

Development of Rare-Earth Doped Fiber Amplifiers for Broad Band Wavelength-Division-Multiplexing Telecommunication

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Rare-earth-doped novel oxide glass and glass ceramic materials for optical amplifiers were developed for WDM telecommunication and their spectroscopy and local structure were investigated. In a series of Er-doped glasses with broad 1.5 μm emission, heavy-metal oxide glasses were found to offer specific local environment to Er³⁺ ions. Potential of nano-glass ceramics for U-band amplifier is shown in a YAG precipitated silicate glass ceramic materials. Also, spectroscopic studies on optical properties of Tm³⁺-doped tellurite glasses are presented as candidate materials of S-band amplifier. The Judd-Ofelt analysis showed 96% quantum efficiency of 1.46 μm transition in a tellurite host, which has properties superior to fluoride fibers. Various possibilities of broadband amplifier materials in the system of rare-earth doped glasses are presented.

KEY WORD: optical amplifier, rare-earth, glass, erbium, thulium, optical fiber, telecommunication

1. Introduction

Due to rapid increase of information traffic and the need for flexible networks, there exists urgent demand for optical amplifiers with a wide and flat gain spectrum in the telecommunication window, to be used in the wavelength-division-multiplexing (WDM) network system¹⁾. After the invention of the Er-doped fiber amplifier (EDFA), various types of amplifier devices have been developed in order to broaden the telecommunication bandwidth in the WDM network^[P1]. Tm³⁺-doped and Pr³⁺-doped fluoride fiber amplifiers have been developed for the S-band and O-band applications, respectively. Long-term reliability of fluoride fibers is still an issue for practical use^[P2]. The Raman amplifier composed of conventional silica fiber is also becoming practical use in WDM system that requires small gain (~10dB) in broad wavelength range. The gain range and bandwidth can be controlled by the wavelength and configuration of pumps. However, the pump power required is very high compared with the rare-earth doped fiber amplifiers. Still the rare earth doped amplifiers can be promising in the practical system due to their high power conversion efficiency.

Most of the EDFA utilized at present is made of silica-based glass fiber, where doped Er³⁺ ions show narrow emission band at 1.55 μm resulting in narrow gain spectra. Following the report of wide spectra²⁾, Mori reported excellent performance of a tellurite based EDFA³⁾, which shows 80nm-wide gain around 1.53 ~ 1.61 μm . In order to increase the channels and to improve the performance of WDM network, it is important to investigate a material with wider gain spectra. We have reported that the Bi₂O₃-based borosilicate glass showed broad emission spectra of the 1.55 μm transition and large Ω_6 of Er³⁺ ion⁴⁾. In 2001, a group of Corning reported the MCS (multi-

component silicate) glass containing Sb₂O₃, which shows wider gain than the glasses⁵⁾. The important factor dominating the cross section and its bandwidth is the Judd-Ofelt Ω_6 parameter of Er³⁺ ions⁶⁾ as well as the refractive index. We also reported a strong correlation between the Ω_6 and the ionicity of Er-ligand bond in various glasses and its origin^{7,8)}. Therefore, it is interesting to investigate glass systems giving ionic ligand fields, which would attain a large Ω_6 .

In the first part of this paper, we report the optical properties of the oxide glass based on Sb₂O₃, in which Er³⁺ ions show very broad emission and the local structure of rare-earth ion in this glass. In the second part, possibility of U-band amplifier based on oxide glass ceramics is discussed and an example of Er:YAG glass ceramics is presented. The origin of energy level splitting of ^{2S+1}L_J multiplets of rare earth ions should be considered for spectral design. In the third part, we report spectroscopic studies on Tm-doped oxide glasses for an S-band amplifier^[P21]. At present, a fluoride fiber based TDFA is practically developed for S⁺-band amplifier. However, the chemical durability, long-term reliability of fluoride fiber is an issue to be solved. Also, the gain spectrum of Tm-doped fluoride fiber is a little bit narrow and there exists a gap between the C-band, which is covered by EDFA. We propose that the tellurite glass can be a more practical material.

2. Background

Optically or magnetically active rare earth (RE) ions are characterized by their 4f electrons in seven 4f-orbitals. In addition to the most stable electronic configurations (ground state), various configurations with excited higher energy are possible in the thirteen RE ions from Ce³⁺ to Yb³⁺ ion. The energy of these different electronic configurations is separated by the Coulomb interaction, the spin-orbit interaction and the ligand field interaction,

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resulting in the well-known energy level structures. The electronic transition generally becomes possible between most energy levels, the wavelength of which varies from ultraviolet to mid-infrared regions. It is a fundamental feature of rare earth ions that are utilized as a luminescent centers in many phosphor and laser materials. The wavelength of one of transitions in the Er^{3+} energy level happened to be about $1.55\mu\text{m}$: the telecommunication wavelength of optical fibers.

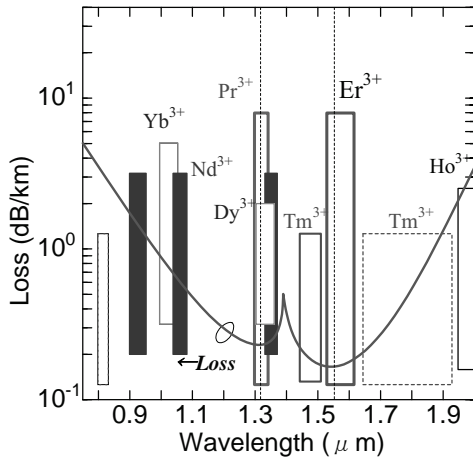


Fig.1. Loss characteristics of silica fiber and emission bands of some rare earth ions.

3. Er-Doped Sb_2O_3 -Glasses

3.1. Preparation and Characterization

Glasses in the composition of $x\text{Sb}_2\text{O}_3\text{-}3\text{Al}_2\text{O}_3\text{-}(97\text{-}x)\text{SiO}_2$ ($x=27,37,47,57,67$) doped with $0.5\text{mol}\%$ Er_2O_3 and those doped with $0.5\text{mol}\%$ Eu_2O_3 were prepared by melting mixed powders in an alumina crucible at $1100\sim 1450^\circ\text{C}$. The obtained glasses were cut into $15\times 10\times 3\text{mm}^3$ shape before polishing into optical surface.

Emission spectra were measured by using a 970nm laser diode (LD) and an InGaAs photodiode (160kHz). The lifetime of the $1.53\mu\text{m}$ emission was measured by pumping with light pulses of the LD and the time evolution of the signal of the detector was collected with a 100MHz digital oscilloscope. Decay curves were analyzed by a least-square fitting to get the lifetime.

The number of Er^{3+} ions in unit volume, ρ_N was calculated with the molecular weight and density. Density of the obtained glass was measured by the Archimedes method using kerosene as an immersion liquid. The refractive index, $n(\lambda)$ was measured by a prism coupling method at wavelength of 633nm , 1304nm and 1550nm . Absorption spectra were measured in $400\text{nm}\sim 1700\text{nm}$ with Shimadzu UV-3101PC spectrophotometer. With an integrated area of the absorption band, spontaneous emission probability, A of the $1.5\mu\text{m}$ was calculated by,

$$A(J \rightarrow J') = \frac{(2J + 1)8\pi c n^2}{(2J' + 1)\lambda^4} \times \int_{0.4\mu\text{m}}^{1.7\mu\text{m}} \frac{k(\lambda)}{\rho_N} d\lambda \quad (1)$$

where c is the light velocity, λ is the mean wavelength of emission, J and J' are the total momentum for the upper and lower levels, $k(\lambda)$ is the absorption coefficient, and n was the refractive index at wavelength of 1530nm .

The Judd-Ofelt parameters of Er^{3+} ions were calculated by the method described elsewhere⁹⁾ with cross sections of five intense bands ($^4\text{F}_{7/2}$, $^2\text{H}_{11/2} + ^4\text{S}_{3/2}$, $^4\text{F}_{9/2}$, $^4\text{I}_{11/2}$, $^4\text{I}_{13/2}$) in $470\text{nm}\sim 1700\text{nm}$.

The excitation spectra of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ emission at 613nm of Eu^{3+} doped glasses was measured in the range of $440\sim 470\text{nm}$. The phonon sideband associated with the pure electronic the $^5\text{D}_2 \leftarrow ^7\text{F}_0$ transition 465nm was multiplied by 50 times to investigate the phonon mode coupled to rare-earth ions¹⁰⁾, which contributes to multiphonon relaxation.

3.2. Properties of Glass and Spectroscopy of Rare Earth Ions

Fig.2 shows the compositional dependence of refractive index, $n(\lambda)$ of the glasses at 633nm and 1550nm increased with decreasing wavelength. The n of the $x\text{Sb}_2\text{O}_3\text{-}3\text{Al}_2\text{O}_3\text{-}(97\text{-}x)\text{SiO}_2$ glasses (in mol%) at $1.55\mu\text{m}$ was $1.66\sim 1.90$, which increased with increasing Sb_2O_3 content.

Fig.3 shows emission spectra of the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ of Er^{3+}

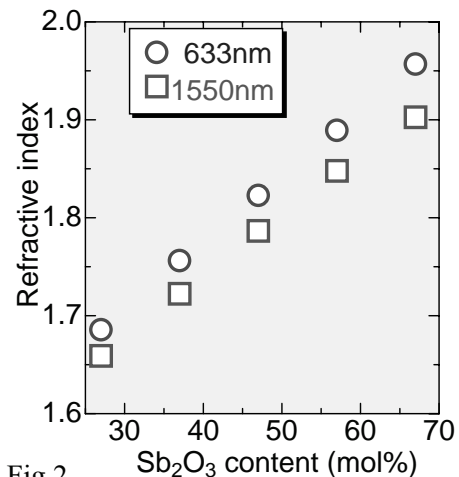


Fig.2 Compositional dependence of refractive index in $x\text{Sb}_2\text{O}_3 \cdot (97\text{-}x)\text{SiO}_2 \cdot 3\text{Al}_2\text{O}_3 \cdot 0.5\text{Er}_2\text{O}_3$ glasses

ions in the $x\text{Sb}_2\text{O}_3\text{-}3\text{Al}_2\text{O}_3\text{-}(97\text{-}x)\text{SiO}_2$ glasses, in the $75\text{TeO}_2\text{-}20\text{ZnO}\text{-}5\text{Na}_2\text{O}\text{-}0.5\text{Er}_2\text{O}_3$ and in the $95\text{SiO}_2\text{-}5\text{GeO}_2\text{-}0.5\text{Er}_2\text{O}_3$ as a reference. The spectrum of the silica shows the narrowest bandwidth of about 30nm and that of the tellurite was 60nm -width. It is seen that the Sb_2O_3 -based glasses show spectra comparable or broader than that of the tellurite. Fig.4 shows the compositional dependence of fluorescence lifetime, τ_f of the $^4\text{I}_{13/2}$ level in the $x\text{Sb}_2\text{O}_3\text{-}$

3Al₂O₃-(97-x) SiO₂-0.5 Er₂O₃ glasses. In the range of Sb₂O₃ content x=37-67, the fluorescence lifetimes of the ⁴I_{13/2} level were almost unchanged, and about 2.5ms, whereas in the Sb₂O₃ content x=27, the lifetime was dramatically decreased.

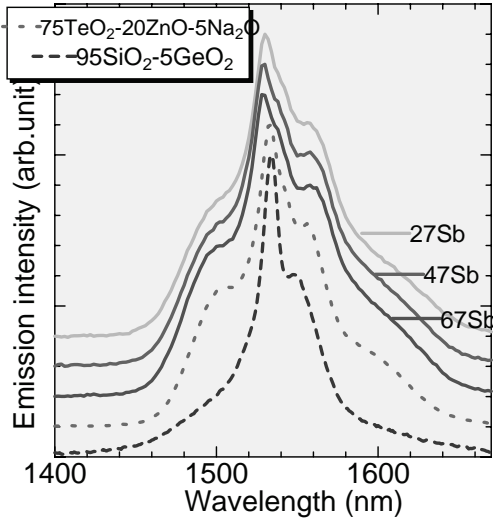


Fig.2. Fluorescence spectra of xSb₂O₃ · (97-x)SiO₂ · 3Al₂O₃ · 0.5Er₂O₃ glasses.

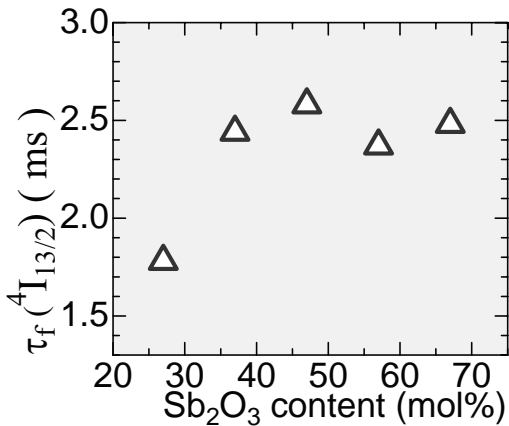


Fig.4 Compositional dependence of lifetime of Er³⁺: ⁴I_{13/2} level in glasses.

The excitation spectrum associated with the Eu³⁺: ⁵D₂←⁷F₀ transition for the xSb₂O₃- 3Al₂O₃-(97-x) SiO₂-0.5 Er₂O₃ glasses are shown in Fig.5. The intense band due to the pure electronic transition (PET) Eu³⁺: ⁵D₂←⁷F₀ transition is located around 464nm, while the phonon sideband (PSB) coupled to the rare earth ions is observed in the higher-energy range¹⁰. The position and shape of the phonon sideband were almost unchanged with Sb₂O₃ content.

3.3. Local Structure of Rare Earth Ions in Sb₂O₃-Glass

Fig.6 shows the calculated spontaneous emission probability, A of the ⁴I_{13/2}→⁴I_{15/2} in the xSb₂O₃- 3Al₂O₃-

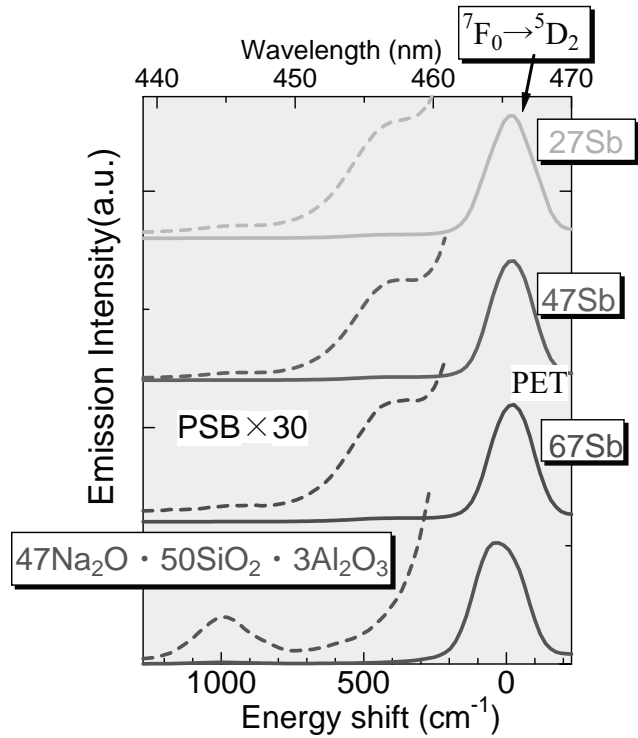


Fig.5. Excitation spectra of Eu³⁺-doped glasses. Phonon sideband can be observed in the higher-energy- side of ⁵D₂←⁷F₀ transition.

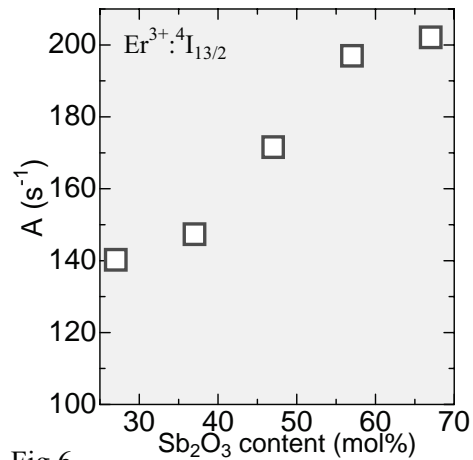


Fig.6 Compositional dependence of spontaneous emission rate of Er³⁺: ⁴I_{13/2} in xSb₂O₃-(97-x)SiO₂-3Al₂O₃-0.5Er₂O₃ glasses.

(97-x) SiO₂-0.5 Er₂O₃ glasses. The A also increased with increasing x, being nearly 200 s⁻¹. The large A is mainly due to large n of the host glasses, which are composed of large amount of Sb³⁺ ion, a p-block element of 5s² electrons having large polarizability¹¹.

With the measured lifetime and A_{JJ'} from Eq.(1), radiative quantum efficiency, η, were calculated by

$$\eta = \frac{\sum A}{\sum A + \sum W_{NR}} = \tau_f \sum A \quad (2)$$

and plotted in Fig.7. Reflecting the compositional variations of $A_{JJ'}$, the η increases with increasing Sb_2O_3 content, x . The η values are relatively small compared with those of EDFA's ever reported, but still much larger than that of Pr-doped fiber amplifiers (4%), which perform large gain at $1.3\mu\text{m}^{12}$. These low values obtained may be due to lower estimation of real local refractive index, i.e., deviation from measured average index. This can be related with no compositional dependence of the local phonon energy obtained from phonon sideband spectra.

Fig.8 shows the compositional dependence of the Judd-Ofelt parameters obtained by using the five electric-dipole bands. It is seen that the Ω_6 values were almost unchanged with Sb_2O_3 content. These results suggest that the Er^{3+} ions are surrounded selectively by Sb_2O_3 -rich phase. Generally the A of the ${}^4\text{I}_{13/2}$ - ${}^4\text{I}_{15/2}$ band is related with the line strengths, S of electric-dipole (ED) and magnetic-dipole (MD) components by¹³,

$$A_{JJ'} = \frac{64\pi^4 e^2}{3h(2J'+1)\lambda^3} \left\{ \frac{n(n^2+2)^2}{9} \times S_{JJ'}^{ED} + n^3 \times S_{JJ'}^{MD} \right\} \quad (3)$$

where e is the elementary charge, h is the Planck constant. The MD transition is independent of the ligand field and

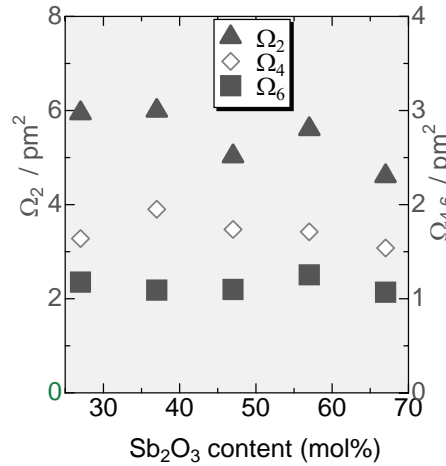
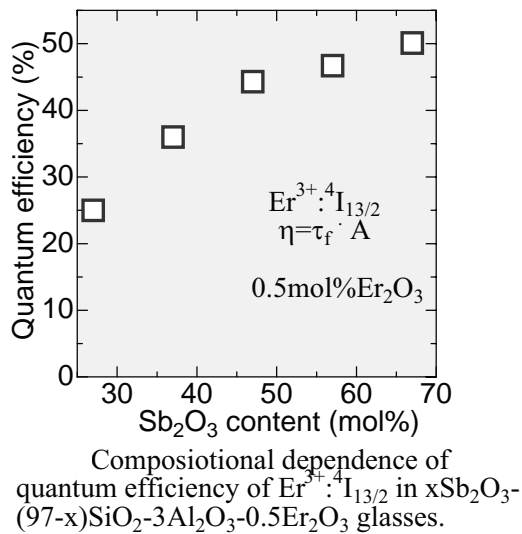


Fig.8. Compositional dependence of Judd-Ofelt Ω_i parameters of Er^{3+} ions

Fig.9. Compositional dependence of vibration phonon energy from PSB spectra.

contributes to a sharp central peak of spectra around $1.53\mu\text{m}$. Because the S^{MD} is characteristic only to the transition determined by the quantum numbers¹⁴, one of the important factors affecting the compositional variations of the emission properties is the ED transition. The S^{ED} of the ${}^4\text{I}_{13/2}$ - ${}^4\text{I}_{15/2}$ is obtained with the Judd-Ofelt parameters and reduced matrix elements by^{15,16},

$$S^{ed} [{}^4\text{I}_{13/2}; {}^4\text{I}_{15/2}] = 0.019\Omega_2 + 0.118\Omega_4 + 1.462\Omega_6 \quad (4)$$

According to Eq.(4), the Ω_6 plays the most dominant role on the cross section of the $1.5\mu\text{m}$ band among three Ω_i 's. Thus in order to increase the bandwidth of spectra, which

is varied with local structure, the increase of the Ω_6 would be effective, because the ED contributes to broader component of the $1.5\mu\text{m}$ band¹⁶. The large Ω_6 value and refractive index may contribute to broad bandwidth in these glasses.

Fig.9 shows the compositional dependence of the phonon energy, $h\omega$ obtained from the wavelength of the phonon sideband and that of the pure electronic transition.

The phonon energy was found to be about 400cm^{-1} in all the compositions up to 70mol% SiO_2 content. Usually in most silicate glasses, the Si-O stretching mode is coupled to the rare earth ions even in low SiO_2 composition. The present results are in contrast to the above facts and thus suggest that the Er^{3+} ions are surrounded selectively by Sb_2O_3 -rich phase and are not affected by Si-O with about 1000cm^{-1} energy

3.4. Origin of “Non-silicate” environment

Fig.10 show the TEM image and a structural model of the glass, where the nano-scale phase separation can be observed. The dark region can be Sb_2O_3 -rich phase and the other can be SiO_2 -rich phase. Since the solubility of rare earth ions in a pure silica or silica-rich glass is very low¹⁷⁾, Er^{3+} ions can be condensed in the Sb_2O_3 -rich phase, as indicated in the spectroscopic results mentioned above. The concentration dependence of lifetime of $\text{Er}^{3+}:^4\text{I}_{13/2}$ shows more rapid decrease in a Sb_2O_3 -poor composition, indicating that Er^{3+} ions are more condensed. The tendency is moderate in glasses with Sb_2O_3 -rich compositions.

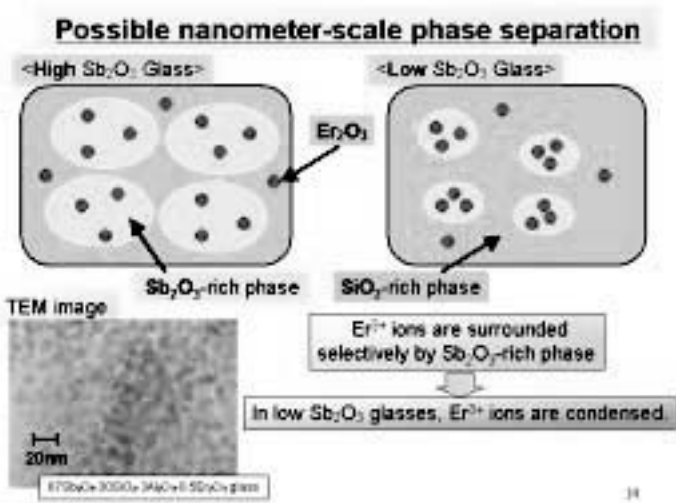


Fig.10. TEM image of the glass and a structural model of nano-scale phase separation.

4. Potential Materials for U-band Amplifier

4.1. Rare earth candidates for 1.6μm emission

Two rare earth ions have been reported to show emission in the U-band wavelength range. Choi reported 1.6μm emission for the $\text{Pr}^{3+}:^4\text{F}_{3,4} \rightarrow ^3\text{H}_4$ in a selenide glass¹⁸⁾ and Lee reported the $\text{Ho}^{3+}:^5\text{I}_5 \rightarrow ^5\text{I}_7$ transition in a sulfide glass¹⁹⁾. Fig.11 shows the energy level diagrams of candidate ions with 1.6μm transition^[P22]. As can be seen from Fig.11, the energy gap of the $\text{Pr}^{3+}:^4\text{F}_{3,4}$ and $\text{Ho}^{3+}:^5\text{I}_5$ are 1400 cm^{-1} and 2500 cm^{-1} ,

respectively. The gain efficiency of amplifiers is dominated by the quantum efficiency of the initial level, which is largely dependent on the multiphonon decay loss. For the levels with the energy gap to the next lower level, ΔE is 3000 cm^{-1} , oxide glasses with phonon energy, $\hbar\omega$, higher than 600 cm^{-1} cannot be a practical host with good efficiency, because the multiphonon decay rate, W_p increases drastically when $\Delta E/\hbar\omega$ is less than 5. In the case of U-band emissions for Pr^{3+} and Ho^{3+} , even the phonon energy of typical fluoride glasses such as ZBLAN (~500 cm^{-1}) is too high to suppress the nonradiative loss. That is the main reason why the 1.6μm emission is reported only in chalcogenide glasses, $\hbar\omega$ of which is less than 400 cm^{-1} . However, the fiberizability and reliability of nonoxide glasses are issue for practical application. On the other hand, ΔE of the $\text{Er}^{3+}:^4\text{I}_{13/2}$ is 6500 cm^{-1} , large enough to obtain quantum efficiency over 90% even in oxide hosts with high phonon energy.

4.2. Do we really know spectra of Er^{3+} ?

In addition to the C-band and L-band EDFA, the S-band EDFA was reported in a conventional silica-based EDF²⁰⁾. It requires a special and tricky pumping configuration with several C-band ASE-suppression filters and much higher pumping power is required than normal EDFAs for the C+L band. Due to the energy distribution, mainly to the Stark level structure of major Er^{3+} ions in glasses, most of glass-based EDFAs usually cover only C+L-band (1520~1610nm) by normal pumping scheme.

Fig.12 shows the origin of spectral broadening due to energy level splitting of $^{2S+1}\text{L}_J$ state of lanthanide ions in crystalline ligand field and in disorderd solids. In a crystalline host, depending on its structure, a unique ligand

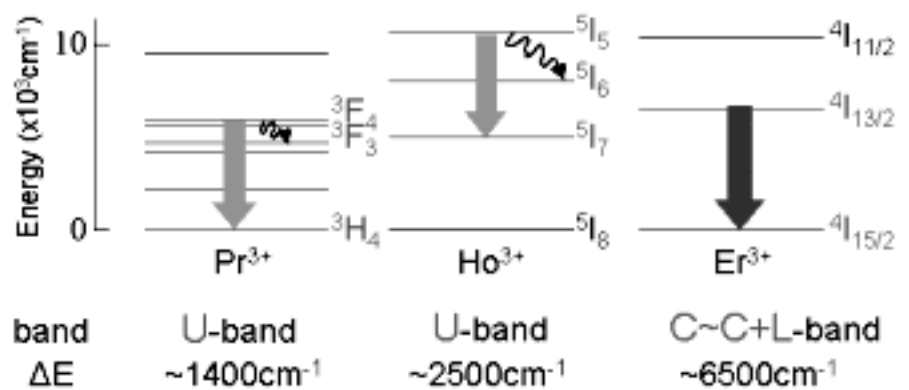


Fig.11 . Energy level diagrams of Pr^{3+} , Ho^{3+} , and Er^{3+} ions. The energy gap of the initial level of 1.6μm emission is also shown.

field can be expected for anomalous Stark splitting. Possibility of homogeneous doping of Er^{3+} ions in crystals is determined by the availability of crystallographic sites suitable for lanthanide substitution. Crystals composed of Y^{3+} , La^{3+} or Gd^{3+} ions, such as yttrium aluminum garnet, YAG, can accommodate substantial amount of other optically 4f-active lanthanide ions in the rare earth site. The spectral shape of doped crystals usually become discrete, while those of doped glasses are continuously broadened. The spectral features of glasses are advantageous for obtaining a flat gain spectrum as a WDM amplifier, but we might not be able to expect anomalous Stark splitting for Er^{3+} ions, since the absence of structural restriction of the crystallographic site in glass may usually result in well-observed “averaged” spectrum centered at 1530nm.

with Ca^{2+} and Si^{4+} at octahedral and tetrahedral sites, respectively. Er^{3+} ions can substitute the Y^{3+} site, the structural configuration of the second nearest cations around which can be varied in the solid solution. This variation results in variation of the ligand field based on the eight nearest oxygen ions and thus can lead to the inhomogeneous broadening of spectra. Our glass ceramics is a $CaO-Y_2O_3-Al_2O_3-SiO_2$ system, in which the Er:YAG phase contains a certain amount of Ca^{2+} and Si^{4+} [P22]. As shown in Fig.14, the emission spectra of the glass ceramics are slightly broadened compared with that of Er:YAG crystal. More detailed studies are necessary to clarify the effect of nano-sized crystals and solid solution on the inhomogeneous broadening of emission spectra [P4].

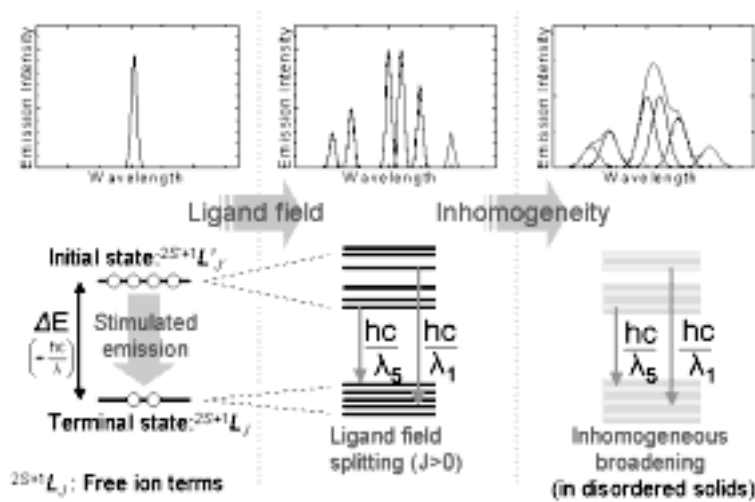


Fig.12 Origin of spectral broadening due to energy level splitting of $^{2S+1}L_J$ state of lanthanide ions in crystalline ligand field and in disordered solids.

4.3. Line Broadening in Er:YAG Glass Ceramics

In 2003, we have reported the U-band emission in a glass ceramics containing Er:YAG [P22]. Fig.13 shows the comparison of $Er^{3+}: ^4I_{13/2} \rightarrow ^4I_{15/2}$ emission in glasses and YAG crystal. Due to its unique Stark level structure, the emission bands are observed in the U-band range. Sharp spectral bands can be moderated by introducing inhomogeneity to the Y^{3+} -site in disordered structure by means of formation of solid solution. The $Ca_3Al_2(SiO_4)_3$ crystal has a cubic garnet structure, the lattice constant of which is only 1% different ($a_0=11.849A$) from that of cubic YAG ($a_0=12.009A$). Solid solution can be formed in the composition $Y_{3-x}Ca_xAl_{5-x}Si_xO_{12}$. Charge neutrality is maintained by substitution of same amount of Y^{3+} and Al^{3+}

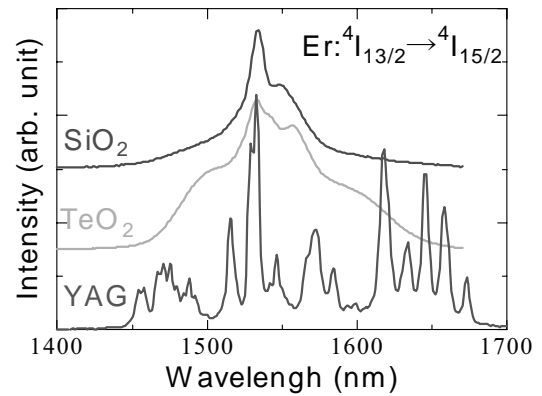


Fig.13. Emission spectra of Er^{3+} in glasses and YAG crystal.

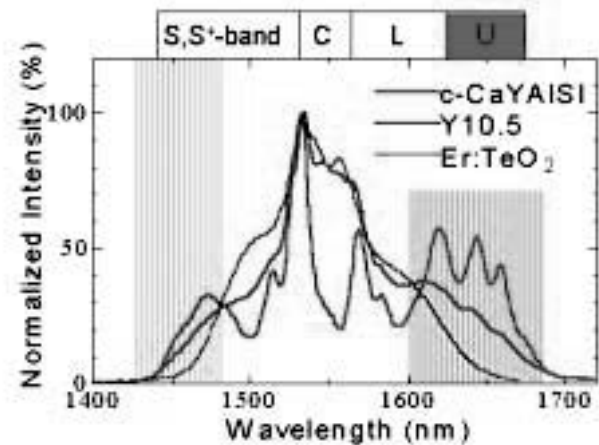


Fig.14. Emission spectra of Er:YAG glass ceramics and a tellurite glass.

5. Tm-doped glasses for S-band amplifier

5.1. Optical Transitions in Tm³⁺ ion

Because the silica-based transmission fiber has a wide window from 1.4μm to 1.65μm, there is emergent demand for optical amplifiers, which can be used around 1.4μm and 1.6μm, in addition to the present silica-based Er-doped fiber amplifiers (EDFA). Tellurite-based EDFA was reported to have 80nm-wide gain up to 1.6μm (L-band), which also shows various excellent material properties³. For the 1.45~1.49μm band (S⁺-band), the fluoride-based Tm-doped fiber (TDF)²¹ can be used as an amplifier, although it still presents difficulties compared with the use of EDFA. One of the reasons for inferior performance of TDFA is the longer lifetime of the terminal ³F₄ level than that of the initial ³H₄ level²². The performance of the TDFA is improved by use of an upconversion-pumping scheme with a 1.06μm laser, which produces a population inversion²². Codoping of other lanthanide ion, such as Ho³⁺, was also found to improve the population inversion by means of the energy transfer from the ³F₄ level²³. In addition, a larger branching ratio, β of the ³H₄→³H₆ band at 0.80μm than that of the 1.45μm make it difficult to realize amplification, because the fiber can easily lase at 0.80μm, resulting in the gain saturation²⁴. According to the Judd-Ofelt calculation, β of 0.80μm is nearly 90%, which is 11 times larger than that of 1.46μm emission in most glasses^{25,26}. Therefore, the suppression of the 0.80μm amplified spontaneous emission (ASE) is important to avoid lasing at unexpected wavelength for improving the amplifier performance. In either case, in spite of difficulty as practical materials, non-oxide fiber hosts with lower phonon energy have been used, because the ³H₄ level is more easily quenched in high-phonon-energy environment due to its small energy gap. However, the energy gap of the ³H₄ level is not so small as that of the Pr:¹G₄ for 1.3μm amplifiers and thus good performance can be expected in some oxide hosts with low phonon energy and better fiberizability.

In this study, the tellurite glass was chosen as a host because it has relatively low phonon energy, excellent properties for fiber fabrications^{3,27}[P21] and thus considered as a candidate material for TDFA.

5.2. Glass preparation and measurements

Glasses in the composition of 72TeO₂-20ZnO- 5Na₂O-3Ln₂O₃ (3Ln=(3-x)Y+xTm, (2.9-y) Y + 0.1Tm + yHo, Tb, or Eu) were prepared. High-purity (99.999%) starting oxide and carbonate materials were mixed and melted in a gold crucible at 900°C for 45 minutes, then poured into preheated stainless-steel molds and annealed around glass transition temperature for 2 hours. The samples were cut and polished into 10x10x2mm³.

Absorption spectra were measured with a Shimadzu

UV-3101PC Spectrophotometer in the range of 300~2200 nm. The Judd-Ofelt analysis was done with absorption cross sections of four electric-dipole transitions to obtain three Ω_t parameters (t=2,4,6), which were used to calculate the spontaneous emission probabilities, A and the branching ratios, β from the ³H₄ level.

Emission spectra were measured by using a 792nm laser diode, LD, (Sony 304XT) and a monochromator (Nikon-G250) from 700nm to 2300nm. InGaAs and PbS photodiodes were used as a detector. The sensitivity calibration of this measurement system was done with the spectra of a standard halogen lamp to evaluate the branching ratio of bands of Tm³⁺ at separated wavelengths. For the lifetime measurement, the LD was electrically modulated to get short pulses and the luminescence decay curves were recorded with a digital storage oscilloscope (LeCroy, LS140, 100MHz) to calculate the lifetime by least-square-fitting with a single or double exponential function. In the fluorescence measurement the sample temperature was controlled from 15K to 300K with a helium-cycling cryostat (Iwatani Plantec Co., TCU4).

5.3. Spectroscopy of Singly Doped Glass

5.3.1. Fluorescence spectra

Figure 15 show the Tm³⁺ energy level and related fluorescence transitions, excited by 790nm. The emission bands at 0.80μm, 1.46μm, and 1.80μm are due to the ³H₄→³H₆, ³H₄→³F₄, and ³F₄→³H₆, respectively. The wavelength region longer than 1.3μm is multiplied by 30 times. The relative intensity ratio of 0.80μm to 1.46μm was about 11, almost unchanged with glass compositions and Tm-concentration. On the other hand, that of 1.46μm to 1.80μm was largely changed with these factors, which is due to the effect of the nonradiative relaxations.

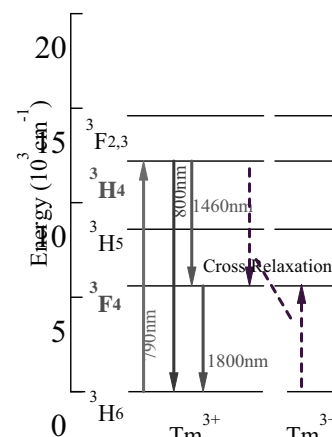


Fig.15. Energy level of Tm³⁺ ion.

5.3.2. Judd-Ofelt analysis and quantum efficiency in tellurite

The obtained Judd-Ofelt parameters of Tm³⁺ in the

present glass were; $\Omega_2= 4.69\text{pm}^2$, $\Omega_4=1.83\text{pm}^2$, $\Omega_6 = 1.14\text{pm}^2$. According to our calculations of spontaneous emission probabilities, A and β , from the $^3\text{H}_4$ level of Tm^{3+} ions in the tellurite glass, the β of $0.80\mu\text{m}$ emission is 11 times larger than that of $1.4\mu\text{m}$ emission, which is almost similar to the case in fluoride and other oxide glasses. The calculated τ_R was $366\mu\text{s}$, while the measured lifetime was $350\mu\text{s}$. This indicates that the quantum efficiency of the $^3\text{H}_4$ level is 96% in tellurite glass, which is comparable to that in ZrF_4 -based fluoride glasses ($\sim 100\%$).

5.3.3. Concentration dependence of emission

Figure 16 shows the Tm_2O_3 - concentration dependence of ratios of the $\tau_f(^3\text{F}_4)/\tau_f(^3\text{H}_4)$ and the integrated intensity of $(1.80\mu\text{m})/(1.46\mu\text{m})$ of fluorescence spectra. Both ratios increase drastically with increasing Tm_2O_3 content. These phenomena are well understood by so-called "Two-for-One process"^[P21], which is a result of the cross relaxation between two Tm^{3+} ions; $[^3\text{H}_4, ^3\text{H}_6] \rightarrow [^3\text{F}_4, ^3\text{F}_4]$ and unfavorable for population inversion between the $^3\text{H}_4$ and $^3\text{F}_4$ levels. Therefore, a low concentration is desirable to keep a high quantum efficiency of the $^3\text{H}_4$ level for $1.4\mu\text{m}$ application.

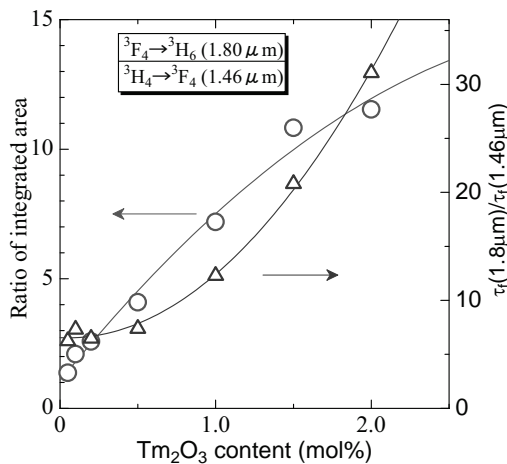


Fig.16. Tm-concentration dependence of ratio of integrated intensity and lifetime of $1.4\mu\text{m}/1.8\mu\text{m}$ emissions.

5.3.4. Temperature dependence of spectra

Figure 17 shows temperature variation of the fluorescence spectra. The peak intensity of the $1.46\mu\text{m}$ - band increases with lowering temperature, while the line shape of the $1.8\mu\text{m}$ -band becomes sharp. It can be seen that the mean wavelength of both bands shift to the longer side. The temperature dependence of integrated intensities of both bands are plotted in Fig.18. The integrated area of the $1.46\mu\text{m}$ - band is almost unchanged at lower temperature and drops with temperature above 150K . On

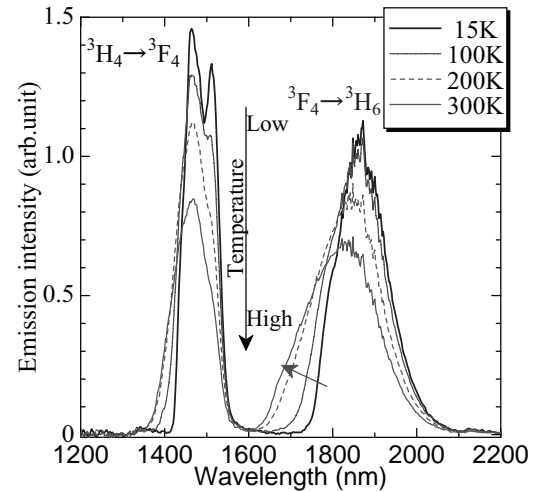


Fig.17. Temperature variation of emission spectra of a Tm-doped tellurite glass

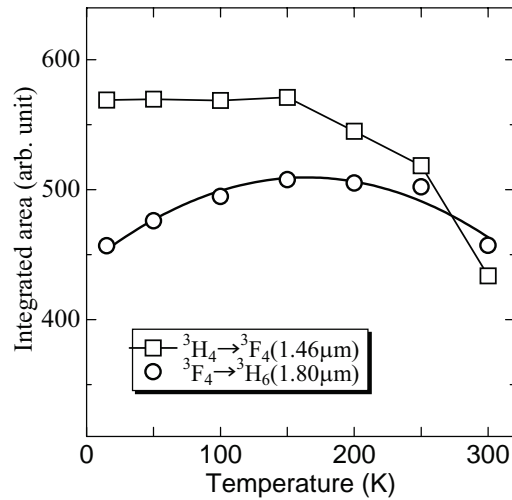


Fig.18. Temperature dependence of emission intensity of $1.46\mu\text{m}$ and $1.80\mu\text{m}$ in a Tm-doped tellurite glass

the other hand, that of the $1.8\mu\text{m}$ -band increases slightly and decreases above 250K . The tendency of the $1.46\mu\text{m}$ emission can be explained by considering the temperature dependence of the nonradiative decay from the $^3\text{H}_4$ level, which has smaller energy gap to the next lower level. The increasing tendency of the $1.8\mu\text{m}$ -band is ascribed to the improved population from the upper level by nonradiative processes. Therefore, the lower the temperature is, the better the population inversion becomes. Another advantage of the lower temperature can be the much improved intensity at $1.50\sim 1.52\mu\text{m}$, which is hardly obtained by conventional EDFA, though not impossible by T DFA²⁸⁾.

5.4. Effect of Codoping of Ho, Tb, Eu

Several studies on the codoping of other lanthanide ions in the Tm-doped fluoride glass have been carried out by

several authors^{25),29-31)}. The role expected for a codopant is to quench the 3F_4 level selectively without quenching the 3H_4 level. From this viewpoint, the Eu^{3+} , Tb^{3+} and Ho^{3+} can be a candidate among thirteen 4f-active lanthanide ions. The energy level diagrams of these ions are shown in Fig.19.

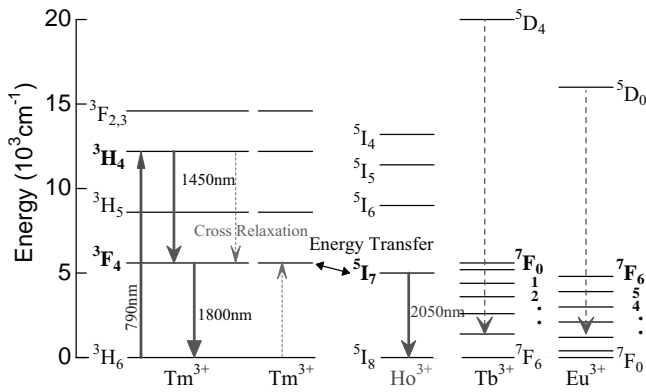


Fig.19. Energy level of Tm^{3+} , Ho^{3+} , Tb^{3+} , and Eu^{3+} ions

The Ln-concentration dependence of the lifetimes of the $Tm^{3+}:^3H_4$ and 3F_4 levels are plotted in Fig.20. Among three codopants, the Eu^{3+} ion quenches both levels most significantly and the Ho^{3+} ion shows the best selectivity; i.e., the least effect on the 3H_4 lifetime with a large quenching effect on the 3F_4 .

The variation of the fluorescence spectra of Tm-Ho codoped tellurite glasses are shown in Fig.21. The spectra are normalized by the intensity of 1.46 μ m-band, because it showed the least change. We see a drastic decrease of the 1.8 μ m-band and a rapid increase of the

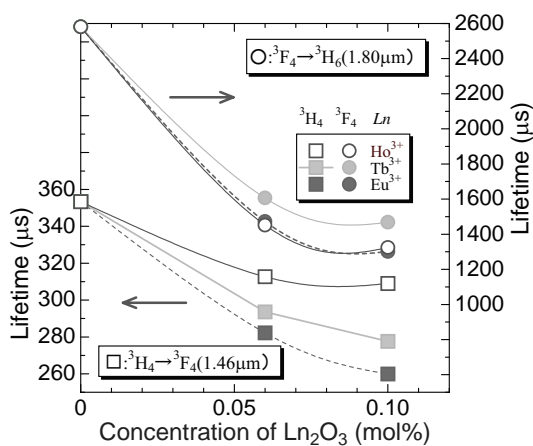


Fig.20. Effect of codopants on lifetimes of Tm-levels in tellurite glasses

$Ho^{3+}:^5I_7 \rightarrow ^5I_8$ emission intensity at 2 μ m. This result is an evidence of the $Tm: ^3F_4 \rightarrow Ho: ^5I_7$ energy transfer, which can contribute to the population inversion.

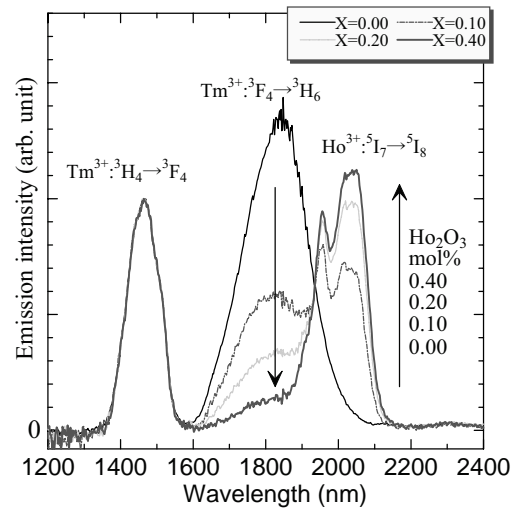


Fig.21. Variation of emission spectra of Tm-Ho-codoped tellurite glasses.

Conclusions

The Sb_2O_3 -silicate glasses offers specific local environment to RE ions and shows broad emission spectra of 1.5 μ m with a large cross section of Er^{3+} ions. It is suggested that the nano-scale phase separation exist in these glasses and the Er ions are selectively condensed in the Sb_2O_3 -rich phase. In the YAG-glass ceramics, Er^{3+} ions show U-band emission, the bandwidth of which became broader than that in a bulk crystal. The Tm^{3+} -doped tellurite glasses can be a potential candidate for an S-band amplifier as an oxide glass fiber.

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