence in the green region.[7–10] This intense green emission is caused by $^5D_4 \rightarrow {}^7F_5$ transition.[7–10] It is also known that Tb^{3+} has a blue emission due to the $^5D_4 \rightarrow {}^7F_6$. The mixed valence state (Tb^{3+}/Tb^{4+}) is needed to achieve an orange emission.[11–14] This state is generally obtained by X-ray radiation to some glasses containing Tb^{3+} because the oxidizing melting condition for Tb^{3+} seems to be very difficult.

In this study, a new fluoride oxide glass with a large Tb^{3+} content around 30 wt% was prepared. This glass contains both oxide and fluoride ions. The change in the fluorescence spectra is shown. Some of the samples in this study exhibited the orange fluorescence emission without X-ray irradiation. No alternative method for preparing glass with the (Tb^{3+}/Tb^{4+}) mixed valence state except for X-ray irradiation treatment has been found yet.

TbF_3 (4N, Shin-Etsu Chemical Co. Ltd.), AlF_3 (99.9% up, Nakarai Chemical Co. Ltd.), BaF_2 (99% up, Koujyunndo Chemical. Co.Ltd) and GeO_2(5N, Mitsuwa Chemical Co. Ltd.) were used as starting materials. The starting materials were thoroughly mixed in Ar atmosphere with alumina mortar and pestle. The mixture was dried under dynamic vacuum (less than 2.6×10^{-1} Pa) for at least 12 h at 120 °C. Then the mixture was packed in a platinum boat and set in an electric furnace filled with argon. The mixture was heated to 1200 °C at a heating rate of 8 °C min^{-1} and held for 1.5 h. The melt was quenched on molecular sieves cooled with liquid nitrogen. The cooling rate was approximately 120 °C s^{-1}.

The products were characterized by optical microscopic observation (Nikon Optiphoto-2) and X-ray powder diffraction measurements (XRD; Shimadzu XD-3A, 30 kV, 20 mA, Cu Kα). Fluorescence spectra of the glasses were measured with a Hitachi Fluorescence Spectrophotometer 850. The light source was an Xe lamp. The excitation wavelength was 366 nm. Glass transition temperature was measured by differential thermal analysis (DTA; SII TG/DTA 32). Glass products were obtained in the $x = 10$–40 in $xTbF_3{\cdot}20BaF_2{\cdot}10AlF_3{\cdot}(70-x)GeO_2$ compositions. Glass formation was judged by the transparency in observation by an optical microscope and the detection of no sharp peak in XRD pattern. EPMA measurements revealed that a small amount of fluorine in the starting mixture was lost by pyrohydrolysis during melting. A change in cation composition was so small that it was very difficult to detect it. Ge vaporized from the melt as GeF_4 since very small amount of germanium compounds were found at the cold part of furnace after melting. The glass transition temperature of $30TbF_3{\cdot}20BaF_2{\cdot}10AlF_3{\cdot}40GeO_2$ was 700 °C.

Figure 1 shows the fluorescence spectra of $xTbF_3{\cdot}20BaF_2{\cdot}10AlF_3{\cdot}(70-x)GeO_2$ glasses ($x = 10$ and 30) melted at 1200 °C. The peak positions, relative peak height, and transition assignments for the glasses are listed in Table 1. In the case of $x = 10$, the fluorescence spectra exhibited a typical profile for compounds containing Tb^{3+}. The color of the emission light was green, as reported in the literatures.[6–9] In the case of $x = 30$, on the other hand, the color of the emission light was yellow-orange and the fluorescence spectrum exhibits very different profile from typical one. Generally it has been reported that Tb^{3+} gives intense fluorescence in the green region when it presents in a salt or glass matrix.[6–9]

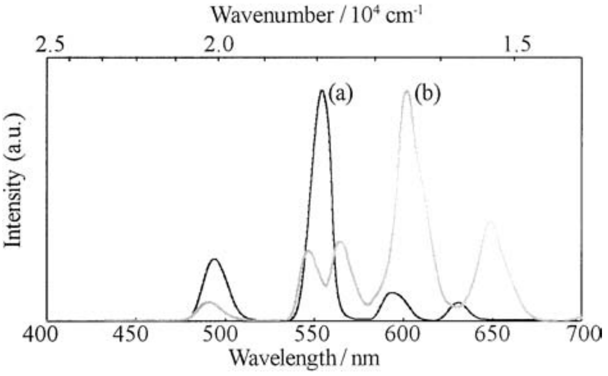

Figure 1. Fluorescence spectra of (a) $10TbF_3{\cdot}20BaF_2{\cdot}10AlF_3{\cdot}60GeO_2$ and (b) $30TbF_3{\cdot}20BaF_2{\cdot}10AlF_3{\cdot}40GeO_2$ glasses.

Table 1. Peak positions, relative peak-heights, and transition assignments of fluorescence of $xTbF_3{\cdot}20BaF_2{\cdot}10AlF_3{\cdot}(70-x)GeO_2$ glasses ($x = 10$ and 30)

Assignment	$x = 10$		$x = 30$	
	λ/nm	I/I_{max}	λ/nm	I/I_{max}
$^5D_4 \rightarrow {}^7F_6$	494	30	491	9
$^5D_4 \rightarrow {}^7F_5$	549	53	547	37
	556	100	565	15
$^5D_4 \rightarrow {}^7F_4$	591	11	588	100
	599	8	601	54
$^5D_4 \rightarrow {}^7F_3$	629	5	610	49
$^5D_4 \rightarrow {}^7F_2$	632	4	648	49
$^5D_4 \rightarrow {}^7F_1$	662	0	662	7

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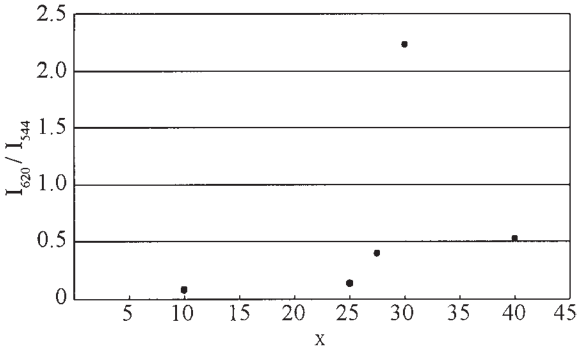

Figure 2. A change in the intensity ratio of the peaks at 620 ($^5D_4 \rightarrow {}^7F_3$) and 544 ($^5D_4 \rightarrow {}^7F_5$) nm, $I_{620/544}$ with x value of $xTbF_3 \cdot 20BaF_2 \cdot 10AlF_3 \cdot (70 - x)GeO_2$.

Figure 2 shows a change in the intensity ratio of the peaks at 620 ($^5D_4 \rightarrow {}^7F_3$) and 544 ($^5D_4 \rightarrow {}^7F_5$) nm, $I_{620/544}$, with x value. In $x = 20 - 30$, the value of $I_{620/544}$ increased and the peak at 620 nm became the most intense at $x = 30$. $I_{620/544}$ value decreased at $x > 30$ and almost zero at $x > 40$. There have been a few reports in which orange emission is observed for terbium-containing glasses.[11–14] It has been reported that X-ray irradiation to the terbium-containing glasses gives orange emission because Tb^{4+} is generated in the glasses. The preparation of Tb^{4+}-containing glass is very difficult by a simple cooling method of a melt. Stabilization of Tb^{4+} has been very difficult in the known melts. The melts in this study have a possibility to be used for stabilizing Tb^{4+} in them. The electron acceptance ability of high valence ions favors charge transfer transitions from surrounding ions to the rare-earth ions. By the way, the emission light of the crystallized sample with $x = 60$ was also orange. It has been hard to interpret the relationship between the color of the emission light and the terbium content. However, the fluorescence of these glasses would be influenced by the glass networking structure with both oxide and fluoride ions constructed in the melt. Structural analysis and magnetic measurements will provide some informations about the present results.

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