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# Compositional dependence of local vibration around rare earth ions in $\text{SiO}_2\text{-PbF}_2$ glass–ceramics

M Takahashi<sup>†</sup>, M Kano<sup>‡</sup> and Y Kawamoto<sup>‡</sup>

<sup>†</sup> Venture Business Laboratory, Kobe University, Nada, Kobe 657, Japan

<sup>‡</sup> Department of Chemistry, Faculty of Science, Kobe University, Nada, Kobe 657, Japan

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**Abstract.** Compositional dependence of local vibration around  $\text{Eu}^{3+}$  in  $\text{SiO}_2\text{-PbF}_2$  glass–ceramics is investigated by analysing the phonon sideband associated with the  $\text{Eu}^{3+}:^5\text{D}_2 \leftarrow ^7\text{F}_0$  transition. Two kinds of sideband peak are observed in a high-energy region of the  $^5\text{D}_2 \leftarrow ^7\text{F}_0$  transition. Phonon energies of these sideband peaks are about  $950\text{ cm}^{-1}$  and  $250\text{ cm}^{-1}$ . Intensities of the sidebands are greatly dependent on the composition; the phonon sideband at  $950\text{ cm}^{-1}$  increases and that at  $250\text{ cm}^{-1}$  decreases with increasing  $\text{SiO}_2$  content. The calculated multiphonon relaxation rate depends only on the intensity of the sideband at  $950\text{ cm}^{-1}$ . This indicates that multiphonon relaxation of the excited rare earth ion is reduced in lower- $\text{SiO}_2$ -content regions. Infrared-to-visible upconversion luminescence of  $\text{Er}^{3+}$  is also measured for glass–ceramics doped with  $\text{Er}_2\text{O}_3$  substituted for  $\text{Eu}_2\text{O}_3$ . Efficient upconversion luminescence is observed at  $550\text{ nm}$  under  $800\text{ nm}$  excitation. The intensity of the upconversion luminescence becomes remarkably higher in lower- $\text{SiO}_2$ -content regions.

## 1. Introduction

Fluoride glasses are one of the promising hosts in developing active optical devices which utilize the intra-4f transitions of rare earth ions, i.e. upconversion phosphors/lasers [1], optical amplifiers [2], visible/infrared lasers [3] and so on. The efficiency of these optical functional materials is greatly dependent on the multiphonon relaxation rate of excited rare earth ions because the dominant nonradiative process is multiphonon relaxation. The multiphonon relaxation rate exponentially increases with increasing maximum phonon energy of host matrix [4]. The maximum phonon energies of fluoride glasses are considerably lower than those of oxide glasses. Therefore, multiphonon relaxation occurs much less frequently in fluoride glasses than in most oxide glasses. In other words, the radiative efficiency of rare earth ions is higher in fluoride glasses than in oxide glasses. This characteristic is greatly related to the improvement in active optical function of rare earth ions. However, properties such as the low chemical and mechanical stability become serious in fabrication of fibers and waveguides of fluoride glasses [5].

Oxide glasses are chemically and mechanically more stable than fluoride glasses. Especially,  $\text{SiO}_2$ -based glasses are chemically stable and easy to fabricate into various waveguide structures. Although the  $\text{SiO}_2$ -based glasses have such peculiar characteristics, the multiphonon relaxation across excitation states take place at high frequency as compared with fluoride glasses because of their large phonon energies. Therefore, silicate glasses are unsuitable for host materials of rare earth doped optical devices.

It has been reported that lead oxyfluoride glass–ceramic, which comprises a oxide glass phase and a fluoride crystal phase, is noteworthy in order to develop a chemically and

mechanically stable and also effective host for rare earth ions. The first report on such glass–ceramic hosts for rare earth luminescence was made by Auzel and his co-workers [6]. The glass–ceramics developed are  $M_nO_m$ – $PbF_2$  (M: B, Si, P, Ge, Te) doped with rare earth oxides such as  $Er_2O_3$  and  $Tm_2O_3$ . They have found that the green upconversion efficiency of  $Er^{3+}$ -doped materials is as high as that obtained for  $Er^{3+}:YF_3$ . Recently, Wu *et al* have investigated the blue upconversion luminescence properties of  $Er^{3+}$  in  $GeO_2$ – $PbF_2$  glass–ceramics doped with  $Yb^{3+}$  [7]. They have reported that the blue upconversion emissions centred at 406 and 480 nm are due to three- and two-photon absorption processes, respectively, and that the energy transfer between  $Yb^{3+}$  and  $Er^{3+}$  depends on temperature. A transparent glass–ceramic host for rare earth ions was first reported by Wang and Ohwaki [8]. They have found that the transparent glass–ceramic co-doped with  $Er^{3+}$  and  $Yb^{3+}$  exhibits efficient upconversion luminescence. Tick and his co-workers have examined the ability of glass–ceramics as host material for an optical amplifier for 1.3  $\mu m$  optical telecommunication [9]. The above authors have suggested that some or most of the rare earth ions may be present in fluoride crystal phases.

The difference in vibration energy between the oxide glass phase and the fluoride crystal phase is significantly large. Therefore, it must be clarified by investigation of the local vibration environment around rare earth ions where rare earth ions are embedded in the glass–ceramics. To investigate the local vibration environment around rare earth ions, phonon sideband analysis is one of the most powerful tools [10].

In this study the compositional dependence of the local vibration environment around rare earth ions in  $SiO_2$ – $PbF_2$  glass–ceramics is examined by employing  $Eu^{3+}$  ion as a probe of rare earth ions. The  $Eu^{3+}$  ion has a suitable transition, which is  ${}^5D_2 \leftarrow {}^7F_0$  transition, to measure phonon sideband because fluorescence excitation band of the pure electronic transition is observed as single peak and the energy gap to the next higher level is large enough. The phonon sideband is hardly observed for other rare earth ions because of complex spectral profiles. Therefore, we analysed the local vibration environment by means of the phonon sideband associated with the  $Eu^{3+}:{}^5D_2 \leftarrow {}^7F_0$  transition. The compositional dependence of the multiphonon decay rate of the rare earth ion is calculated from the experimental results. Furthermore, the compositional dependence of the  $Er^{3+}$  upconversion luminescence intensity is examined for glass–ceramics of the same composition in which  $Eu_2O_3$  is substituted for  $Er_2O_3$ . Correlation between upconversion luminescence intensity and the local vibration environment of the rare earth ion is also discussed.

## 2. Experimental procedure

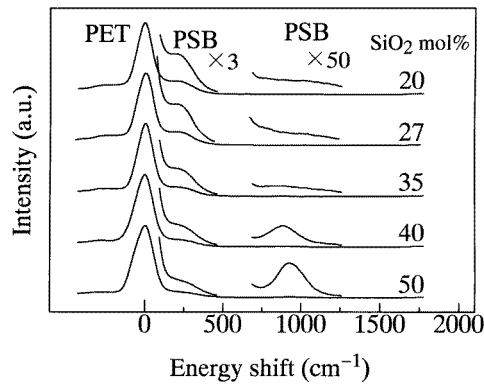
The glass–ceramic compositions employed were  $xSiO_2 \cdot (95 - x)PbF_2 \cdot 2.5La_2O_3 \cdot 2.5Eu(Er)_2O_3$  ( $x = 20, 27, 35, 40, 50, 60$ ). High-purity reagents  $SiO_2$ ,  $PbF_2$ ,  $La_2O_3$ ,  $Eu_2O_3$  and  $Er_2O_3$  were used as the starting materials.  $La_2O_3$  should be added to the batches as a stabilizing agent. Batches were well mixed and melted in covered Pt crucibles at 1000 °C for 1 hour. The melts were then poured into brass moulds preheated at about 200 °C to obtain precursor glasses. The precursor glasses were then annealed at 350 °C for 4 hours for crystallization.

The fluorescence excitation spectra of the  $Eu^{3+}:{}^5D_2 \leftarrow {}^7F_0$  transition were measured by monitoring the  $Eu^{3+}:{}^5D_0 \rightarrow {}^7F_2$  transition with a Hitachi F-3010 fluorescence spectrophotometer. The  $Er^{3+}$  upconversion spectra were measured with the same spectrometer by using an AlGaAs diode laser ( $\lambda = 802$  nm,  $P = 250$  mW) as an excitation source.

### 3. Results

#### 3.1. Phonon sideband

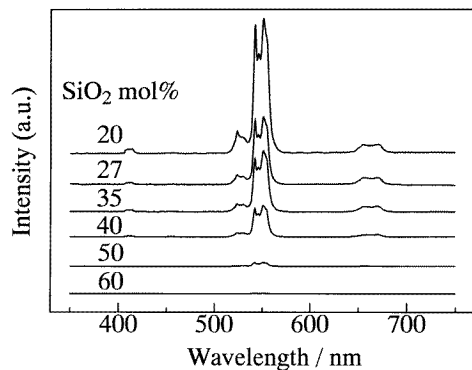
Figure 1 shows the fluorescence excitation spectra of the  $\text{Eu}^{3+} : ^5\text{D}_2 \leftarrow ^7\text{F}_0$  transition. The centre of gravity of the peak area in the  $^5\text{D}_2 \leftarrow ^7\text{F}_0$  transition was taken as zero energy shift. Phonon sidebands associated with the pure electronic  $\text{Eu}^{3+} : ^5\text{D}_2 \leftarrow ^7\text{F}_0$  transition (PET) can be observed in the higher-energy regions of the PET. In the respective spectra, two kinds of phonon sideband (PSB) peaks can be seen at around  $250 \text{ cm}^{-1}$  and  $950 \text{ cm}^{-1}$ . Hereafter the PSB peaks are referred to as PSB(250) and PSB(950) depending on the energy shifts. The intensities of both PSB peaks change with  $\text{SiO}_2$  content, that is, the intensity of PSB(250) decreases and that of PSB(950) increases with increasing  $\text{SiO}_2$  content.



**Figure 1.** Fluorescence excitation spectra of the  $\text{Eu}^{3+} : ^5\text{D}_2 \leftarrow ^7\text{F}_0$  transition.

#### 3.2. Upconversion luminescence

Figure 2 shows the changes in  $\text{Er}^{3+}$  upconversion luminescence spectra under 800 nm excitation with  $\text{SiO}_2$  content. Four upconversion emission bands, which locate around 410, 525, 550 and 660 nm, can be seen in each spectrum. The intensity of upconversion luminescence drastically decreases with increasing  $\text{SiO}_2$  content.



**Figure 2.** Compositional dependence of  $\text{Er}^{3+}$  upconversion luminescence spectra under 800 nm excitation.

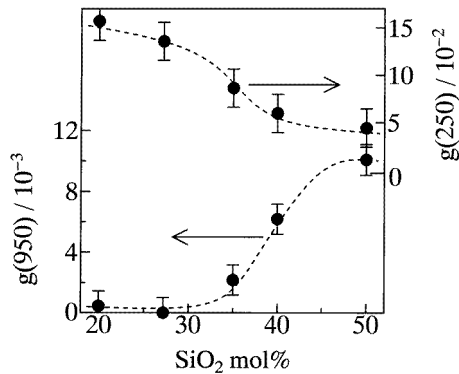
## 4. Discussion

### 4.1. Local vibration environment around $\text{Eu}^{3+}$

As shown in figure 1, the phonon energies of both peaks are independent of the  $\text{SiO}_2$  content. The intensity of PSB(250) decreases whereas that of PSB(950) increases with increasing  $\text{SiO}_2$  content, i.e. decreasing  $\text{PbF}_2$  content. This fact suggests that PSB(250) and PSB(950) closely relate to the Pb–F and Si–O vibrations, respectively.

The vibrational spectroscopic study of lead oxyfluorosilicate glasses has been reported by Osaka *et al* [11]. They reported that the vibrational energies of the  $\text{SiO}_4$  unit in the glasses range from 830 to 1060  $\text{cm}^{-1}$ , depending on the number of nonbridging oxygens in the tetrahedron. The similarity of the energy of the PSB(950) band with vibrational energies of  $\text{SiO}_4$  units, and its increase of intensity when increasing  $\text{SiO}_2$  content, support the assignment of the PSB(950) band to Si–O vibrations.

The electron–phonon coupling strength can be calculated from the intensity ratio of PSB to PET [12]. Figure 3 shows the  $\text{SiO}_2$  content dependence of electron–phonon coupling strength of PSB peaks. Hereafter, the electron–phonon coupling strengths of PSB(250) and PSB(950) are referred to as  $g(250)$  and  $g(950)$ , respectively. The  $g(950)$  value increases and the  $g(250)$  value decreases with increasing  $\text{SiO}_2$  content. The  $g(950)$  values are almost zero up to about 25 mol%  $\text{SiO}_2$  content. This fact suggests that  $\text{Eu}^{3+}$  ions are preferentially embedded in lead fluoride phase and that most of the  $\text{Eu}^{3+}$  ions are in a lead fluoride crystal phase up to about 25 mol%  $\text{SiO}_2$  content. The increase in  $g(950)$  value with increasing  $\text{SiO}_2$  amount indicates that some of the  $\text{Eu}^{3+}$  ions exists in a silicate glass phase in higher- $\text{SiO}_2$ -content regions.



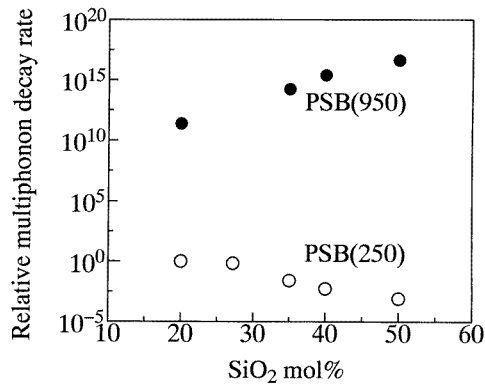
**Figure 3.**  $\text{SiO}_2$  content dependence of electron–phonon coupling strength of PSB peaks. The dotted lines are guides for the eye.

### 4.2. Multiphonon relaxation rate

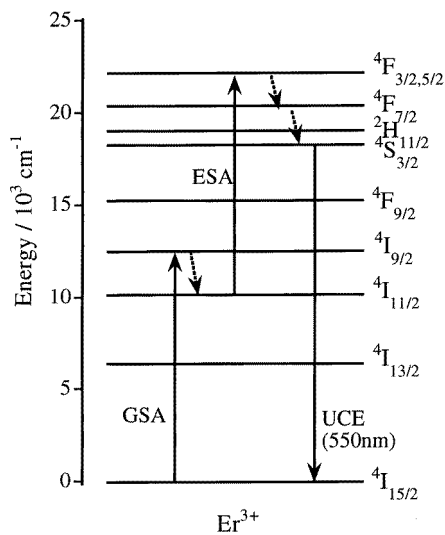
The multiphonon relaxation rate of excited rare earth ions,  $W_p$ , is expressed by the Miyakawa–Dexter equation [4, 13],

$$\begin{aligned}
 W_p &\propto \exp(-\alpha \Delta E) \\
 \alpha &= \hbar\omega^{-1} \{ \ln(p/g) - 1 \} \\
 p &\sim \Delta E / \hbar\omega
 \end{aligned}
 \tag{1}$$

where  $g$  is the electron-phonon coupling strength,  $\Delta E$  is the energy gap to the next lower level,  $\hbar\omega$  is the phonon energy and  $p$  is an integer equal to the number of phonon quanta concerned with multiphonon decay. As shown in (1), the relative multiphonon relaxation rate can be calculated from the phonon energy and the electron-phonon coupling strength determined from a PSB spectrum. Figure 4 shows the  $\text{SiO}_2$  content dependence of the relative multiphonon relaxation rate across the energy gap of  $3500\text{ cm}^{-1}$ , which was calculated from PSB(250) and PSB(950) as an example. This energy gap is almost equal to the energy gap of the  $\text{Er}^{3+}:^4\text{I}_{11/2} \rightarrow ^4\text{I}_{13/2}$  transition. As shown in figure 5, the  $\text{Er}^{3+}:^4\text{I}_{11/2}$  state is considered to be an intermediate state of the  $\text{Er}^{3+}$  upconversion process [14]. The multiphonon relaxation rate calculated from the  $g(950)$  value is several orders of



**Figure 4.**  $\text{SiO}_2$  content dependence of the relative multiphonon decay rate across the energy gap of  $3500\text{ cm}^{-1}$ . Relative multiphonon decay rates were calculated by regarding the value calculated from PSB(250) for the glass-ceramics containing 20 mol%  $\text{SiO}_2$  as unity.



**Figure 5.** Schematic illustration of energy level and upconversion mechanism under 800 nm excitation of  $\text{Er}^{3+}$  in fluoride glass host; GSA—ground state absorption, ESA—excited state absorption, UCE—upconversion emission.

the magnitude larger than that from the  $g(250)$  value. Since the phonon energy of PSB(950) varies little with composition, the multiphonon relaxation rate of excited rare earth ions in the present glass–ceramics depends only on the  $g(950)$  value.

As shown in figure 2, the upconversion luminescence intensity drastically decreases with increasing  $\text{SiO}_2$  content. Assuming that the local environment around  $\text{Er}^{3+}$  is similar to that around  $\text{Eu}^{3+}$  in the glass–ceramics, the higher multiphonon relaxation rate at higher  $\text{SiO}_2$  content contributes to the decrease in upconversion intensity. In other words, Si–O vibration coupled with the 4f electrons of  $\text{Er}^{3+}$  ions may play a dominant effect on the efficiency of  $\text{Er}^{3+}$  upconversion in the present glass–ceramics.

It should be mentioned here that the radiative transition rates between 4f energy states of rare earth ions are also dependent on the local environment. Considering the previous reports on the radiative rate of  $\text{Er}^{3+}$  in lead silicate [15] and fluoride [14] hosts, the difference in radiative rates of intra-4f transitions of  $\text{Er}^{3+}$  is within a factor of 1.5. The upconversion intensity decreases by a factor  $>10^{-2}$  with increasing  $\text{SiO}_2$  content. Therefore, we suggest that the multiphonon relaxation of the excited  $\text{Er}^{3+}$  ion dominates the upconversion efficiency.

## 5. Concluding remarks

The local vibrations around  $\text{Eu}^{3+}$  in  $\text{SiO}_2$ – $\text{PbF}_2$  glass–ceramics have been investigated by means of the phonon sideband analysis. Two kinds of vibration which correspond to Si–O and Pb–F vibration are observed. In lower  $\text{SiO}_2$  contents, rare earth ions are preferentially embedded in the fluoride crystal phase and upconversion luminescence can be observed with high efficiency. The multiphonon relaxation rate of excited rare earth ions greatly depends on the density of Si–O vibration around the rare earth ion.

## Acknowledgments

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