

OPTICAL PROPERTIES OF RARE EARTH IONS IN HEAVY METAL OXIDE GLASSES

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ABSTRACT

Various heavy metal oxide glasses were prepared, and the optical properties of Pr and Tm ions were investigated. Among the glasses, the infrared emissions of Pr: 1.3 μm and Tm: 1.46 μm were successfully observed in Bi_2O_3 glasses, and such phenomena were due to the high refractive index and low phonon energy of the Bi_2O_3 glasses. According to the results from the Judd-Ofelt analyses, the radiative transition probabilities A of Pr: $^1\text{G}_4 \rightarrow ^3\text{H}_5$ transition at 1.3 μm were dependent on the refractive index n and the line strength of electric dipole transition S_{ed} . On the other hand, A of Tm: $^3\text{H}_4 \rightarrow ^3\text{F}_4$ transition at 1.46 μm mainly depended on n . The Pr: $^1\text{G}_4$ level was successfully populated by Pr/Yb Co-doping, and Pr: 1.3 μm emission intensity increased. In Tm $^{3+}$ doped 10K70Bi25Ga glasses, it was confirmed that emission intensity of 1.46 μm band increased with increasing the Tm $_2\text{O}_3$ content.

INTRODUCTION

Recently, the construction of a high-speed, mass communication network is done by the spread of the internet, and further development is desired. Optical amplifier magnifies the light signal attenuated in optical fiber, and such device is required in the long-distance transmission of information. Optical amplifier is hence the key device in the optical communication. Moreover, WDM (Wavelength Division Multiplexing) system that can amplify two or more weakened light signals has been developed to enlarge the telecommunication capacity. SiO_2 glasses have been mainly used for the optical fibers. Er^{3+} ion shows a luminescence of at 1.55 μm at which SiO_2 glasses show the lowest transmission loss, and hence Er^{3+} ion has been used as an active ion in the optical amplifiers. They are known as EDFA (Er^{3+} Doped Fiber Amplifier).

The rare earth ions such as Pr^{3+} , Tm^{3+} , and Dy^{3+} etc. are enumerated as a prospective candidate of the active ions other than Er^{3+} , but they hardly show fluorescence in SiO_2 host and have never been attracted. Recently, the amplifiers other than EDFA have been brought to attention; T DFA (Tm^{3+} Doped Fiber Amplifier) for 1.46 μm band and P DFA (Pr^{3+} Doped Fiber Amplifier) for 1.3 μm band, etc. The research and development have been extensively done.

Figs.1 and 2 show the energy level diagrams of Pr^{3+} and Tm^{3+} ions, respectively. In case of Pr^{3+} and Tm^{3+} , non-radiative transitions easily occur, because the energy gap between the upper level of their emissions and the next lower level is very small, and it is hence very difficult to obtain highly efficient emissions in the high phonon energy host glasses like SiO_2 glasses. Therefore, the low phonon energy materials, such as fluoride glasses, have been aggressively studied. Bi_2O_3 glasses have low phonon energy and high refractive index. In this study, rare earth

ions were introduced to Bi_2O_3 glasses, and their optical properties were investigated.

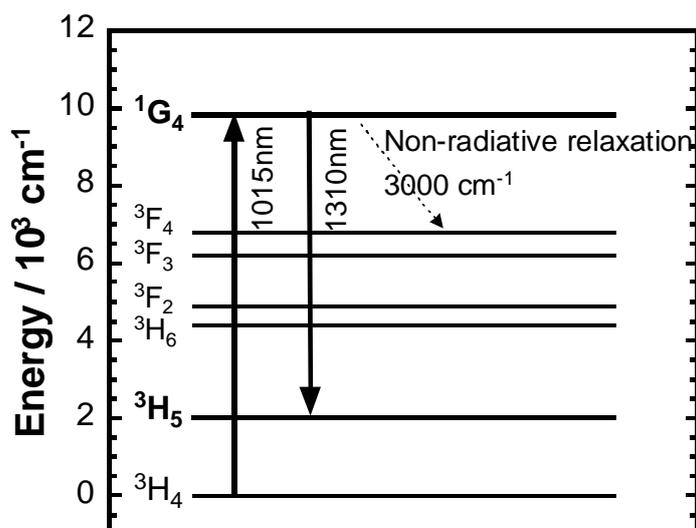


Fig. 1. Energy level diagram of Pr^{3+} .

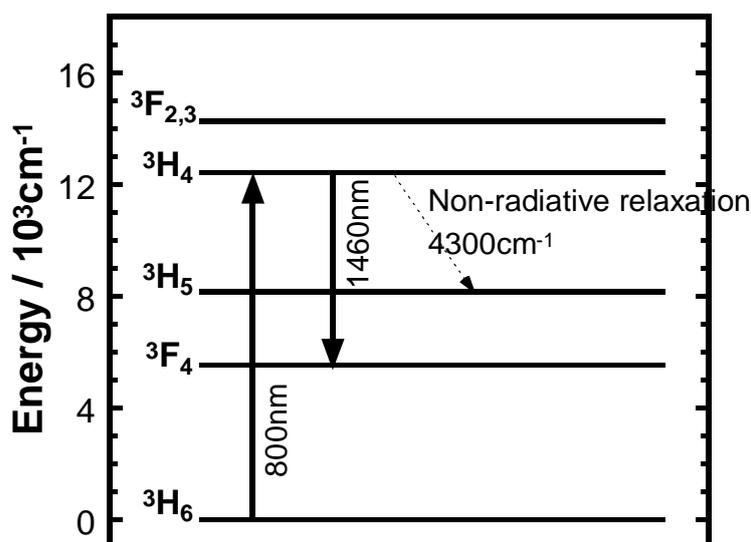


Fig. 2. Energy level diagram of Tm^{3+} .

EXPERIMENTAL PROCEDURE

Table 1 shows the glass composition. 0.1-1.0 mol% Pr_2O_3 or Tm_2O_3 were also added to the starting materials. The composition of $5\text{Na}_2\text{O}-20\text{ZnO}-75\text{TeO}_2$ glasses were prepared for Pr-Yb co-doping. By co-doping Yb with Pr, the fluorescing $^1\text{G}_4$ level is more populated, and high emission efficiency is expected. Also, this glass composition has high solubility of rare earth ions, which reduces clustering of Pr ions and concentration quenching.¹ Tm-doped conventional oxide glasses, $45\text{Ca}45\text{Al}10\text{Si}$, $5\text{Na}60\text{Ca}35\text{Al}$, $15\text{Na}85\text{Ge}$, $15\text{Na}85\text{Si}$ and $15\text{Na}85\text{B}$ were prepared for comparing with the Bi_2O_3 glasses.

Table 1 Glass composition

Dopant	Abbreviation	Composition (mol%)	
Pr	xBi(40-x)W60Te	xBi ₂ O ₃ -(40-x)WO ₃ -60TeO ₂	x=5-15
	xBi ₂ xW(100-3x)Te	xBi ₂ O ₃ -2xWO ₃ -(100-3x)TeO ₂	x=7.5-25
	xW(100-x)Te	xWO ₃ -(100-x)TeO ₂	x=10-30
	xBi(100-x)Ga	xBi ₂ O ₃ -(100-x)Ga ₂ O ₃	x=65-80
	5Na ₂ OZn75Te	5Na ₂ O-20ZnO-75TeO ₂	(Yb ₂ O ₃ codope)
Tm	60Bi20Li20Ba	60Bi ₂ O ₃ -20Li ₂ O-20BaO	
	xK70Bi(30-x)Ga	xK ₂ O-70Bi ₂ O ₃ -(30-x)Ga ₂ O ₃	x=0-10
	10KxBi(90-x)Ga	10K ₂ O-xBi ₂ O ₃ -(90-x)Ga ₂ O ₃	x=50-70
	xBi20W(80-x)Te	xBi ₂ O ₃ -20WO ₃ -(80-x)TeO ₂	x=0-12.5
	50Bi50B	50Bi ₂ O ₃ -50B ₂ O ₃	
	45Ca45Al10Si	45CaO-45Al ₂ O ₃ -10SiO ₂	
	5Na60Ca35Al	5NaO-60CaO-35Al ₂ O ₃	
	15Na85Ge	15Na ₂ O-85GeO ₂	
	15Na85Si	15Na ₂ O-85SiO ₂	
	15Na85B	15Na ₂ O-85B ₂ O ₃	

The powders were mixed and melt for 30 minutes by using Au or Pt crucible. The melts were quenched in a brass mold, and the samples were annealed at near the glass transition temperatures for 1 h and finally polished.

The density was measured by an Archimedes method. The refractive index was measured with a prism coupler method (Metricon, Model 2010). The optical absorption spectra were measured with a UV/VIS/NIR spectrophotometer (JASCO, V-570) in the wavelength range of 190 – 2500 nm. From these results, the Ω parameters and radiative transition probability were calculated by the Judd-Ofelt analysis. The Raman spectra of RE-undoped glasses were obtained with RAMANOR T64000 (Jobin Yvon). The phonon side band (PSB) spectra were measured for the samples doped with 1.0 mol% Eu₂O₃ instead of Pr₂O₃ or Tm₂O₃. From the PSB spectra, local structure around rare earth ions and phonon energy of these glasses were estimated. Also, the fluorescence spectra were measured with Nd:YAG laser (1064 nm) as excitation, OPO (Optical Parametric Oscillator) for conversion of wavelength, and liquid-nitrogen cooled photomultiplier (HAMAMATSU Photonics) as a detector. The wavelengths of the excitation beams were 1015 nm for Pr, 975 nm for Pr/Yb codoped, and 800 nm for Tm-doped samples.

RESULTS AND DISCUSSION

Raman spectra and phonon side band spectra

Fig. 3 shows the Raman spectra of the host glasses, and Fig. 4 shows the phonon side band (PSB) spectra of 1.0 mol% Eu₂O₃ doped glasses. The information of local structure around rare earth ions is obtained from PSB. In the typical oxide glasses having high phonon energy, such as borate (15Na85B) and silicate (15Na85Si) glasses, the PSB peaks are observed at more than 1000 cm⁻¹. In these host glasses, it is difficult to obtain highly efficient emissions because of the multi-phonon relaxation.

In Raman spectrum of 10Bi20W70Te glass, the peaks at 460 and 660 cm⁻¹ are attributed to the TeO₄ trigonal bi-pyramid, the peak at 760cm⁻¹ to the TeO₃ trigonal pyramid, and the peaks at 840 and 930 cm⁻¹ to W-O and W=O bonds, respectively. In PSB spectra of 10Bi20W70Te glass, the peaks are seen at 600 – 900 cm⁻¹, whose phonon energies are relatively high, and hence

highly efficient emissions cannot be expected.

In 10K70Bi20Ga glass, the Raman bands observed at 400, 550, and 500 – 600 cm^{-1} are attributed to Bi-O-Ga, Ga-O-Ga, and Bi-O-Bi groups, respectively, and the band at 660 cm^{-1} is assigned to non-bridging oxygens in GaO_4 tetrahedra. In this glass, it is difficult to obtain the local structure around rare earth ions from PSB because of the weak intensity. In the Bi_2O_3 glasses, however, it is suggested from the Raman spectrum that the glasses have low phonon energy.

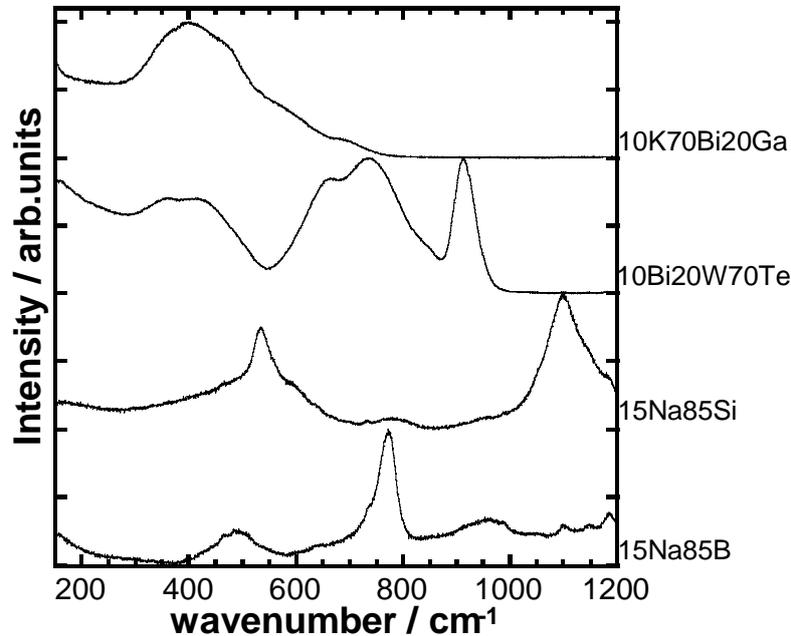


Fig. 3. Raman spectra of RE_2O_3 undoped glasses.

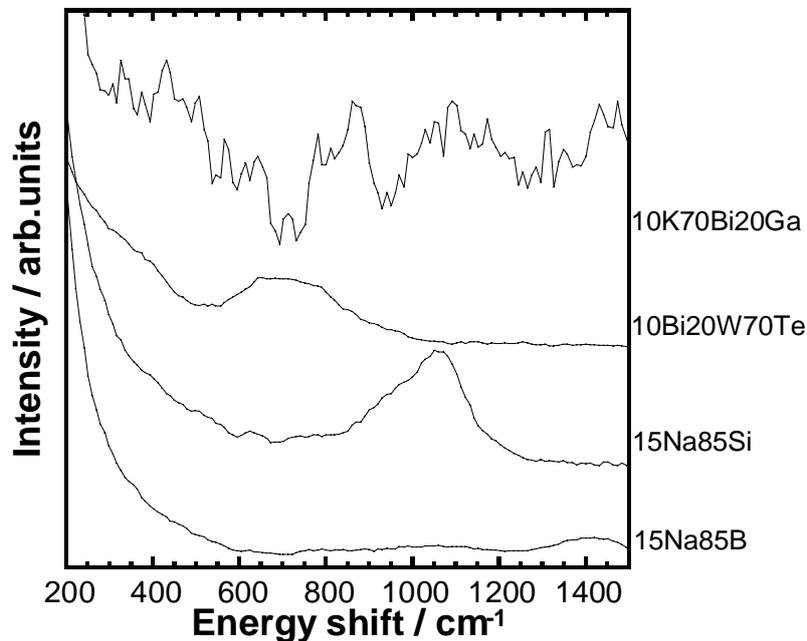


Fig. 4. PSB spectra of 1.0mol% Eu_2O_3 doped glasses.

Absorption spectra

Fig. 5 shows the absorption spectra of Pr doped $x\text{Bi}-(100-x)\text{Ga}$ glasses. The absorption from ground state $^3\text{H}_4$ level to $^1\text{G}_4$ level, which is the upper level for the Pr:1.3 μm emission, is quite weak. Fig. 6 shows the absorption spectrum of Tm doped $70\text{Bi}_2\text{O}_3-30\text{Ga}_2\text{O}_3$ glass. The absorption from ground state $^3\text{H}_6$ level to $^3\text{H}_4$ level which is upper level for Tm: 1.46 μm emission is large enough.

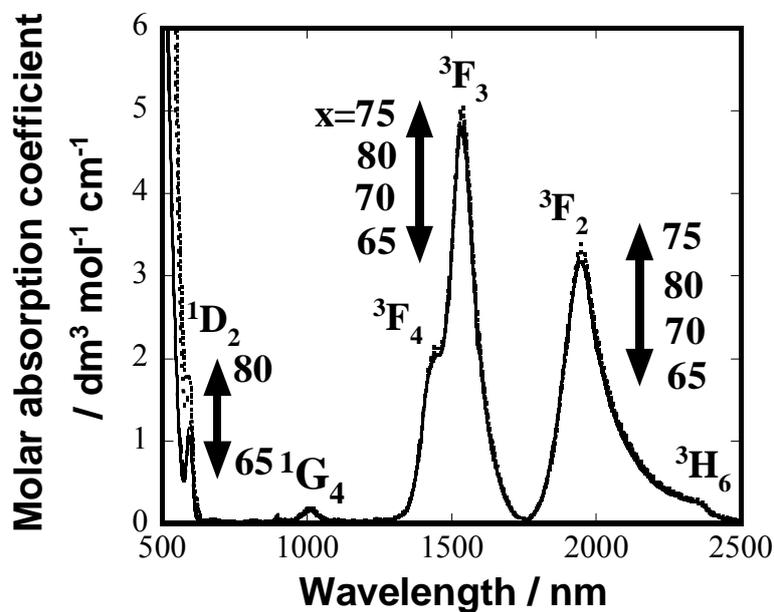


Fig. 5. Absorption spectra of 1.0 mol% Pr_2O_3 doped $x\text{Bi}_2\text{O}_3-(100-x)\text{Ga}_2\text{O}_3$ glasses.

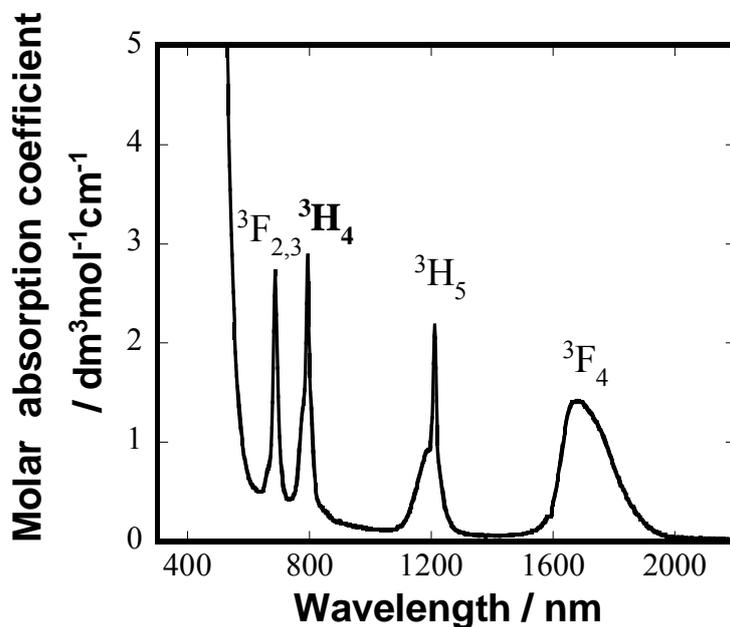


Fig. 6. Absorption spectrum of 1.0 mol% Tm_2O_3 doped $70\text{Bi}_2\text{O}_3-30\text{Ga}_2\text{O}_3$ glass.

Judd-Ofelt analysis

The radiative transition probability, A , is calculated from the equation,²

$$A = \frac{64\pi^4\nu^3e^2}{3hc^3(2J+1)} \left[\frac{n(n^2+2)^2}{9} S_{ed} + n^3 S_{md} \right]. \quad (1)$$

where n is the refractive index of host glass, S_{ed} and S_{md} indicate the line strength of electric and magnetic dipole transitions, respectively, and S_{ed} , is calculated from Eq. 2 for Pr³ and Eq. 3 for Tm.

$$S_{ed} = 0.0307\Omega_2 + 0.0715\Omega_4 + 0.334\Omega_6 \quad (2)$$

$$S_{ed} = 0.1215\Omega_2 + 0.1329\Omega_4 + 0.2258\Omega_6 \quad (3)$$

The correlation between A of Pr: $^1G_4 \rightarrow ^3H_5$ transition and n at 1310 nm is shown in Fig. 7, and the correlation between A and S_{ed} is shown in Fig. 8. To obtain high radiative transition probabilities, high refractive index and high electric-dipole line strength, that is high Ω parameter, are needed. The highest radiative transition probability is obtained in 25Bi50W25Te glass. But the actual emission intensity would be relatively small because of the multi-phonon relaxation.

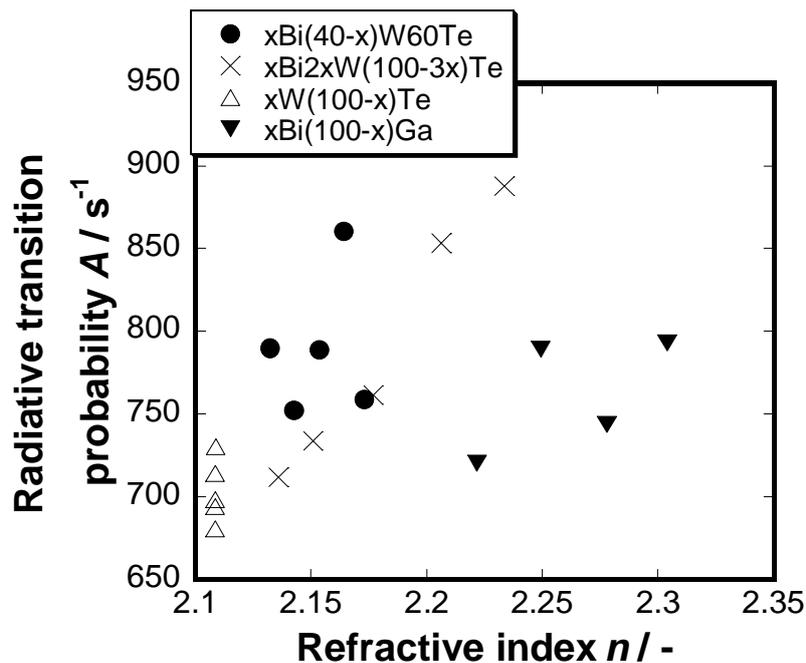


Fig. 7. Relation between refractive index n and radiative transition probability A (Pr: $^1G_4 \rightarrow ^3H_5$ transition).

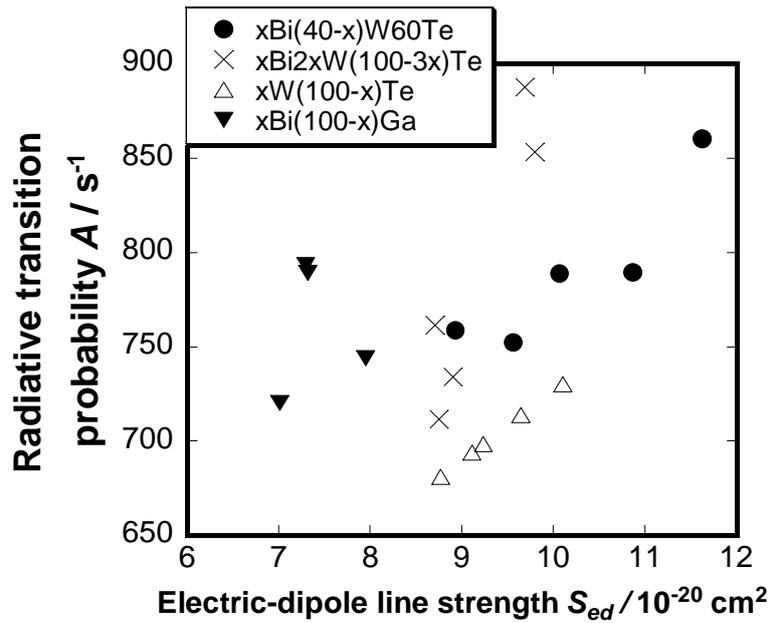


Fig. 8. Relation between electric-dipole line strength S_{ed} and radiative transition probability A (Pr: $^1G_4 \rightarrow ^3H_5$ transition).

Fig. 9 shows the correlation between A of Tm: $^3H_4 \rightarrow ^3F_4$ transition and n at 1460 nm. As for S_{ed} , a strong correlation to A is not confirmed, but a strong correlation was seen between n and A . 70Bi30Ga glass having the highest n showed the highest A .

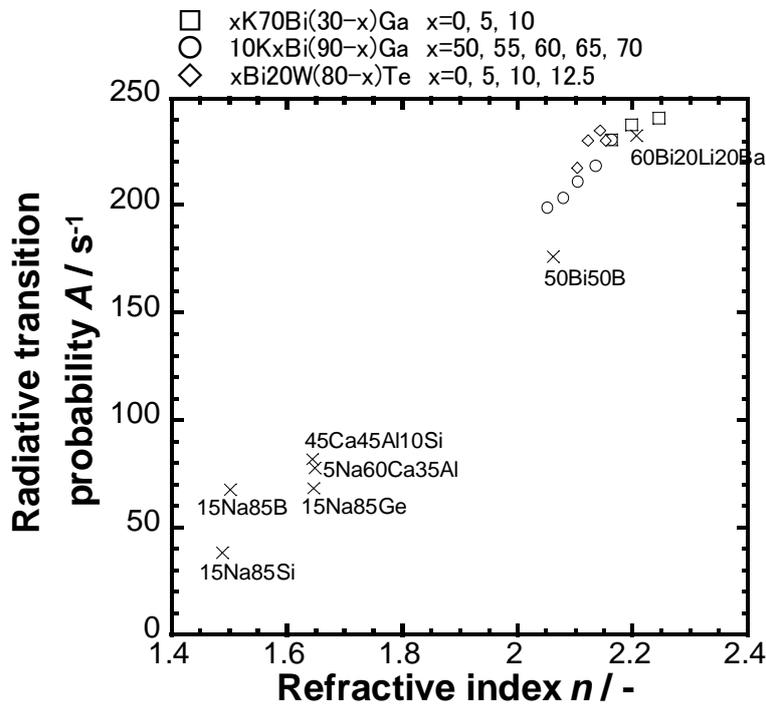


Fig. 9. Relation between refractive index n and radiative transition probability A (Tm: $^3H_4 \rightarrow ^3F_4$ transition).

Fluorescence spectra

Fig. 10 shows the fluorescence spectra of 0.1mol% Pr_2O_3 doped 75Bi25Ga glass and 0.1mol% Pr_2O_3 / 5.0mol% Yb_2O_3 co-doped 5Na20Zn75Te glass. The mechanism of 1.3 μm emission of $\text{Pr}^{3+}/\text{Yb}^{3+}$ -codoped is shown in Fig. 11. As shown in Fig.5, absorption from the ground state $^3\text{H}_4$ level to $^1\text{G}_4$ level in Pr^{3+} is very small. It is necessary to increase the population of $^1\text{G}_4$ level to obtain 1.3 μm emission, and the population of $^1\text{G}_4$ level should increase by using the absorption of Yb^{3+} . Due to the successful energy transfer of $\text{Yb}:^2\text{F}_{5/2} \rightarrow \text{Pr}:^1\text{G}_4$, the 1.3 μm emission of Pr occurred in 0.1mol% Pr_2O_3 doped 75Bi25Ga glass. However, the emission in Pr-Yb co-doped 5Na20Zn75Te glass is much larger than the Pr single doped glass (Fig. 10), indicating that the co-doping Yb with Pr enhances Pr: 1.3 μm emission extremely. The peaks at 1425 and 1480 nm are considered as the noise for the experimental equipments.

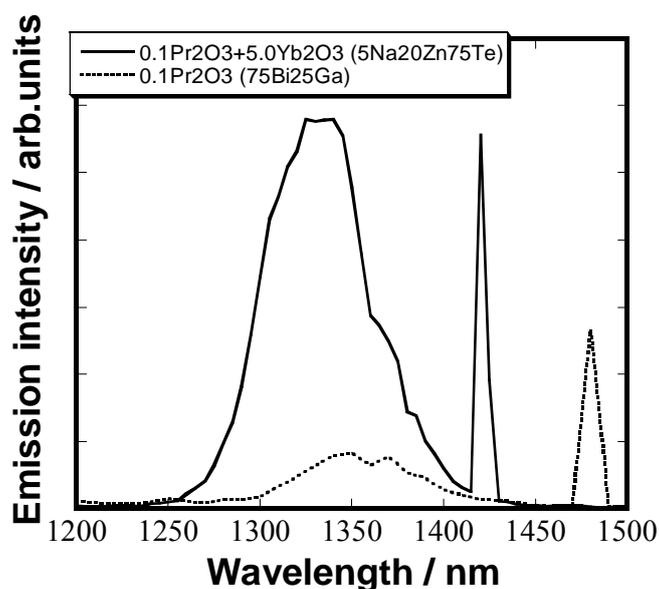


Fig. 10. Fluorescence spectra of Pr: $^1\text{G}_4 \rightarrow ^3\text{H}_5$ transition at 1.3 μm band in 0.1mol% Pr_2O_3 single-doped 75Bi25Ga glass and Pr/Yb codoped 5Na20Zn75Te glass.

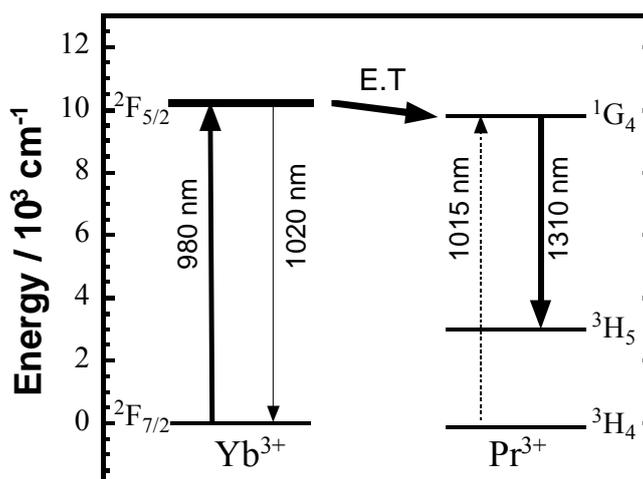


Fig. 11. Promotion mechanism of Pr: 1.3 μm emission by Yb \rightarrow Pr energy transfer.

Fig. 12 shows fluorescence spectra of x mol% ($x=0.1 - 1.0$) Tm_2O_3 doped 10K70Bi20Ga glasses. Tm: 1.46 μm emission is observed. With increasing Tm_2O_3 content, the 1.46 μm band increases in intensity, and it reaches to a saturation at $x=1.0$, which is probably due to the concentration quenching.

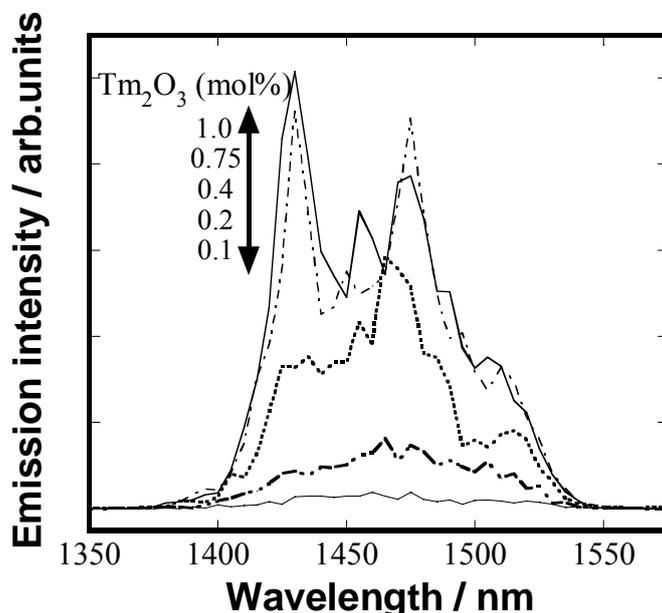


Fig. 12. Fluorescence spectra of Tm: $^3\text{H}_4 \rightarrow ^3\text{F}_4$ transition at 1.46 μm band in x mol% ($x = 0.1 - 1.0$) Tm_2O_3 doped 10K70Bi20Ga glasses.

CONCLUSION

The infrared emissions of Pr: 1.3 μm and Tm: 1.46 μm were confirmed in Bi_2O_3 glasses, which was due to the high refractive index and low phonon energy of the Bi_2O_3 glasses. According to the results from the Judd-Ofelt analyses, the radiative transition probability A of Pr: $^1\text{G}_4 \rightarrow ^3\text{H}_5$ transition was dependent on the refractive index n and the line strength of electric dipole transition S_{ed} . On the other hand, A of Tm: $^3\text{H}_4 \rightarrow ^3\text{F}_4$ transition mainly depended on n . Co-doping Yb with Pr successfully populated the Pr: $^1\text{G}_4$ level, and Pr: 1.3 μm emission intensity increased. In 10K70Bi25Ga glasses doped with Tm, it was confirmed that emission intensity of 1.46 μm band increased with increasing the Tm_2O_3 content.

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