Journal of Alloys and Compounds 408–412 (2006) 845–847

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Effect of counter ions on the reduction process of Sm^{3+} ions in TiO_2–ZrO_2–Al_2O_3–SiO_2 glasses

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Received 31 July 2004; accepted 25 November 2004
Available online 3 June 2005

Abstract

The radio-chemical reaction of Sm^{3+} reduction in xTiO$_2$(ZrO$_2$)–$(10 - x)$Al$_2$O$_3$–90SiO$_2$ glasses ($x = 0$–10 mol%) was examined by a photoluminescence technique with fluorescence intensities at 560–650 nm (Sm^{3+}; $^4G_{5/2} \rightarrow {}^6H_J$) and 680–720 nm ($Sm^{2+}$; $^5D_0 \rightarrow {}^7F_J$). It was found that the reduction of Sm^{3+} ions by X-ray irradiation was significantly decreased by the introduction of TiO_2 and no reduction occurred in the glasses containing TiO_2 above 5%. On the other hand, in the ZrO_2 containing glasses, the reduction of Sm^{3+} ions was almost monotonous up to 5% of ZrO_2. Electron spin resonance (ESR) spectra revealed the presence of some defect centers; hole-trap center (HTC) and electron-trap center (ETC). Hole centers trapped by oxygen ions bound to the Al^{3+} ions were strongly related to the reduction process from Sm^{3+} to Sm^{2+} ions; the released electrons from the Al-related HTC were captured by the nearest Sm^{3+} ions, forming Sm^{2+}. On the other hand, in the TiO_2-containing glasses, electrons generated were preferably trapped in Ti^{4+} ions so as to form ETC, resulting in no reduction of Sm^{3+} ions.

Keywords: Sm; Reduction; Sol–gel glass; Fluorescence; ESR; Point defect

1. Introduction

Rare-earth ions-doped glasses have widely been studied because of their unique optical properties and applications for opto-telecomunication, such as laser action, upconversion, amplifier and spectral hole burning [1,2]. Persistent spectral hole burning (PSHB) phenomena are especially interesting due to its application to frequency-domain optical data storage. Glasses are more preferred as a host matrix of rare-earth ions for their inhomogeneously broadened line width of optical transitions, facile compositional variation and easy mass production. Recently, using a sol–gel technique, we prepared Sm^{2+} ions-doped aluminosilicate glasses and demonstrated the PSHB up to room temperature [3–5]. Spectral holes are considered to be burnt by photoinduced chemical reactions within the rare-earth ions or between the rare-earth and matrix glass structure [6].

So far, we have investigated the reduction of Sm^{3+} into Sm^{2+} ions by X-ray or femtosecond laser irradiation and the formation of the PSHB. These glasses give faster and more efficient hole burning compared to the H_2-gas treated glasses [3–5]. It was also noted that in the glasses irradiated with X-ray there were an amount of aluminium–oxygen hole centers (Al–OHC), which were hole centers trapped with oxygen bounded to the Al ions, and the generated quantity were closely correlated with the quantity of Sm^{3+} reduction [7].

In this study, a X-ray reduction process of Sm^{3+} ions in TiO_2(ZrO_2)–Al_2O_3–SiO_2 glasses was investigated in relation with various point defects generated in each of these glasses.

2. Experiments

2.1. Sample preparation

xTiO$_2$ (or ZrO$_2$)–$(10 - x)$Al$_2$O$_3$–90SiO$_2$ (mol%) glasses doped with 10 wt% Sm_2O_3 were prepared by the sol–gel process of $Si(OC_2H_5)_4$, $Al(OC_4H_9)_3$, $Ti(OC_3H_7)_4$, $Zr(OC_3H_7)_4$

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0925-8388/$ – see front matter
doi:10.1016/j.jallcom.2004.11.084

and $SmCl_3 \cdot 6H_2O$. Gels were synthesized through hydrolysis of the mixed materials in ethanol, a detailed explanation of which is given elsewhere [8,9]. The gels were heated in air at 40 °C/h to 800 °C and held at that temperature for 2 h. Some of the glasses were irradiated with X-rays. The X-ray irradiation was performed by the Cu Kα line for 14 h at room temperature with 40 kV and 20 mA using a conventional X-ray diffractometer (Rigaku RAD-B system).

2.2. Measurement of properties

The fluorescence spectra were recorded at right angles using a Hamamatsu, R955 photomultiplier. A xenon lamp passed through a monochromator for excitation. Electron spin resonance (ESR) measurement was performed using a Jasco, JES-FE 1XG spectrometer at 77 K. The *g*-values and the quantities of spin obtained ESR signals were calibrated by the utilization of diphenylpicrylhydrazal (DPPH) and 2,2,6,6-tetramethyl-1-poperidinyloxy (TEMPO), respectively.

3. Results and discussion

3.1. Reduction of samarium ions in glasses

Fig. 1 shows the fluorescence spectra of Sm^{3+} ion doped $10Al_2O_3$–$90SiO_2$ glasses before and after X-ray irradiation. The sharp fluorescence lines observed around 565, 600 and 650 nm before the irradiation are ascribed to $^4G_{5/2}$–$^6H_{5/2,7/2,9/2}$ transitions, respectively, of the Sm^{3+} ions. After the irradiation, new fluorescence lines noticeably emerges around 680, 700 and 720 nm. These bands are characteristic bands of Sm^{2+} ions arising from $^5D_0$–$^7F_{0,1,2}$ transitions, respectively. For evaluating the variation of the reduction of Sm^{3+} ions with the substitution of Al_2O_3 with $TiO_2(ZrO_2)$, the fluorescence intensity ratio of the Sm^{2+} ions, $I_{Sm^{2+}}/(I_{Sm^{2+}} + I_{Sm^{3+}})$, is shown in Fig. 2, where $I_{Sm^{2+}}$ is the fluorescence intensity of Sm^{2+} ions and $I_{Sm^{3+}}$ is that of Sm^{3+} ions. In case of the substitution by TiO_2, the fluorescence intensity ratio drastic ally decreases, and no reduction occurs in the glasses containing TiO_2 above 5%. On the other hand, in the case of ZrO_2, the ratio is almost monotonous up to 5% of ZrO_2, then the fluorescence of Sm^{2+} ions disappears when Al_2O_3 is reached to 0%.

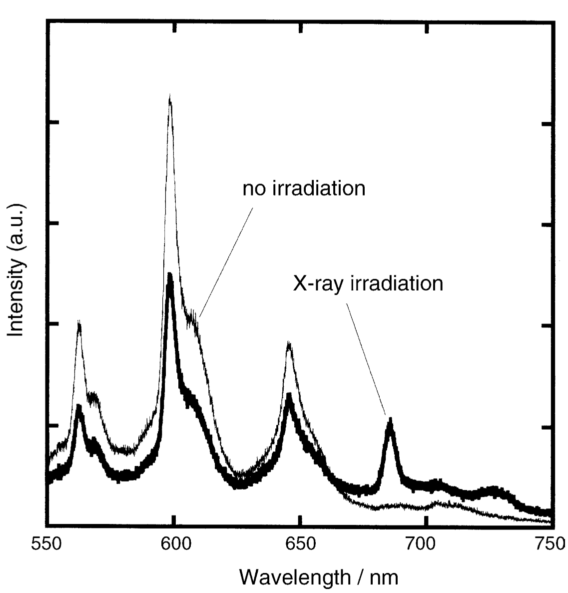

Fig. 1. Fluorescence spectra of Sm^{3+}-doped Al_2O_3–SiO_2 glass before and after X-ray irradiation (λ_{ex} = 404 nm).

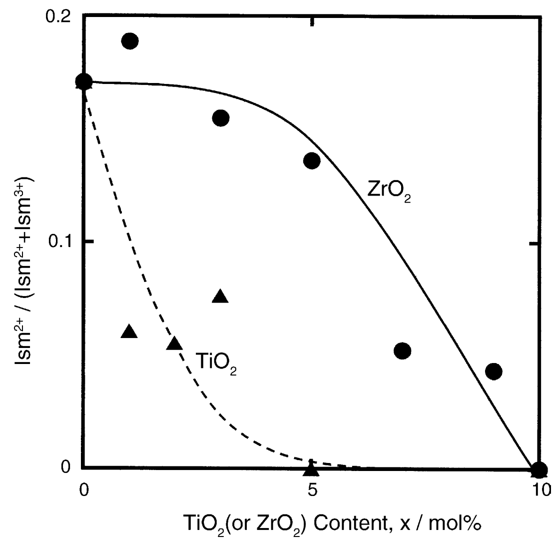

Fig. 2. The variation of the reduction of Sm^{3+} ions in different matrices.

3.2. Generation of point defects in glasses

Fig. 3 shows ESR spectra of the glasses irradiated with X-ray. In $10Al_2O_3$–$90SiO_2$ glass, there is one signal of defects

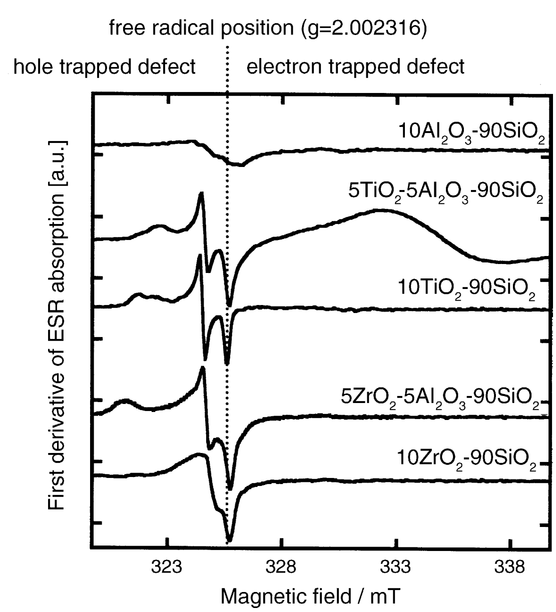

Fig. 3. ESR spectra of the glasses irradiated with X-ray irradiation.

Table 1
The quantities of hole- or electron-trap centers

Composition	HTC (spin/g)	ETC (spin/g)
$10Al_2O_3$–$90SiO_2$	3.8×10^{16}	None
$5TiO_2$–$5Al_2O_3$–$90SiO_2$	3.9×10^{16}	3.6×10^{17}
$10TiO_2$–$90SiO_2$	2.3×10^{16}	None
$5ZrO_2$–$5Al_2O_3$–$90SiO_2$	2.4×10^{16}	None
$10ZrO_2$–$90SiO_2$	4.3×10^{16}	None

with magnetic anisotropy in the glass. It is defined as hole-trap centers trapped by the oxygen ions bound to Al^{3+} ions (Al–OHC: $g = 2.0075$) [7]. The defects which are generated with cutting of Al-related bonding are more effective about the reduction of Sm^{3+} ions, because Sm ions tend to exist near to Al [7,10]. Thus, Sm^{3+} ions experience no reduction by X-ray when Al_2O_3 is not one of the glass components (see Fig. 2). In the other glasses, they have each hole-trap center with different g-value. Furthermore, only in the glass containing TiO_2, Al_2O_3 and SiO_2, electron-trap centers are clearly observed. With three component glasses contained Al_2O_3, SiO_2 and TiO_2, the quantity of reduction of Sm^{3+} ions was exceedingly small (see Fig. 2). This suggests that Sm^{3+} ions cannot be supplied with electrons in such glasses because electron-trapped centers are attracting them strongly.

Table 1 summarizes the quantities of hole- or electron-trapped defects generated by X-ray (see also Fig. 3). In $5TiO_2$–$5Al_2O_3$–$90SiO_2$ glass, electron-trap centers of 3.6×10^{17} spin/g are generated, which are by 10 times more than hole-trap centers. It is found that the electron-trap centers are generated enough to prevent the reduction of Sm^{3+} ions. For this reason, the fluorescence intensity ratio about Sm^{2+} ions was very small in the aluminosilinate based glasses in which TiO_2 was added.

4. Conclusions

We studied the reduction process of Sm^{3+} ions and generation of defects with X-ray irradiation in $xTiO_2$ (or ZrO_2)–$(10 - x)Al_2O_3$–$90SiO_2$ glasses. In the glasses not containing Al_2O_3, no reduction of Sm^{3+} ions occurred because the reduction process of Sm^{3+} ions closely correlated with Al–OHC. On the other hand, in case of three component glasses containing Al_2O_3, SiO_2 and TiO_2, the Sm^{3+} ions were hardly reduced with X-ray irradiation. This suggested that electron-trap centers generated in the glass matrix were attracting electrons strongly. Therefore, Sm^{3+} ions were not supplied with electrons required for reduction.

Acknowledgement

This research was partly supported by The NIT-21st Century COE Program for Environmental Friendly Ceramics.

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