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# Compositional Dependence of Upconversion Luminescence of $Er^{3+}$ in $ZrF_4$-Based Glasses

## III. Anion Substitution Effect

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As one of the compositional designs for enhancing the unconversion luminescence efficiency of $Er^{3+}$ in $ZrF_4$-based glasses, the anion substitution effect has been examined in glasses $58ZrF_4 \cdot (39\text{-}x)BaF_2 \cdot xBaX_2 \cdot 3Er(\text{or } Eu)F_3$ ($x = 0$–$29$ for $X$ = Cl and $x = 0$–$10$ for $X$ = Br in batch compositions). Prominent enhancement of upconversion emission intensity was observed on the substitution of Cl for F. The Cl substitution brought about two effects, of which one was an increase in the deviation from inversion symmetry in the $F^-$ coordination around $Er^{3+}$ and the other was an increase in both phonon energy and electron–phonon coupling strength. The former raises the transition probability in the upconversion process, leading to an enhancement of the emission intensity, while the latter increases the multiphonon relaxation in the upconversion process, leading to a reduction of the emission intensity. Due to these antithetical effects on the upconversion process, the upconversion emission intensity of the Cl substituted glasses exhibits a maximum value around the $58ZrF_4 \cdot 20BaF_2 \cdot 19BaCl_2 \cdot 3ErF_3$ composition. *The substitution of small amounts of Cl for F is concluded to be quite effective for enhancing the* upconversion efficiency of $ZrF_4$-based glasses. © 1993 Academic Press, Inc.

## I. Introduction

The conversion of infrared radiation to shorter wavelengths, i.e., frequency upconversion luminescence, by rare earth-doped glasses presently receives much interest since the development of near-infrared semiconductor diode lasers has made the upconversion pumping of rare-earth laser systems possible (*1*). Among various glass-forming systems, heavy metal fluoride glasses are considered to be the best candi-

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dates for producing upconversion luminescence with high emission efficiency. This is because the maximum phonon frequencies of the glasses are so small that the nonradiative loss due to multiphonon relaxation can be substantially reduced (2). Until now, therefore, upconversion luminescence phenomena have been intensively examined in heavy metal fluoride glasses based on $ThF_4$ (*3*), $HfF_4$ (*4*), and so on. Accordingly, compositional designs for upconversion laser glasses also are an important subject in heavy metal fluoride-based systems. However, there are few reports thus far on the compositional dependence of upconversion luminescence in these glasses.

The present authors are advancing a series of experiments as to how the upconversion luminescence of $Er^{3+}$ in fluoride glasses is affected by the kinds and quantities of glass-constituting ions. So far the effect of glass-modifying cations on $Er^{3+}$ upconversion luminescence has been examined in the $21.25MF \cdot 21.25LiF \cdot 52.5ZrF_4 \cdot 5ErF_3$ ($M$: Li, Na, K, Rb or Cs) and $5M'F_2 \cdot 25BaF_2 \cdot 65ZrF_4 \cdot 5ErF_3$ ($M'$: Mg, Ca, Sr or Ba) glasses (*5*, *6*). Also the difference in $Er^{3+}$ upconversion luminescence with the kinds of glass-forming cations has been examined on the $MF_n$-$BaF_2$-$YF_3$ ($M$: Zr, Hf, Al, Ga, In, Sc, or Zn) glasses (*7*).

This paper reports the effect of anion substitution on the upconversion properties of $Er^{3+}$ in fluoride-based glasses. The glass composition chosen was a $ZrF_4$-based one in which part of the $F^-$ ions was replaced by other anions such as $Cl^-$, $Br^-$, $I^-$, or $O^{2-}$ ions.

## Experimental Procedure

### (*a*) *Sample Preparation*

The glass composition employed is $58ZrF_4 \cdot (39\text{-}x)BaF_2 \cdot xBaX_2 \cdot 3LnF_3$ ($Ln$: Er or Eu, $X_2$: $Cl_2$, $Br_2$, $I_2$ or O) in mol%. The $x$ values for the respective $X$s are given in Table I. High purity reagents $ZrF_4$, $BaF_2$, $BaCl_2$, $BaBr_2$, $BaI_2$, $BaCO_3$, $ErF_3$, and $EuF_3$ were used as raw materials in preparing the glasses. About 4 g batches of the raw materials were melted at 700°C for about 20 min in Pt crucibles under an Ar gas stream. Then the melts were poured into brass molds kept at a temperature of about 100°C. The glasses obtained were annealed at the respective glass transition temperatures determined by a differential thermal analysis. In the samples of O substitution (i.e., $BaX_2$ = BaO), small but numerous crystals precipitated in the glass matrices, giving no good quality glasses with high transparency.

Glasses obtained by Cl, Br, or I substitution were subjected to X-ray fluorescence analysis to determine the substituted halogen contents. The analyzed values of Cl, Br, and I contents are given in Table I, where glass-transition temperature, density and $Er^{3+}$ concentration are also given for the Cl or Br substituted glasses. Since no significant amounts of I were found to remain in the I substituted glasses, no experiments were performed on these glasses.

Since the Cl or Br substituted glasses were prepared without the addition of a fluoridizing agent, $NH_4F \cdot HF$, to the batches, appreciable amounts of oxygen might be included as an impurity. Thus, the oxygen content was analyzed in some of the Cl substituted glasses by using an oxygen and nitrogen analyzer for metals (HORIBA, EMGA-2200). The analyzed oxygen contents in glasses of $x$ = 0, 15, and 24 were 0.469(18), 0.223(8) and 0.357(16)ppm, respectively. Therefore the oxygen amounts of the Cl substituted glasses are concluded to be negligibly small regardless of the Cl content.

### (*b*) *Upconversion Luminescence Spectra of $Er^{3+}$*

The upconversion luminescence spectra of $Er^{3+}$ in the $58ZrF_4 \cdot (39\text{-}x)BaF_2 \cdot xBaX_2 \cdot 3ErF_3$ ($X$ = Cl or Br) glasses were measured in the wavelength range 380–780 nm

TABLE I

COMPOSITIONS AND SOME PROPERTIES OF GLASSES $58ZrF_4 \cdot (39\text{-}x)BaF_2 \cdot xBaX_2 \cdot 3ErF_3$ ($X_2$ = $Cl_2$, $Br_2$, $I_2$ or O)

| $X$ | $x$ (Mol%) batch | Substituted F (Anion%) | | $T_g$ (°C) | Density ($g \cdot cm^{-3}$) | $Er^{3+}$ concentration ($10^{-4}$ $mol \cdot cm^{-3}$) |
|---|---|---|---|---|---|---|
| | | Batch | Analyzed | | | |
| Cl | 0 | 0 | ~0.00 | 309 | 4.909 | 8.193 |
| | 5 | 3 | 1.71 | 287 | 4.653 | 8.029 |
| | 10 | 6 | 3.20 | 285 | 4.603 | 7.868 |
| | 15 | 9 | 5.09 | 276 | 4.492 | 7.609 |
| | 19 | 12 | 6.23 | 271 | 4.453 | 7.485 |
| | 24 | 15 | 7.50 | 262 | 4.550 | 7.400 |
| | 29 | 18 | 8.95 | 249 | 4.394 | 7.251 |
| Br | 5 | 3 | 2.7 | 297 | 4.655 | 7.863 |
| | 10 | 6 | 5.4 | 287 | 3.463 | 7.538 |
| I | 5 | 3 | ~0.0 | | | |
| | 10 | 6 | ~0.0 | | | |
| O | 2.5 | 1.5 | | | | |
| | 5 | 3 | | | | |

with a fluorescence spectrophotometer (HITACHI, 850) at room temperature, using 800.0 nm radiation from an AlGaAs diode laser (SONY, SLD303XT-22) with a 250 mW power excitation source. Glass plates of size 3.0 × 4.0 × 1.0 mm with optically flat surfaces were used.

### (c) *Emission Spectra of $Eu^{3+}$*

The emission spectra of the $^5D_0 \rightarrow {}^7F_J$ ($J$ = 0, 1 and 2) transitions of $Eu^{3+}$ in the $58ZrF_4 \cdot (39\text{-}x)BaF_2 \cdot xBaCl_2 \cdot 3EuF_3$ glasses were measured in the wavelength range 550–650 nm with a fluorescence spectrophotometer (HITACHI, 850) at room temperature, using 395 nm light of a Xe lamp as the excitation source.

### (d) *Phonon Sideband Spectra of $Eu^{3+}$*

The excitation spectra of $Eu^{3+}$ in the $58ZrF_4 \cdot (39\text{-}x)BaF_2 \cdot xBaCl_2 \cdot 3EuF_3$ glasses were measured by monitoring the $^5D_0 \rightarrow {}^7F_2$ emission at 616 nm. The measurement was carried out in the wavelength range 420–475 nm at room temperature with the same apparatus as that in (c). The phonon sidebands associated with the $^5D_2 \leftarrow {}^7F_0$ transition were observed for all the glasses at high energy sides of the electronic bands.

## Results and Discussion

### (a) *Change in Upconversion Luminescence Spectra with Anion Substitution*

The upconversion luminescence spectra of the $58ZrF_4 \cdot (39\text{-}x)BaF_2 \cdot xBaCl_2 \cdot 3ErF_3$ glasses are shown in Fig. 1. The upconver-

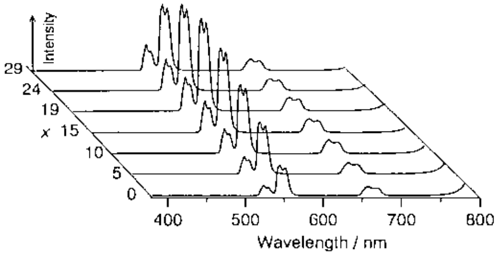

FIG. 1. Upconversion luminescence spectra of $Er^{3+}$ in glasses $58ZrF_4 \cdot (39\text{-}x)BaF_2 \cdot xBaCl_2 \cdot 3ErF_3$.

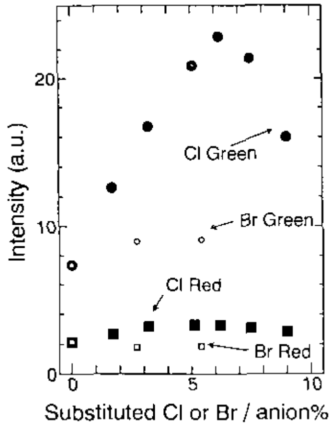

FIG. 2. Anion substitution dependences of upconversion emission intensities in glasses $58ZrF_4\cdot(39\text{-}x)BaF_2\cdot xBaX_2\cdot 3ErF_3$ ($X$ = Cl or Br).

sion luminescences of $Er^{3+}$ were observed at about 525 and 550 nm, due to the $^2H_{11/2}\to{}^4I_{15/2}$ and $^4S_{3/2}\to{}^4I_{15/2}$ transitions, respectively, and at about 660 nm due to the $^4F_{9/2}\to{}^4I_{15/2}$ transition. A faint emission band was observed at about 410 nm, corresponding to the $^2H_{9/2}\to{}^4I_{15/2}$ transition. Peak wavelengths of these emission bands were almost the same in all of the Cl or Br substituted glasses.

Figure 2 shows the Cl- and Br-content dependences of the emission intensities of the green color (525 and 550 nm) and red color (660 nm) bands. The following three features can be seen from the figure: (1) The magnitude of the change in the emission intensities with anion substitution is much more remarkable for the Cl substitution than for the Br substitution. (2) In the Cl substituted glasses the emission intensities of both green and red colors become larger with substitution, although substitution beyond about 6 anion% leads to a reduction of the emission intensities. (3) In the Br substituted glasses the emission intensity of the green color slightly increases with substitution, while that of the red color remains almost unchanged.

### (*b*) $F^-$ *Coordination Environment of* $Eu^{3+}$

The observed emission spectra of $Eu^{3+}$ in the $58ZrF_4\cdot(39\text{-}x)BaF_2\cdot xBaCl_2\cdot 3EuF_3$ glasses are shown in Fig. 3. In the luminescence spectral bands, the $^5D_0\to{}^7F_2$ emission band is due to the electric-dipole transition, depending largely on a local symmetry of the coordination environment around $Eu^{3+}$, while the $^5D_0\to{}^7F_1$ emission band is due to the magnetic-dipole transition, which is independent of a local symmetry (*8*). Therefore the ratio of the $^5D_0\to{}^7F_2$ to $^5D_0\to{}^7F_1$ emission intensities gives information about the deviation from inversion symmetry in the coordination environment of $Eu^{3+}$ (*9*).

In the emission spectra of $Eu^{3+}$ ions observed for the $58ZrF_4\cdot(39\text{-}x)BaF_2\cdot xBaCl_2\cdot 3EuF_3$ glasses, the $^5D_0\to{}^7F_0$, $^5D_1\to{}^7F_3$ and $^5D_0\to{}^7F_1$ emission bands overlap one another, as can be seen from the assignment given in Fig. 3. Thus the deconvolution of each band was necessary in order to calculate the ratio of the $^5D_0\to{}^7F_2$ to $^5D_0\to{}^7F_1$ emission intensities. The band deconvolu-

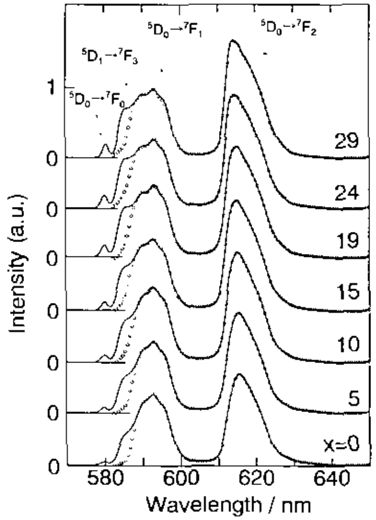

FIG. 3. Emission spectra of $Eu^{3+}$ in glasses $58ZrF_4\cdot(39\text{-}x)BaF_2\cdot xBaCl_2\cdot 3EuF_3$. (Dotted lines of open circles are $^5D_0\to{}^7F_1$ and $^5D_0\to{}^7F_2$ emission spectra obtained by convolution fitting.)

tion was performed using a curve-fitting program of the least squares method. An example of the convolution fitting is shown for the $x = 5$ glass in Fig. 4. The $^5D_0 \rightarrow {}^7F_1$ bands obtained for all the Cl substituted glasses by convolution fitting are shown by dotted lines of open circles in Fig. 3, together with the $^5D_0 \rightarrow {}^7F_2$ bands.

Figure 5 shows the ratios of the $^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$ emission intensities in the $58ZrF_4 \cdot (39\text{-}x)BaF_2 \cdot xBaCl_2 \cdot 3EuF_3$ glasses, which are plotted against the substituted Cl content in anion%. The compositional dependence of the $^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$ ratios clearly indicates that a deviation from inversion symmetry in the $F^-$ coordination of $Eu^{3+}$ increases with an increase of the substituted Cl content. Since the $Er^{3+}$ and $Eu^{3+}$ ions can be considered to be chemically equivalent and thus to play almost the same role in the glasses, the $F^-$ coordination environments of $Er^{3+}$ are presumed to be the same as those of $Eu^{3+}$.

Therefore, the increasing tendency of upconversion intensities in the $58ZrF_4 \cdot (39\text{-}x)BaF_2 \cdot xBaCl_2 \cdot 3ErF_3$ glasses is ascribed to the increased transition probability in the upconversion process with successive substitution of the $Cl^-$ ions for the $F^-$ ions around the $Er^{3+}$ ions. In actual, however, the upconversion luminescence intensities were reduced in the Cl substitution beyond about 6 anion%, as seen from Fig. 2. Accordingly there must be other factors by which upconversion luminescence intensities are reudced with the Cl substitution.

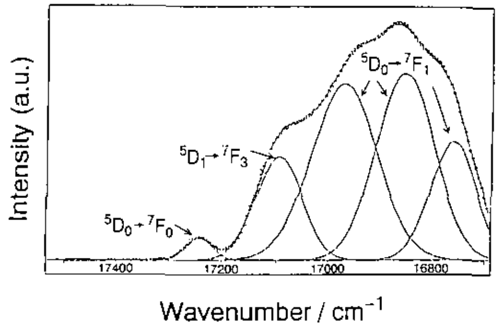

FIG. 4. Convolution fitting for emission spectrum of $Eu^{3+}$ in glass $58ZrF_4 \cdot 34BaF_2 \cdot 5BaCl_2 \cdot 3EuF_3$.

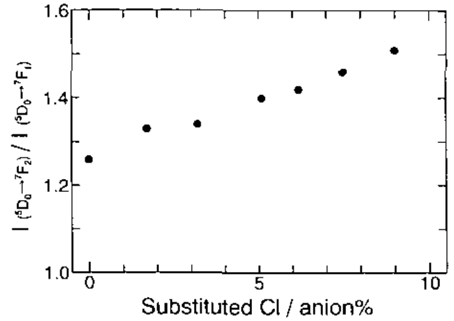

FIG. 5. Intensity ratios of emissions $^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$ in glasses $58ZrF_4 \cdot (39\text{-}x)BaF_2 \cdot xBaCl_2 \cdot 3EuF_3$.

### (*c*) *Phonon Energy and Electron–Phonon Coupling Strength*

According to the Miyakawa–Dexter equation (*10*), the nonradiative decay rate due to the multiphonon relaxation process is governed by the phonon energy and the electron–phonon coupling strength. The larger the phonon energy and/or the electron–phonon coupling strength, the larger becomes the decay rate. Consequently an increase in phonon energy and/or electron–phonon coupling strength reduces the lifetime and quantum efficiency of excited levels, and thus reduces the emission intensity of upconversion luminescence.

The phonon sideband (PSB) spectra observed for the $58ZrF_4 \cdot (39\text{-}x)BaF_2 \cdot xBaCl_2 \cdot 3EuF_3$ glasses are shown in Fig. 6, where all the spectra are normalized to the intensity of the pure electronic transition (PET) in order to facilitate a comparison. The phonon energy corresponds to the mean energy difference between the pure electronic transition and the phonon sideband, and the electron–phonon coupling strength is estimated as the ratio of the integrated intensity of

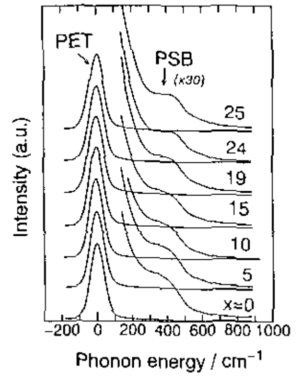

FIG. 6. Excitation spectra of $^5D_0 \leftarrow {}^7F_2$ emission of $Eu^{3+}$ in glasses $58ZrF_4 \cdot (39\text{-}x)BaF_2 \cdot xBaCl_2 \cdot 3EuF_3$.

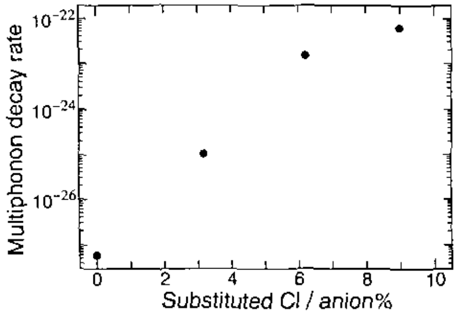

FIG. 7. Multiphonon decay rates in transition $^4I_{9/2} \rightarrow {}^4I_{11/2}$ *obtained for glasses* $58ZrF_4 \cdot (39\text{-}x)BaF_2 \cdot xBaCl_2 \cdot 3ErF_3$ by the Miyakawa–Dexter equation.

phonon sideband to that of pure electronic transition (*11*). It can be seen from the figure that the phonon sidebands overlap very closely with the pure electronic transition bands, making the evaluation of both phonon frequency and electron–phonon coupling strength extremely difficult. Thus, deconvolution of the phonon sidebands from the pure electronic transition bands was attempted for the Cl substituted glasses of $x = 0$, 10, 19 and 29, using a curve-fitting program of the least squares method. The phonon energy and the electron–phonon coupling strength values obtained from the extracted phonon sidebands are given in Table II. From the table it can be seen that the phonon energy becomes considerably higher with the successive substitution and the electron–phonon coupling strength is slightly increased. From these values, the multiphonon decay rate of the $^4I_{9/2} \rightarrow {}^4I_{11/2}$ transition was calculated for the glasses of $x = 0$, 10, 19 and 29 according to the Miyakawa–Dexter equation and the results are plotted in Fig. 7 as a function of the substituted Cl content in anion%. The calculation result, though it might be a tentative estimate, suggests that the nonradiative decay rate increases with the successive Cl substitution.

TABLE II

PHONON ENERGIES, $\hbar\omega$, AND ELECTRON–PHONON COUPLING STRENGTHS, $g$, OF GLASSES $58ZrF_4 \cdot (39\text{-}x)BaF_2 \cdot xBaCl_2 \cdot 3EuF_3$

| $x$ (Mol%) batch | Substituted F (Anion%) batch | $\hbar\omega$ (cm$^{-1}$) | $g$ |
|---|---|---|---|
| 0 | 0 | 375 | 0.0058 |
| 10 | 6 | 395 | 0.0072 |
| 19 | 12 | 425 | 0.0072 |
| 29 | 18 | 435 | 0.0074 |

Such a dependence of the nonradiative decay rate on the Cl content implies that the emission intensity of upconversion luminescence in the $58ZrF_4 \cdot (39\text{-}x)BaF_2 \cdot xBaCl_2 \cdot 3ErF_3$ glasses decreases with the successive substitution of the $Cl^-$ ions for the $F^-$ ions. On the other hand, as described in Section (b), the substitution of the $Cl^-$ ions for the $F^-$ ions gains the emission intensity of upconversion luminescence by increasing the transition probabilities in a multistep excitation and emission process. These two antithetical effects can explain the results shown in Fig. 2, where the upconversion luminescence intensity exhibits a maximum value at the Cl substitution of 6 anion% in the $58ZrF_4 \cdot (39\text{-}x)BaF_2 \cdot xBaCl_2 \cdot 3ErF_3$ glasses.

## Conclusions

The effect of anion substitution on the upconversion luminescence properties of $Er^{3+}$ in $ZrF_4$-based glasses was investigated by substituting a part of the $F^-$ ions in the $58ZrF_4 \cdot 39BaF_2 \cdot 3ErF_3$ composition by $Cl^-$, $Br^-$, $I^-$, or $O^{2-}$ ions. The substitution was possible only for the $Cl^-$ and $Br^-$ ions and the substitution ranges for the respective ions were 0–8.95 and 0–5.4 in anion%. The upconversion luminescence of $Er^{3+}$ of the glasses, which was measured by 800 nm excitation of a 250 mW power, gave three intense emissions around 525, 550, and 660 nm, and a faint emission around 410 nm. The substitution effect on emission intensity is much more prominent in the Cl substitution than in the Br substitution. The emission intensities of the Cl substituted glasses is largely increased by substitution, exhibiting a maximum value around 6 anion%. To investigate the local structure around $Er^{3+}$, the emission and the phonon sideband spectra were measured for the Cl substituted glasses containing $Eu^{3+}$ instead of $Er^{3+}$. The Cl substitution was found to cause the following two changes for the glasses: An increased deviation from inversion symmetry in the $F^-$ coordination around $Er^{3+}$, which raises the radiative transition probability, and an increase in both phonon energy and phonon–electron coupling strength, which increases the nonradiative decay rate due to multiphonon relaxation. The Cl substitution dependence of emission intensity was deduced to be due to the competition of these two factors. The present study concludes that the substitution of $Cl^-$ for a small amount of $F^-$ in $ZrF_4$-based glasses is highly effective for enhancing the upconversion luminescence of $Er^{3+}$.

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