Efforts of Gd^{3+}-Tb^{3+} energy transfer and Luminescence properties of Terbium-activated fluoride oxide tellurite glasses

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Tb-activated fluoride oxide tellurite glasses were synthesized by high-temperature melting method. The effects on the density, transmission, lifetimes and luminescence properties under UV and X-ray were investigated and the energy transfer mechanisms between Gd^{3+} and Tb^{3+} analyzed and discussed. These glass scintillators have a unique combination of properties including high scintillating light output, high density. The results also show that, with increasing concentrations of Tb^{3+} and Gd^{3+}, a monotonic increase in the energy transfer efficiencies from Gd^{3+} to Tb^{3+} is observed followed by enhance emission centered under UV and X-ray excitation.

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1. Introduction

Scintillating glasses are promising alternatives to single crystals and ceramic scintillators for applications in high energy physics and in X-CT for industrial and medical imaging. The main advantages of scintillating glasses [1] lie in the possibility of low-cost production, in the ease of manufacture for different sizes and shapes, such as fibers [2,3], and the glasses composition of matrix could adjust at a broad arrangement. Compared with crystal[4], scintillating glasses have some disadvantages, such as low transfer efficiency, low density and low light yield. However, density and light yield are two important features for scintillators in some applications.

Tellurite glasses have high density and low phonon energy, the luminescence properties have been reported in some papers [5,6,7,8]. In this work, Tb-activated fluoride oxide tellurite glasses with different concentration of rare-earth ions were prepared. The density, transmission and luminescence properties under X-Ray and UV excitation have been investigated.

A variety of scintillating glasses with high density and high scintillating light output have been reported, but the comprehensive performance of scintillators, especially in the scintillation light output, is not very satisfactory and needs further improvement.

2. Experiment

Compositions of as-studied glasses are shown in Table.1, They were prepared using high purity (99.9%) TeO_2, PbF_2, BaF_2, Gd_2O_3 as starting materials while Tb^{3+} ions were introduced from reagent grade Tb_4O_7. Then, they were carefully mixed in appropriate proportions and 20g batches were placed in alumina crucibles at 900 ^oC for 25 min. The melts were constantly poured onto a preheated stainless-steel plate and pressed into the glasses with 7 mm thickness, then annealed at 300 ^oC for 2 h followed by cooling in the furnace at its natural cooling rate. The glass were cut and polished to 4 mm thickness for various spectroscopic measurements.

Table.1. Composition and density of the Glass

Serial number	Glass Name	Glass composition(mol %)	Density(g/cm^3)
1	TPBT1	$74TeO_2$-$15PbF_2$-$10BaF_2$-$1Tb_2O_3$	5.18
2	TPBT2	$73TeO_2$-$15PbF_2$-$10BaF_2$-$2Tb_2O_3$	5.20
3	TPBT3	$70TeO_2$-$15PbF_2$-$10BaF_2$-$5Tb_2O_3$	5.27
4	TPBT4	$67TeO_2$-$15PbF_2$-$10BaF_2$-$8Tb2O_3$	5.36
5	TPBTG1	$72TeO_2$.$15PbF_2$-$10BaF_2$-$1Tb_2O_3$-$2Gd_2O_3$	5.51
6	TPBTG2	$70TeO_2$-$15PbF_2$-$10BaF_2$-$1Tb_2O_3$-$4Gd_2O_3$	5.72
7	TPBTG3	$68TeO_2$-$15PbF_2$-$10BaF_2$-$1Tb_2O_3$-$6Gd_2O_3$	5.93
8	TPBTG4	$69TeO_2$.$15PbF_2$-$10BaF_2$-$2Tb_2O_3$-$4Gd_2O_3$	5.97
9	TPBTG5	$66TeO_2$.$15PbF_2$-$10BaF_2$-$5Tb_2O_3$-$4Gd_2O_3$	6.05

Density was measured by Archimedes method. Ultraviolet/Visible transmission spectra were measured by Perkin-Elmer Lamda35 spectrometer. Excitation and emission spectra under UV excitation was measured by Hitachi F-4500 spectrometer. The scintillation light output was measured using an 80 KeV/c X-ray beam (made in Shanghai Institute of Ceramic, Chinese Academy of Sciences, China). All the above measurements were performed at room temperature.

3. Results and discussion

3.1 Density of various samples

The density of different samples are also shown in the Table.1. As expected, all samples have a density over 5g/cm^3. Particularly, the density of TPBTG5 is up to 6 g/cm^3. The high density indicates that these glasses could be used as a good scintillating material.

3.2 Transmission spectra

Fig. 1 shows the transmission spectra of samples with different composition. All the samples have a good transparent property. A sharp absorption band was occurred at 485 nm, especially TPBT4 whose mole concentration of Tb^{3+} is 8%. This is the characteristic absorption band of Tb^{3+} due to the transition from $^7F_6$ to $^5D_4$.

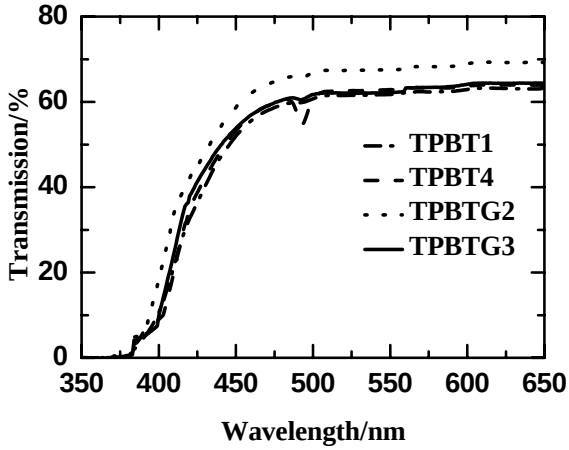

Fig.1. Transmission spectra of glass samples.

3.3 Excitation spectra

The excitation spectrum of glass samples is shown in Fig. 2. The photoluminescence spectra of TPBT3 were obtained at four different excitation wavelength of 317, 352, 358 and 373 nm, which can be attributable to the $^7F_6 \rightarrow {}^5H_7$, $^7F_6 \rightarrow {}^5L_9$, $^7F_6 \rightarrow {}^5L_{10}$ and $^7F_6 \rightarrow {}^5D_3$ transition of Tb^{3+} ion respectively. The highest peak appears at 373 nm. The excitation spectra of TPBTG5 is two peaks more than TPBT3, which are located at 270 and 312 nm, due to the transition of $^8S_{7/2} \rightarrow {}^6I$ and $^8S_{7/2} \rightarrow {}^6P_{7/2}$ of Gd^{3+} ion. This is clear evidence that efficient energy transfer Gd^{3+}-Tb^{3+} should occur.

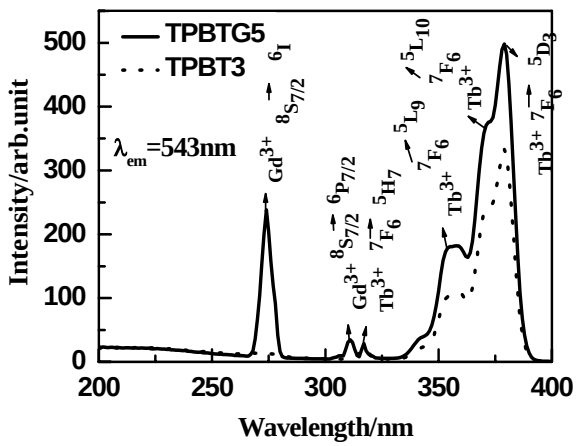

Fig.2 Excitation spectra of TPBT3 and TPBTG5

3.4. Emission spectra

3.4.1 Emission spectra under UV

Fig.3 shows the Emission spectra for different concentration of Tb^{3+} ions glasses excited with 373 nm. As illustrated in Fig.3. Four main emission peaks are located at 490 nm, 543 nm, 583 nm, 620 nm respectively, which can be attributable to the $^5D_4 \rightarrow {}^7F_J$ (J = 6, 5, 4, 3) transition of Tb^{3+}ion. The highest peak appears at 543nm. It demonstrates that as the increase in the concentration of Tb^{3+} in the matrix, the intensity of emission will be increased rapidly. It could be speculated that the distance between Tb^{3+} ions will decrease caused by the increasing concentration of Tb^{3+} ions, so the emission of Tb^{3+} will be increased. For the mole concentration of Tb^{3+} ions arrived at 8 %, emission peak at 543nm show much higher than that of 1 %. Almost the same results are observed under X-ray as shown in Fig.5. When excited by X-ray, the mole concentration of Tb^{3+} ions arrived at 5%, emission peak at 543 nm were 2 times higher than that of 1 %. Thus, with improving the concentration of Tb^{3+}ions, the intensity of luminescence will be increased. It could be speculated that the distance between Tb^{3+} ions will decrease caused by the increasing concentration of Tb^{3+} ions, consequently the ratio of energy transfer from the matrix to Tb^{3+} will be increased.

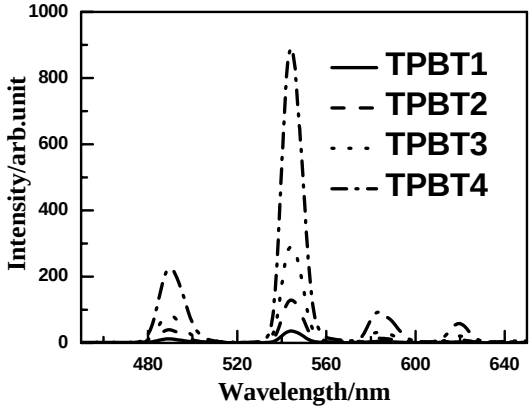

Fig.3. Emission spectra for different concentration of Tb^{3+} ions glasses excited with 373nm.

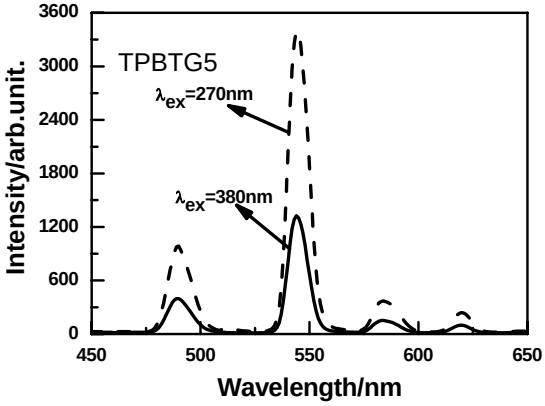

Fig.4. Emission spectra under 270nm and 380nm excitation.

The Fig.4 show the emission spectra under 270 nm and 380 nm excitation. As observed from Fig.4, at the excitation wavelength of 270nm($^8S_{7/2} \rightarrow {}^6I$ transition of Gd^{3+} ion), the fluorescence intensity is very strong, as it is commonly known that Gd^{3+} and Tb^{3+} co-doped materials exhibit relatively strong absorption line at 270 nm. Also this demonstrates efficient energy transfer from Gd^{3+} ion to Tb^{3+} ion.

3.4.2 Emission spectra under X-ray radiation

Analogous to the above, the Emission spectra for different concentration of Gd^{3+} ions under X-ray excitation is shown in Fig.6. It should be noted that four main emission peaks were also obtained while the wavelength of highest peak was 543 nm. With the increase of the concentration of Gd^{3+} ions, the intensity of emission of Tb^{3+} will be increased [9]. The results implied that Gd^{3+} ions

sensitize the luminescence of Tb^{3+} in these matrix, moreover Gd^{3+} ions transmit energy to Tb^{3+} efficiently.

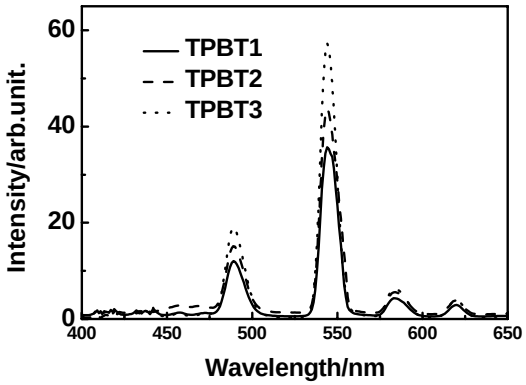

Fig.5. Emission spectra for different concentration of Tb^{3+} ions glasses under X-ray excitation.

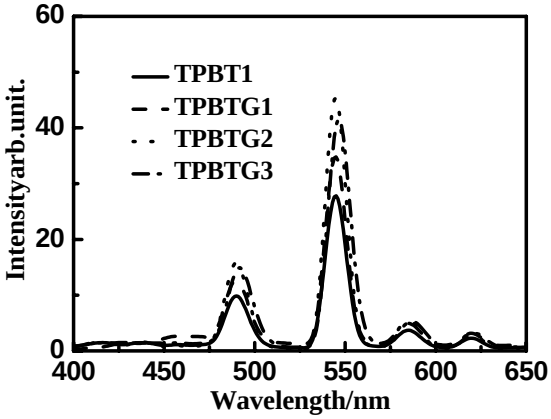

Fig.6. Emission spectra under X-ray excitation.

3.5 energy levels of Gd3+ and Tb3+

A energy levels diagram of Tb^{3+} and resonant energy transfer process from Gd^{3+} to Tb^{3+} was plotted in Fig.7 [10]. When Tb3+ ions are excited by ultraviolet light or X-Ray, electronic transition of $^5D_4 \rightarrow F_J$ is observed in these glasses, where J = 3,4,5,6. Gd^{3+} ions could also be excited to ^6I_J, then down to the level $^6P_{7/2}$ rapidly, through resonant energy transfer. Meanwhile, part of the energy in the $^6P_{7/2}$ level of Gd^{3+} is transferred to the $^5H_7$ level of Tb^{3+} by resonant energy transfer, then relaxes to $^5D_3$ and $^5D_4$, enhancing the luminescence of Tb^{3+}.

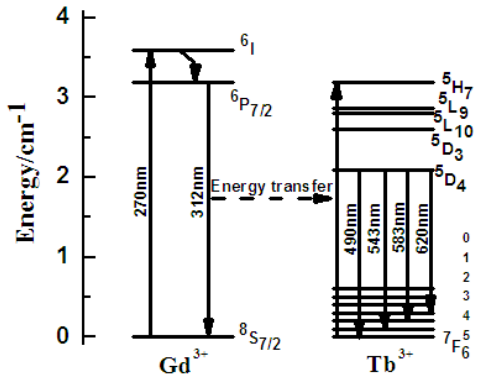

Fig.7. energy levels diagram of Tb^{3+} and energy transfer from Gd^{3+} to Tb^{3+}.

The efficiency of energy transfer depend on the concentration of Gd^{3+} ions[11]. As the Tb^{3+} content increased, the distances of Gd^{3+}-Tb^{3+} become shorter, leading to more energy transferring from Gd^{3+} to Tb^{3+}. Then the luminescence of Tb^{3+} become higher than before. Because $^6P_{7/2}$ level of Gd^{3+} is very closer with $^5H_7$ level of Tb^{3+}, the probability of energy transfer improve at these two levels. Meanwhile, the energy transfer from Gd^{3+} to Tb^{3+} ions is irreversible, as the $^6P_{7/2}$ level of Gd^{3+} is higher than the $^5H_7$ level of Tb3+, $^6P_{7/2}$ level of Gd^{3+} could transfer to $^5H_7$ level of Tb^{3+} easily by resonant energy transfer.

3.6 Decay curves

Their decay curve may be fitted using single-exponential function, The lifetime of all samples are listed in Table.2. With the increasing of Tb^{3+} and Gd^{3+}, the lifetime of glass will be decreased. But all data points start to converge to a single point at ~1.5ms.

Table.2 fluorescence lifetimes of all samples

Serial number	1	2	3	4	5	6	7	8	9
Lifetimes (ms)	1.51	1.50	1.47	1.44	1.50	1.49	1.47	1.43	1.42

4. Conclusion

In the present work, Tb-activated scintillating glasses with different concentration of rare-earth have been studied. Because of the energy transfer from Gd^{3+} to Tb^{3+}, Gd^{3+}-containing glasses show higher scintillating light output than Gd^{3+}-free glasses. But when Gd^{3+} ions concentration reach a certain value, with the increasing of the Gd^{3+} ions concentration, scintillating properties will decrease instead of increase. The optimal mole concentration of Gd^{3+} ions is 4%. These glasses have a remarkable effect on the increase of the scintillating light output. The high scintillating light output and high density over 5.0 g/cm^3 indicates the present glasses are attractive for use in some physical applications.

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