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Persistent spectral hole burning of Eu^{3+} ions in TiO_2–SiO_2 glass prepared by sol–gel method

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Abstract

The $15TiO_2$–$85SiO_2$ glass containing Eu^{3+} ions was prepared by sol–gel method. The excitation spectrum in the range from 220 to 360 nm exhibits the absorption of the charge-transfer bands of the Eu^{3+} and Ti^{4+} ions, indicating an energy transfer from the Ti charge-transfer band to the Eu^{3+} ions. The emission spectrum consists of the transitions from the $^5D_0$ to ^7F_J ($J = 0, 1, 2, 3, 4$), respectively. PSHB spectra were recorded on the excitation spectrum of the $^7F_0 \rightarrow {}^5D_0$ transition by monitoring the fluorescence of the $^5D_0 \rightarrow {}^7F_2$ transition. A hole was burned at 8 K. The multiholes of the Eu^{3+} ions in the glass can be burned with different burning wave numbers.

Keywords: TiO_2–SiO_2 glass; Eu^{3+}; Sol–gel; Persistent spectral hole burning

1. Introduction

In recent years, the persistent spectral hole burning (PSHB) has attracted tremendous interest due to its potential application in high-resolution spectral probes and high-density optical-storage devices [1–5]. These studies involved organic materials, inorganic crystals, and glasses. Among these materials, glass materials containing rare earth ions are advantageous for application in frequency-domain optical devices because of their large inhomogeneous linewidth of transition, high transparency, and easy mass production. Therefore, the PSHB of rare earth ions, such as Eu^{3+} and Sm^{2+} ions have been extensively investigated in the glasses based on the silicate containing several metal ions, such as Na^+, B^{3+}, Al^{3+}, Sn^{4+}, and P^{5+} ions [1–5]. These investigations have exhibited that many glasses possess the property of PSHB. However, there are still some problems about the practical application of these materials. Moreover, the PSHB mechanism is not very clear now. Therefore, the search for new materials is stimulated both by the desire to understand mechanisms of PSHB and by the need to obtain efficient PSHB property for frequency-domain optical storage.

On the other hand, the PSHB of rare earth ions in the glasses based on the silicate containing Ti^{4+} ions have pay little attention. One possible reason is that the glass containing Ti^{4+} ions is quite difficult to prepare by the traditional melting process. However, it is feasible to use sol–gel method for preparing the glass containing Ti^{4+} ions. While the glasses prepared by sol–gel method have shown the good properties of PSHB, indicating that sol–gel method is an excellent route to prepare the doped glasses for PSHB.

To the best of our knowledge, the PSHB of Eu^{3+} ions in TiO_2–SiO_2 glass has not yet been reported. Here, we report the property of the PSHB of the Eu^{3+} ions in TiO_2–SiO_2 glasses by sol–gel method.

2. Experiment

2.1. Sample preparation

The sample with the composition $15TiO_2$–$85SiO_2$ containing 1% Eu_2O_3 was prepared by the sol–gel process

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using tetraethoxysilane (TEOS), ethanol, deionized water, $Ti(OC_4H_9)_4$, and $EuCl_3 \cdot 6H_2O$ as the starting materials. A small amount of concentrated hydrochloric acid was added as a catalyst. The $Si(OC_2H_5)_4$ was first hydrolyzed with a mixed solution of ethanol and deionized water. $Ti(OC_4H_9)_4$ was then introduced into the partially hydrolyzed TEOS solution, followed by stirring for 1 h at about 70 °C. When the solution was cooled to room temperature, $EuCl_3 \cdot 6H_2O$ dissolved in C_2H_5OH was added to this solution and stirred for 30 min. After this period, the mixed solution of H_2O and C_2H_5OH was added, and the resultant solution was stirred for another 30 min to form homogeneous solution. The obtained homogeneous solutions were cast into plastic containers, where they were allowed to gel at room temperature. Gel times varied from 4 to 8 weeks depending on the composition and room temperature. The final gel was heated at 500 °C in air for 4 h. The obtained samples are transparent and colorless.

2.2. Characterization

X-ray diffraction (XRD) pattern of the sample was obtained with X-ray diffractometry (Rigaku RAD-B system). The excitation and emission spectra at room temperature were recorded using a monochromator (Jobin Yvon, HR 320) and a photomultiplier (Hamamatsu, R955). A 500-W xenon lamp with light that passed through a monochromator (Jobin Yvon, H 20) was used for excitation. The PSHB was observed on the excitation spectra of the $^5D_0$–$^7F_0$ transition. The excitation spectra were obtained by scanning the output of a continuous wave Ar^+ ion laser-pumped Rhodamine 6G dye laser monitoring the fluorescence of the $^5D_0 \rightarrow {}^7F_2$ transition band. The sample was irradiated for 30 min using a Rhodamine 6G dye laser operating at 560 mW. After irradiation, the excitation spectra were recorded in the same way. The laser power for scanning was attenuated by neutral-density (ND) filters to less than 0.2% of that for burning. The spectra were recorded at 8 K using the Jobin Yvon HR 320 monochromator.

3. Results and discussion

3.1. X-ray diffraction pattern of the $15TiO_2$–$85SiO_2$ glass containing Eu^{3+} ions

Fig. 1 shows the X-ray diffraction pattern of $15TiO_2$–$85SiO_2$ glass containing Eu^{3+} ions. It is a typical amorphous glass pattern.

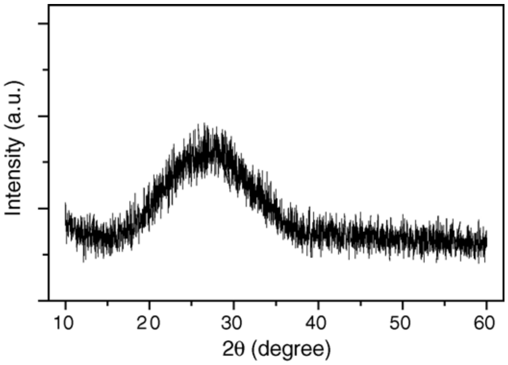

Fig. 1. XRD pattern of $15TiO_2$–$85SiO_2$ glass containing Eu^{3+} ions.

3.2. Excitation and emission spectra of the $15TiO_2$–$85SiO_2$ glass containing Eu^{3+} ions

Fig. 2 shows the excitation spectrum of the $15TiO_2$–$85SiO_2$ glass containing Eu^{3+} ions. The excitation spectrum of TiO_2–SiO_2 glasses containing Eu^{3+} ions consists of broad bands and several narrow bands. The broad bands in the range from 220 to 360 nm are due to the charge-transfer bands of the Eu^{3+} and Ti^{4+} ions [6]. The narrow bands at about 364, 385, 396, 416, 467, and 536 nm are attributed to the f–f transitions within the Eu^{3+} $4f^6$ configuration. The appearance of the charge-transfer bands of the Ti^{4+} ions in the glass indicates an energy transfer from the charge-transfer bands of the Ti^{4+} ions to the Eu^{3+} ions.

Fig. 3 shows the emission spectrum of the $15TiO_2$–$85SiO_2$ glass containing Eu^{3+} ions. It consists four group bands at about 579, 592, 614, 653, and 703 nm. These bands are due to the $^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2, 3, 4$) transitions, respectively. Note that emission bands exhibit inhomogeneous properties. Since amorphous glasses do not have the ordered structure normally found in crystals, the environment of a Eu^{3+} ion is not sufficiently well defined to enable a simple characterization of its optical properties. The emission band from Eu^{3+} ions in glasses consists of a superposition of contributions from individual ions distributed among the entire ensemble of local environments. The resulting statistical distribution of Stark components leads to a significant degree of inhomogeneous broadening of the emission lines [7]. Therefore, this phenomenon is associated with the change of the environment of the Eu^{3+} ions in the glass due to the disorder microstructure of the glass.

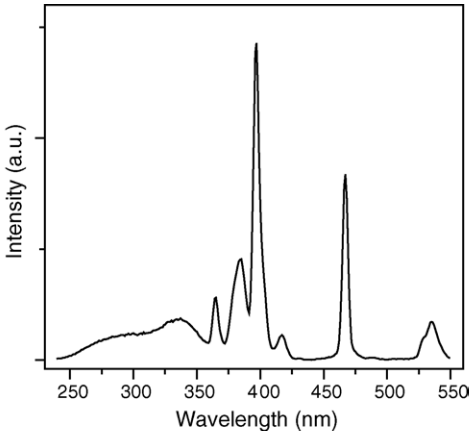

Fig. 2. Excitation spectrum of the $15TiO_2$–$85SiO_2$ glass containing Eu^{3+} ions.

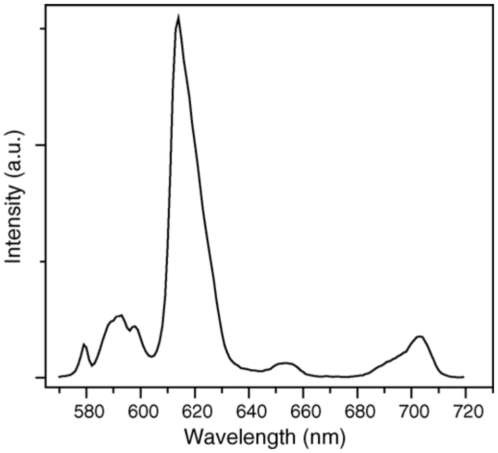

Fig. 3. Emission spectrum of the 15TiO$_2$–85SiO$_2$ glass containing Eu^{3+} ions.

3.3. *Persistent spectral hole burning*

PSHB spectrum was recorded on the excitation spectrum of the$^7F_0 \rightarrow {}^5D_0$ transition by monitoring the fluorescence of the $^5D_0 \rightarrow {}^7F_2$ transition. Fig. 4 shows the typical excitation spectra before and after hole burning at 8 K. A hole is clearly observed at the burning wave number of about17260 cm^{-1}. The hole depth is estimated as ∼24% by comparing the fluorescence intensity. The width (FWHM) of the spectral hole is about 1.7 cm^{-1}. No obvious antiholes were observed around the burned holes.

Fig. 5 shows the multihole spectra of the glass. It can be seen that five holes were burned in the order of the increasing number. It is obvious that the earlier holes were partially refilled, when the later holes were burned. This behavior was also observed in the some glasses containing Eu^{3+} ions, where the earlier holes were partially refilled, when the later holes were burned [8,9]. Although the mechanism of hole burning in the system is not clear at the present stage of the study, this situation may be associated with redistribution of electrons during hole burning because hole spontaneous refilling is very slow. Possible explanation is that the hole-burnt state has a higher energy than the unburned state and electrons, relax across the activation barrier into the unburned state, when they obtain some energy during a new hole burning [8]. As a result, the earlier holes were partially refilled, when the later holes were burned. The detailed mechanism of PSHB in the system is still open. Further investigation is in progress for thorough comprehension of the mechanism for spectral hole burning of the Eu^{3+} ion in the 15TiO$_2$–85SiO$_2$ glass.

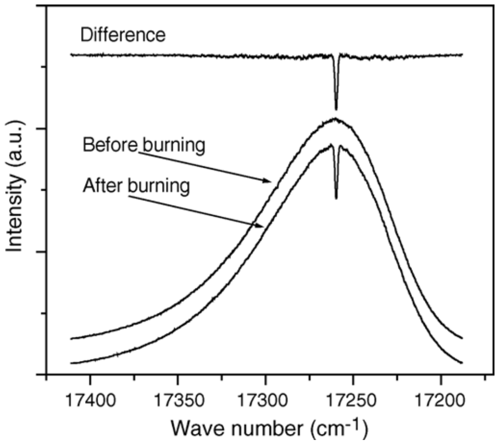

Fig. 4. Excitation spectra for $^7F_0 \rightarrow {}^5D_0$ of the Eu^{3+} ions in the glass before and after hole burning, and the difference signal (upper). Measured at 8 K and burned at 17260 cm^{-1} with a power of 560 mw for 30 min.

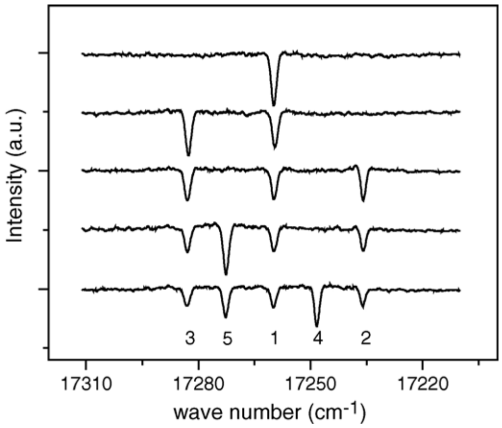

Fig. 5. Multihole spectra of the Eu^{3+} ions in the glass. Holes were burned at five wave numbers in the order of numbers.

4. Conclusion

The 15TiO$_2$–85SiO$_2$ glass containing Eu^{3+} ion was prepared by the sol–gel processing of metal alkoxides. The luminescent properties of the 15TiO$_2$–85SiO$_2$ glass containing Eu^{3+} ion exhibit an energy transfer from Ti charge band to the Eu^{3+} ions. Persist spectral holes were burned into the $^5D_0$–$^7F_0$ for the first time in the 15TiO$_2$–85SiO$_2$ glass containing Eu^{3+} ion. The multiholes of the Eu^{3+} ions in the glass can be burned with different burning wave numbers.

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