Novel Photonic Glasses for Fiber-Optic Amplifiers

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ABSTRACT

Development of novel glass hosts for the fiber-optic amplifiers was introduced with a special attention on the O-band amplifiers operating at 1.31μm. Upon the addition of alkali halide (especially CsBr) into Ge-Ga-S glasses, the intensity of the 1.31 μm emission from Dy^{3+} ($^6F_{11/2}$.$^6H_{9/2}$→$^6H_{15/2}$) increased sharply at the expense of the 1.75 μm emission intensity ($^6H_{11/2}$→$^6H_{15/2}$). The lifetimes of the 1.31 μm emission level also increased up to 1580 μs. The nearest neighbors of Eu^{3+} ions, or rare-earth ions in this glass, are composed of halogen ions that are part of well-structured complex such as tetrahedral $[GaS_{3/2}Br]^-$ subunit and/or Ga_2Br_6. Similar enhancement in the emission properties was also observed in Tm^{3+} and Ho^{3+}-doped glasses with the addition of an appropriate amount of CsBr into sulfide glasses.

1. Introduction

Commercial success of fiber-optic telecommunication using erbium-doped fiber-optic amplifiers (EDFA) at the 1.55μm-wavelength band has realized the worldwide optical communication network [1]. However, explosion in the amount of information drove the transmission capability of the current 1.55μm window to the limit even with state-of-art dense wavelength division multiplexing (DWDM) techniques. As a result, commercial services using wavelengths other than 1.55μm band (C-band:1530-1565nm) have to be established. There are several bands identified within the wavelength region where silica glass fibers show attenuation losses low enough to be used. They are O-band (1290-1330nm), S-band (1460-1530nm), L-band (1565-1625nm) and U-band (1625-1675nm). All these bands offer

opportunities as optical communication window if one can identify efficient and economical ways of signal amplification.

2. Glasses for the New Communication Bands

One of the most important steps for the development of new amplifiers is the identification of proper rare-earth ions that can emit the fluorescence at the wavelength of interest. In fact, many rare-earth ions have already been known for each proposed communication band. For example, Pr^{3+} and Dy^{3+} ions can provide emissions for O-band [2,3] while Tm^{3+} ions are the most promising active ions for the S-band amplification [4]. In addition, Pr^{3+} and Ho^{3+} also provide potentials for the U-band amplifiers [5,6]. However, one of the most serious difficulties associated with all these rare-earth ions is existence of the strong multiphonon relaxation (MPR) from the upper emission level. Therefore, one needs to use host glasses with low phonon vibration energy to decrease the coupling of the lattice vibration with the f-f transition in activator ions. In this respect, glasses other than conventional SiO_2- or B_2O_3-based ones need to be used as host materials of rare-earth ions. Specific examples associated with Pr^{3+} and Dy^{3+} are provided as follows.

Pr^{3+} can provide 1.31μm emission from the Pr^{3+}:$^1G_4 \rightarrow {}^3H_5$ transition [2], but this transition suffers from large multiphonon relaxation (MPR) that degrades the efficiency of the 1.31 μm fluorescence. This is due to the small energy separation (ΔE) of ~3300cm^{-1} between the emission level and the one located immediately below. Dy^{3+} also emits fluorescence from the $^6F_{11/2}$.$^6H_{9/2} \rightarrow {}^6H_{15/2}$ transition that is useful for this communication window [3]. A stimulated emission cross-section of this transition (4.35×10^{-20} cm^2) in sulfide glass matrix is approximately 4-times larger than the value of a similar transition in Pr^{3+} [2]. Again, the value of ΔE is only 1850cm^{-1} and as a result, the measured lifetime of the emission level is only about 38 μs with a quantum efficiency of 17% [3]. This is approximately one tenth of the lifetime of the $^1G_4$ level in Pr^{3+}.

Several candidate materials have been considered as hosts for these rare-earth ions. First group of materials are mainly rather uncommon oxide glasses such as tellurites and heavy metal oxides with their highest phonon vibration frequency of ~700cm^{-1} and 500cm^{-1}, respectively [7]. These numbers are well below than that of conventional silicate or borate glasses which are in excess of 1100cm^{-1}. The other group of glasses is non-oxide glasses including heavy metal fluoride and

chalcogenide glasses. They can provide far reduced phonon-coupling strength compared to oxide glasses explained previously. The highest phonon vibration frequencies are ~475cm^{-1} and 350cm^{-1} in fluorides and sulfides, respectively. This paper will briefly introduce the development of new host glasses for amplifiers at the new communication bands with a special emphasis on the O-band amplifier materials doped with Dy^{3+} ions.

3. Novel Glasses for the 1.3 μm Amplification

3. 1. Glass compositions

To secure the high rare-earth solubility and good glass-forming ability, glasses were selected along the stoichiometric line of GeS_2 and Ga_2S_3 [8]. Three compositions, $Ge_{0.29}Ga_{0.05}S_{0.66}$, $Ge_{0.25}Ga_{0.10}S_{0.65}$ and $Ge_{0.18}Ga_{0.18}S_{0.64}$, in atomic fraction were used as starting glasses and will be referred to as GGS1, GGS2 and GGS3, respectively. We added several alkali halides of KBr, KI, CsBr, or CsI to reduce the multiphonon relaxation in glasses. Final compositions of the glasses were (1-x)GGS1[or GGS2, GGS3]-xMX[M=K, Cs and X=Br, I], where x were 0.05, 0.10, 0.16 and 0.20 in mole fraction. Dy^{3+} concentrations in glasses were in the range of 0.01~0.1 in atomic %. Starting powders were batched into the silica ampoule and were melted in the rocking furnace as described in the previous report [9,10].

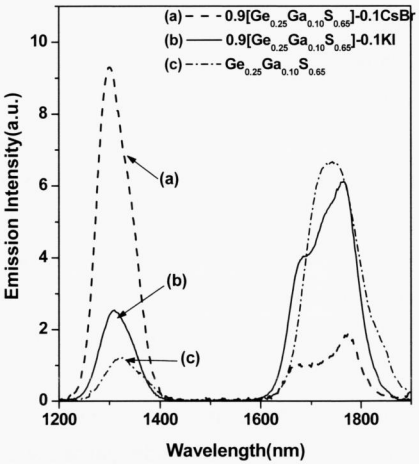

Fig. 1. Emission spectra of the 1.31μm ($^6F_{11/2}$, $^6H_{9/2}$→$^6H_{15/2}$) and 1.75μm ($^6H_{11/2}$→$^6H_{15/2}$) transitions in Dy^{3+}-doped glasses.

3. 2. 1.3μm Emission Properties

When alkali halide was not added, the 1.31 μm emission intensity from the $^6F_{11/2}$·$^6H_{9/2}$→$^6H_{15/2}$ transition remained considerably smaller than the 1.75 μm emission ($^6H_{11/2}$→$^6H_{15/2}$) and it appears similar to the spectra reported previously [3]. However, the 1.31 μm emission intensity increased sharply (Fig. 1) at the expense of the 1.75 μm

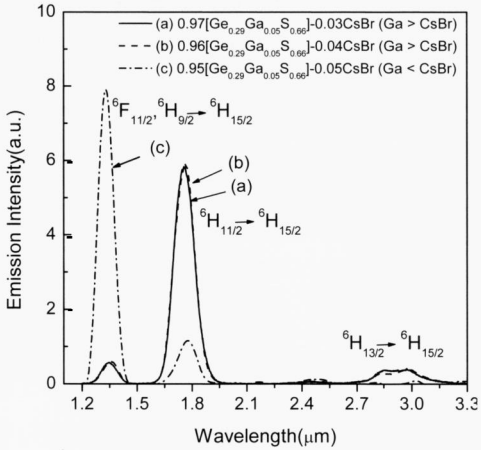

Fig. 2. Compositional dependence of emission spectra from Ge-Ga-S-CsBr glasses doped with 0.1 at.% Dy^{3+}.

emission upon the addition of KBr or CsBr. At the same time, lifetime of the $^6F_{11/2}$.$^6H_{9/2}$ level in the GGS-CsBr glass (0.1 at.% Dy^{3+} doping) increased to 1320 μs, about 35 times increase from the value in GGS glass (Table 1). In the glass with 0.01 at. % Dy^{3+} concentration, lifetime was 1580 μs with the quantum efficiency (η) of the transition approaching ~100 %.

These emission properties, however, are strongly dependent on the CsBr (or KBr) concentration in glasses. For example, emission spectra from GGS1 glasses containing 3% and 4% CsBr showed only a weak 1.31μm emission (Fig. 2). However, a widely different fluorescence spectrum appeared as CsBr concentration reached 5%. Lifetimes also showed an abrupt increase when the CsBr reached a certain concentration. In general, the improvement of the emission intensity and lifetime became possible only when the number of CsBr molecules was equal to or larger than that of Ga atoms.

Table 1. Calculated(τ_R) and measured(τ_m) lifetimes and quantum efficiencies ($\eta=\tau_m/\tau_R$) of 1.31μm fluorescence from 0.1 at.% Dy^{3+}-doped chalcogenide and chalcohalide glasses.

	$0.9[Ge_{0.25}Ga_{0.10}S_{0.65}]$-0.1KBr	$0.9[Ge_{0.25}Ga_{0.10}S_{0.65}]$-0.1CsBr	$0.9[Ge_{0.25}Ga_{0.10}S_{0.65}]$-0.1KI	$0.9[Ge_{0.25}Ga_{0.10}S_{0.65}]$-0.1CsI	$Ge_{0.25}Ga_{0.10}S_{0.65}$[5]
τ_R	840	964	326	317	227
τ_m	735	1320	220	193	38
η	0.88	>1	0.68	0.61	0.17

3. 3. Multiphonon Relaxation

Multiphonon relaxation process becomes a dominant process governing the

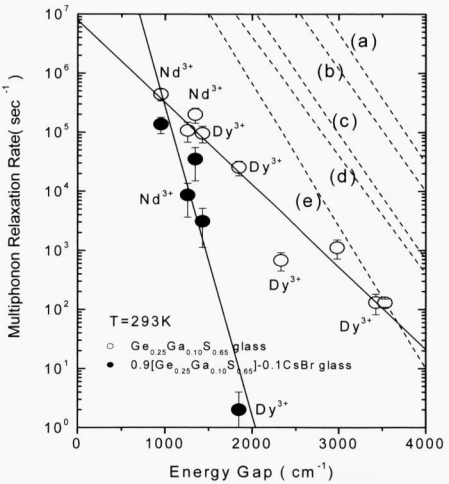

Fig.3. Dependence of multiphonon relaxation rates on energy gap for (a) Phosphate, (b) Silicate, (c) Germanate,(d) Tellurite and (e) Fluoride glasses[10]. Two solid lines are the result of the fitting for Ge-Ga-S and Ge-Ga-S-CsBr glasses.

the lifetime of the excited-state energy levels when there is negligible ion-ion interaction among rare-earths. MPR rates of GGS2 and 0.9GGS2-0.1CsBr glasses were calculated for the several energy levels in Nd^{3+} and Dy^{3+}, using $W_{mp}=(1/\tau_m)-(1/\tau_R)$. Here, W_{mp} is the MPR rates, τ_m and τ_R are measured and calculated lifetimes of the specific energy level, respectively. The two solid lines in Fig. 3 were obtained from the least-squares fitting of the calculated W_{mp} with the energy gap (ΔE) using the $W_{mp}=W_0 exp(-\alpha\Delta E)$ relation-ship [11,12]. In the latter equation, W_0 is the MPR rate extrapolated to zero energy gap and α is a constant depending only on host materials. Upon the addition of the MPR rate decreased by approximately four orders of magnitude especially for the Dy^{3+}: $^6F_{11/2}$-$^6H_{9/2}$ level where 1.3 μm emission starts from. This difference in the MPR rates between Ge-Ga-S and CsBr-containing glasses can explain, at least partially, the changes in the intensity and lifetime of the 1.31μm emission.

3. 4. Local Environment of Rare-Earth Ions

3.4.1. Temperature dependence of multiphonon relaxation

From the significant improvement on the emission properties, one can anticipate that addition of alkali halide resulted in a large change in the local phonon mode around rare-earth ions. Multiphonon relaxation of the excited-state of Dy^{3+} was measured at different temperature and was fitted using the following equation as shown in Fig. 4 [9].

$$W_{mp}(T) = W(0)\prod_i (n_i + 1)^{p_i} \qquad (1)$$

Here, n_i is Bose-Einstein occupation number. P_i is the number of phonons needed to bridge the gap between the excited-states and the one located immediately below. For GGS glass, the measured values fit most precisely by assuming that 375cm^{-1} vibration frequency, the asymmetric stretching vibration mode (υ_3) of GeS_4 tetrahedra, dominates the multiphonon relaxation. On the other hand, it was not possible to obtain a good fit CsBr-containing glass as shown with a dotted line in

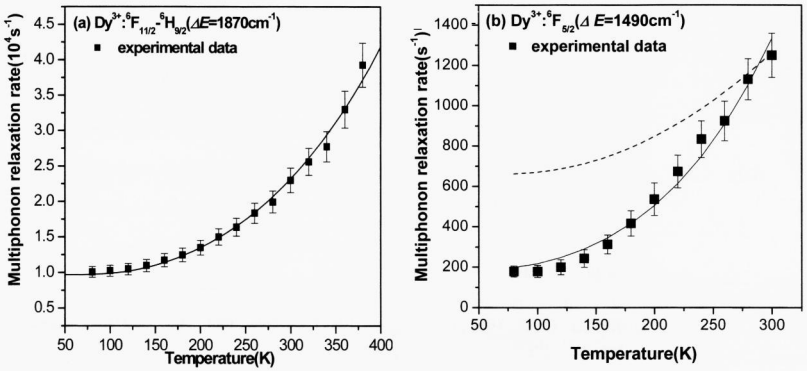

Fig. 4. Temperature dependence of multiphonon relaxation rates in Dy^{3+} from the (a) $^6F_{11/2}$-$^6H_{9/2}$ level in GGS and (b) $^6F_{5/2}$ level in GGSCsBr glasses.

Fig. 4(b). Instead, a reasonable fitting was made possible by assuming a 6-phonon process involving the 245cm^{-1} vibration (solid line). This vibration is due to Ga-Br bonds formed in the glass upon the addition of CsBr [10]. These results suggested that the phonon mode responsible for the MPR process in Ge-Ga-S-CsBr glasses is Ga (or Ge)-Br bonds and it is different from the one found in Ge-Ga-S glasses.

3.4.2. Phonon side band (PSB) spectroscopy

PSB modes represent the Stokes or anti-Stokes fluorescence induced by the phonon modes that are effectively coupled to the fluorescing energy level of rare earth ion [13]. It has been impossible to apply PSB spectroscopy to chalcogenide glasses since fluorescence from Eu^{3+} has not been observed. However, Eu^{3+} formation was confirmed recently from Ga-Ga-S-KBr glass[14] and investigation of the local structure around rare-earth ions [15,16] using PSB spectroscopy became possible.

The PSB spectrum of Eu^{3+}-doped $0.85(Ge_{0.18}Ga_{0.18}S_{0.64})$ + 0.15 CsCl glass (all in atomic or mole fraction) was recorded by measuring the fluorescence of $^5D_0 \rightarrow {}^7F_2$ (~ 615 nm) at 10 K while continuously changing the energy of pumping light in the vicinity of the Eu^{3+}: $^5D_0$ level. Five distinct phonon modes in Fig. 5 fit with the vibration mode of Ga_2Cl_6 dimer and $CsGaS_{1.5}Cl$. In addition, most of the vibration modes from $EuCl_3$ compound [17] also matched the measured phonon side bands. Therefore, it appears that Eu^{3+} ions have Cl^n ions as their nearest neighbors and these Cl^- ions either form 6~8 coordinated $EuCl_3$ or bond to the tetrahedral $[GaS_{3/2}Cl]^-$ subunit and/or Ga_2Cl_6. In any case, Eu^{3+} is surrounded by Cl^n ions and these new Eu-Cl bonds played the most important role on the enhancement of the 1.3μm emission properties of Dy^{3+}.

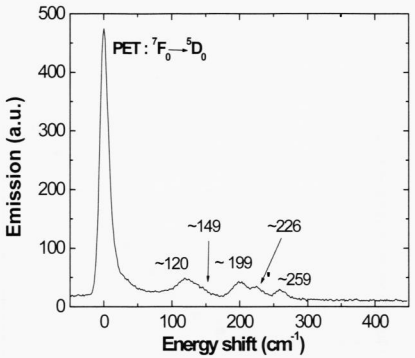

Fig. 5. A phonon side band spectrum of 0.1 mol% Eu-doped 0.85 $(Ge_{0.18}Ga_{0.18}S_{0.64})$ + 0.15 CsCl glass recorded by monitoring fluorescence change of $^5D_0 \rightarrow {}^7F_2$ transition (~ 615 nm) at 10K. PET represents the pure electronic transition

4. Glasses for Additional Communication Bands

Potentials of these chalcohalide glasses toward the S-band amplification were also investigated by doping Tm^{3+} and Tb^{3+} [18]. Similar to previous reports on Dy^{3+} [9,10], the effect of CsBr on the emission properties of Tm^{3+} was evident (Fig. 6). Emission centered at 1.48 μm and 1.8 μm are due to the $^3H_4 \rightarrow {}^3F_4$ and $^3F_4 \rightarrow {}^3H_6$ transitions in Tm^{3+}, respectively. Intensity of the 1.48 μm emission was condsiderably stronger than that of the 1.8 μm emission in glass containing CsBr while the reverse is true for sulfide glass with no CsBr [19]. Lifetimes of the $^3H_4$ level increased from 0.15 ms to 1.2 ms with CsBr addition and it is approximately 8 times longer than the value obtained from the normal sulfide glass. Quantum efficiency of the transition also increased to approximately 90%. Fig. 7 shows the decrease in lifetimes of the Tm^{3+}: $^3H_4$ and $^3F_4$ levels by increasing Tb^{3+} content while Tm^{3+} concentration was fixed at 0.10 mol%. Lifetimes of the $^3H_4$ level

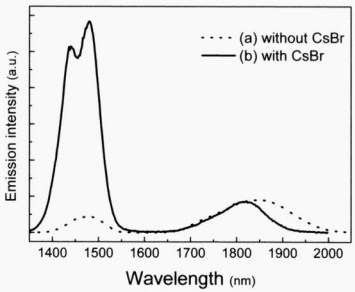

Fig. 6. Emission spectra of (a) $0.85(Ge_{0.25}As_{0.10}S_{0.65})$-$0.15GaS_{3/2}$ and (b) $0.70(Ge_{0.25}As_{0.10}S_{0.65})$-$0.15GaS_{3/2}$-0.15 CsBr glasses doped with 0.2 mol% Tm^{3+}. Spectra were normalized to their maximum intensity at ~1.8 μm.

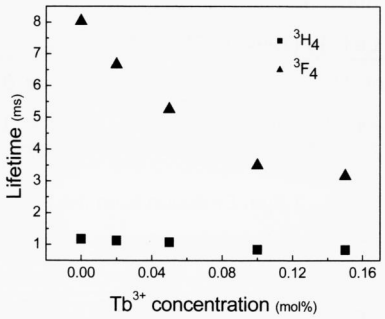

Fig. 7. Changes in lifetimes of the $^3H_4$ and $^3F_4$ levels in Tm^{3+} ions with the addition of Tb^{3+}.

decreased only slightly from 1.2 to 0.8 ms, while those of the $^3F_4$ level experienced a significant decrease from 8.1 to 3.0 ms. These results are due to the energy transfer of Tm^{3+}:$^3F_4 \rightarrow Tb^{3+}$:$^7F_{0,1,2}$ and population inversion became possible when Tb^{3+} concentration reached 0.11 mol %.

Spectroscopic properties of 1.6μm emission from Ho^{3+} doped into sulfide glass were also evaluated for their potential use as U-band fiber-optic amplifiers [6]. Emission from the $^5I_5 \rightarrow ^5I_7$ transition showed a peak wavelength of 1670nm, a full width at half maximum (FWHM) intensity of ~65nm and a cross section of $\sim 4.2 \times 10^{-21}$ cm^2. The lifetime of the fluorescing level ($^5I_5$) under the optimum condition was ~1.3ms. Ho^{3+} concentration in glass should be limited to 0.08mol% to prevent the cross relaxation and cooperative upconversion that decrease the $^5I_5$ level lifetime. Co-doping of Tb^{3+} also decreased terminal $^5I_7$ level lifetimes via the energy transfer of Ho^{3+}: $^5I_7 \rightarrow Tb^{3+}$: $^7F_{0,1,2}$.

5. Summary

Development of novel glass hosts for the fiber-optic amplifiers was introduced with a special attention on the O-band amplifiers operating at 1.31μm. Intensity, lifetime, and other radiative properties of the 1.31μm emission from Dy^{3+} experienced a hugh improvement upon the addition of alkali halides to Ge-Ga-S glasses. The lifetime of the 1.31μm emission level (Dy^{3+}:$^6F_{11/2}$-$^6H_{9/2}$) increased as

much as 35 times with 10 mole % addition of CsBr. Quantum efficiency also approached 100%. In Ge-Ga-S-CsCl glasses, local environment of Eu^{3+} ions is mainly made of Cl^{I} ions and these Cl^{II} ions form $EuCl_3$, tetrahedral $[GaS_{3/2}Cl]^-$ subunit and/or Ga_2Cl_6. Glasses in the Ge-(As)-Ga-S-CsBr system also hold potential as host materials for both S-band and U-band amplifiers.

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