Spectral Properties and Thermal Stability of Er\(^{3+}\) Doped Lead Oxysulfide Silicate Glasses for Broadband Amplification

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Er\(^{3+}\)-doped 50SiO\(_2\)-(50-x) PbO-xPbF\(_2\) glasses were prepared. The effect of PbF\(_2\) content on refractive index, density, absorption spectra, the Judd-Ofelt parameters \(\Omega_i\) (\(i=2, 4, 6\)), fluorescence spectrum and the lifetime of \(^{4}I_{15/2}\) level of the glass samples were investigated, and the stimulated emission cross-section was calculated from McCumber theory. With increasing PbF\(_2\) content in the glass composition, the \(\Omega_i\) parameter, fluorescence full width at half maximum (FWHM) and lifetime of \(^{4}I_{13/2}\) level of Er\(^{3+}\) increase, while refractive index and density decrease. The FWHM value is related to the \(\Omega_6\) parameter, and the larger the \(\Omega_6\) parameter, the broader the FWHM. Compared with other glass hosts, the gain bandwidth properties of Er\(^{3+}\)-doped 50SiO\(_2\)-50PbF\(_2\) glass is close to those of tellurite and bismuth glasses, and has advantage over those of silicate, phosphate and germate glasses. [Received July 11, 2003; Accepted December 11, 2003]

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1. Introduction

In recent years, the demand for increased transmission capacity of wavelength-division multiplexed telecommunication systems requires extension of the transmission window from the conventional C band (1530-1565 nm) to the L band (1570-1610 nm). It is of great importance to flatten the gain spectrum and broaden the amplification bandwidth of Er\(^{3+}\)-doped fiber amplifiers (EDFAs) because of their key function in the wavelength-division-multiplexing (WDM) network system.\(^{1-4}\) Broadening and flattening of the amplification bandwidth of EDFAs are now becoming important for meeting these requirements. From a practical standpoint, the flatness of the gain is also critical important because the light intensity for different channels would be varied by the multistep amplification if the gain of optical amplifiers were not independent of wavelengths. So far, many researchers have paid much attention to phosphate, fluorophosphates, fluoride, germanate, tellurite, and bismuth glasses.\(^{5-12}\) Specifically, Er\(^{3+}\)-doped tellurite and bismuth glasses are capable of providing the broad FWHM and large stimulated emission cross-section around 1.55 \(\mu\)m bands, and thus are attractive host materials for 1.55 \(\mu\)m broadband amplification.\(^{16-18}\) However, chemical and mechanical stability and fiberizability of these glasses as practical materials still remain problems. Silicate glasses are the most chemically and mechanically stable and also are more easily fabricated into various shapes such as a rod and optical fiber.\(^{13}\) Therefore, the design of a new silicate glass host for Er\(^{3+}\) for wide and flat spectra of the \(^{4}I_{13/2} \rightarrow ^{4}I_{15/2}\) transition around 1.55 \(\mu\)m bands is a target at present.

In this work, the new oxysulfide silicate glasses (50SiO\(_2\)-(50-x) PbO-xPbF\(_2\)) were prepared. The physical and thermal properties, the absorption spectra, fluorescence spectra and the lifetime of \(^{4}I_{13/2}\) level of Er\(^{3+}\) of the glasses were investigated. The absorption and stimulated emission cross-sections were calculated from McCumber theory, and the Judd-Ofelt intensity parameters \(\Omega_i\) (\(i=2, 4, 6\)) were determined using the Judd-Ofelt theory.

2. Experimental

Glasses with the compositions of 50SiO\(_2\)-(50-x) PbO-xPbF\(_2\) (x=0, 10, 20, 30, 40, and 50 mol\%\) were prepared. The starting materials are reagent grade SiO\(_2\), PbO, and PbF\(_2\). The Er\(^{3+}\) doping concentration in the glasses was 1.0 mol\%, which was introduced as with 99.99% purity. About 50 g batches of starting materials were fully mixed and then melted between 1000°C and 1100°C in covered silicate crucibles in a SiC Globar furnace with an N\(_2\) atmosphere. When the melting was completed, the glass liquids were cast into stainless steel plates. All glass samples were annealed 2 h at ranging from 320°C to 400°C, depending upon the glass composition. The glass samples were then cooled to room temperature at a rate of 10°C/h, and then were cut and polished carefully in order to meet the requirements for optical measurements.

The glass transition temperature \(T_g\), and crystallization onset temperature \(T_c\) were determined by differential thermal analysis (DTA) at a heating rate of 10°C/min, using aluminum oxide ceramic pan. Density was measured according to the Archimedes’ principle using distilled water as the medium. Refractive index was measured on prism minimum deviation method. UV/VIS/NIR absorption spectra were recorded between 300 and 1700 nm using a spectrophotometer on 3 mm thick glass samples optically polished. Fluorescence spectra were recorded using a laser diode excitation source at 970 nm. The fluorescence lifetimes of \(^{4}I_{13/2}\) level of Er\(^{3+}\) were measured with light pulses of 970 nm laser diode (LD) and a HP54680B 100-MHz oscilloscope. All the measurements were taken at room temperature.

3. Results and discussion

3.1 Physical and thermal stability properties

**Figure 1** shows the compositional dependence of refractive index and density of Er\(^{3+}\)-doped 50SiO\(_2\)-(50-x) PbO-xPbF\(_2\) glasses. With increasing PbF\(_2\) content, refractive index and density decrease. Fig. 2 shows the compositional dependence of \(T_g\), \(T_c\), and \(\Delta T=T_g-T_c\) of Er\(^{3+}\)-doped 50SiO\(_2\)-(50-x) PbO-xPbF\(_2\) glasses. With increasing PbF\(_2\) content, the value of \(T_g\), \(T_c\), and \(\Delta T=T_g-T_c\) decrease. The difference between \(T_g\) and \(T_c\), \(\Delta T=T_g-T_c\), has been frequently used as a rough estimate of the glass formation ability or glass stability. Since fiber drawing is a reheating process and any crystallization during the process will increase the scattering loss of the fiber and then degrade the optical properties.\(^{14}\) To achieve a large working range of temperature during our sample fiber drawing, it is desirable for a glass host to have \(\Delta T\) as large as
possible. From Fig. 2, it can be seen that the smallest value of \( \Delta T \) is 231°C, which is larger than those of tellurite (141.5°C), bismuth (170°C) and fluoride (105°C) glasses, indicating these glass samples are more stable against devitrification.  

3.2 Absorption spectra and Judd-Ofelt analysis

Figure 3 shows the absorption spectra of Er\(^{3+}\)-doped 50SiO\(_2\)-(50-x) PbO-xPbF\(_2\) glasses. Each assignment corresponds to the excited level of Er\(^{3+}\). With the substitution of PbF\(_2\) for PbO, the cut off band shifts to a shorter wavelength by the bandgap absorption of the glass matrix.

The Judd-Ofelt theory\(^{18,19}\) was often used to calculate the spectroscopic parameters such as intensity parameters \( \Omega \) (t = 2, 4, 6), spontaneous emission probability, fluorescence branching ratios, radiation lifetime and the line strength of electric-dipole transition (\( S_{el} \)) and magnetic dipole transition (\( S_{mag} \)) of rare-earth ion doped glasses. The three parameters \( \Omega \), (t=2, 4, 6) can be obtained experimentally from the measured absorption spectra and refractive index of the glass hosts. The value of \( \Omega_2 \), \( \Omega_4 \) and \( \Omega_6 \) for the glass samples are calculated by the procedure provided in Ref.\(^{20,21}\).

Figure 4 shows the compositional dependence of \( \Omega_t \) (t = 2, 4, 6) parameters of Er\(^{3+}\)-doped 50SiO\(_2\)-(50-x) PbO-xPbF\(_2\) glasses. Apparently, with increasing PbF\(_2\) content, the values of \( \Omega_2 \) and \( \Omega_4 \) increase monotonically, and the value of \( \Omega_6 \) decreases monotonically. According to previous studies\(^{21-22}\), \( \Omega_2 \) is related with the symmetry of the glass hosts while \( \Omega_4 \) is inversely proportional to the covalency of Er-O bond. The covalency of Er-O bond is assumed to be related with the local basicity around the rare-earth sites, which can be adjusted by the composition or structure of the glass hosts.\(^5\) On the basis of the electronegativity theory,\(^{23}\) the smaller the difference of electronegativity between cation and anion ions, the stronger the covalency of the bond. The values of electronegativity, for Pb, O, and F elements, are 1.8, 3.5, and 4.0, respectively. As a result, the covalency of Pb-F bond is lower than that of Pb-O bond. Consequently, the value of \( \Omega_2 \) increase with the substitution of PbF\(_2\) for PbO.

3.3 Fluorescence spectra and stimulated emission cross-section

The stimulated emission cross-section and FWHM are very important for optical amplifier to realize broadband and the gain amplification, which can be used to evaluate the gain properties of the optical amplifier.\(^{24,25}\) The fluorescence spectra of Er\(^{3+}\)-doped 50SiO\(_2\)-(50-x) PbO-xPbF\(_2\) glasses are shown in Fig. 5. FWHM is often used as a semiquantitative indication of the bandwidth. Figure 6 shows the composi-
Fig. 5. Compositional dependence of the normalized emission spectra of Er$^{3+}$-doped 50SiO$_2$-(50-x) PbO-xPbF$_2$ (x=0, 10, 20, 30, 40, and 50 mol%) glasses.

Fig. 6. Compositional dependence of FWHM of Er$^{3+}$-doped 50SiO$_2$-(50-x) PbO-xPbF$_2$ (x=0, 10, 20, 30, 40, and 50 mol%) glasses.

Fig. 7. Relationship between FWHM and $\Omega_6$ parameter in Er$^{3+}$-doped 50SiO$_2$-(50-x) PbO-xPbF$_2$ glasses.

Fig. 8. Absorption and stimulated emission cross-sections of Er$^{3+}$ in 50SiO$_2$-50PbF$_2$ glass.

Compositional dependence of FWHM of Er$^{3+}$-doped 50SiO$_2$-(50-x) PbO-xPbF$_2$ glasses. Obviously, FWHM of these glass samples increase monotonically with increasing PbF$_2$ content. In the case of the $^{4}I_{13/2} \rightarrow ^{4}I_{15/2}$ transition of Er$^{3+}$, because the difference in the total angular momentum $\Delta J$ equals 1, there exists the contribution of magnetic dipole transitions ($S_{\text{m}}$).

In order to obtain broadband and flat emission spectrum, it will be effective to increase the relative contribution of electric dipole transition ($S_{\text{e}}$) [2]. $S_{\text{m}}$ is independent of the ligand fields and is characteristic to the transition determined by the quantum numbers, while $S_{\text{e}}$ is a function of the ligand fields, and it is possible to increase $S_{\text{e}}$ by modifying the structure and compositions of the glass hosts. According to the Judd-Olfet theory, the line strength of $S_{\text{e}}$ of the 1.55 $\mu$m $^{4}I_{13/2} \rightarrow ^{4}I_{15/2}$ transition of Er$^{3+}$ is given by [27]:

$$S_{\text{e}} = \frac{\Omega_6}{\Omega_2} \cdot \frac{2}{3} \cdot \frac{1}{\Omega_4} \cdot \frac{1}{\Omega_6}$$

(1)

Consequently, for $S_{\text{e}}$ of $^{4}I_{13/2} \rightarrow ^{4}I_{15/2}$ transition of Er$^{3+}$, the $\Omega_6$ parameter is dominant and consequently is also dominant for 1.55 $\mu$m emission. Therefore, increasing the $\Omega_6$ parameter is helpful in increasing the bandwidth 1.55 $\mu$m emission. Figure 7 shows the relationship between FWHM and the $\Omega_6$ parameter of Er$^{3+}$-doped 50SiO$_2$-(50-x) PbO-xPbF$_2$ glasses. The $\Omega_6$ parameter shows a strong dependence on FWHM of the 1.55 $\mu$m emission band, and the glass sample with a large the $\Omega_6$ parameter generally possesses a broad FWHM. This result demonstrates the validity of the above statement.

The absorption cross-section was determined from the absorption spectra, and the stimulated emission cross-section is calculated from McCumber theory [28]. According to the McCumber theory, the absorption and stimulated emission cross-sections are related by

$$\sigma_a(\lambda) = \sigma_s(\lambda) \exp \left[ \frac{(\epsilon - h\nu)}{kT} \right]$$

(2)

where $\sigma_a$ and $\sigma_s$ are absorption and stimulated emission cross-sections, respectively, $\hbar$ is the plank constant, $k$ is the Boltzmann constant, $\nu$ is the photon frequency, $\epsilon$ is the net free energy required to excite one Er$^{3+}$ from the $^{4}I_{15/2}$ state to $^{4}I_{13/2}$ at temperature $T$. $\epsilon$ was determined using the procedure provided in [29]. Figure 8 illustrates the absorption and stimulated emission cross-sections of Er$^{3+}$ in 50SiO$_2$-50PbF$_2$ glass. The stimulated emission cross-section is proportional to the refractive index of the glass host $[\sigma \sim (n^2+2)^2/n]$. Since glass host has large refractive index, it is expected that Er$^{3+}$ in 50SiO$_2$-50PbF$_2$ glass is capable of providing large stimulated emission cross-section at the 1.55 $\mu$m bands.
The emission parameters FWHM, the peak of the stimulated emission cross-section (\(\sigma_{\text{peak}}^{\text{stim}}\)) and FWHM \(\times\) \(\sigma_{\text{peak}}^{\text{stim}}\) of Er\(^{3+}\) in different glass hosts are listed in Table 1 in order to compare the emission properties of Er\(^{3+}\). The gain bandwidth of optical amplifier can be evaluated by FWHM \(\times\) \(\sigma_{\text{peak}}^{\text{stim}}\) product. The bigger the product, the better the property. From Table 1, it is seen that the value of FWHM, \(\sigma_{\text{peak}}^{\text{stim}}\) and FWHM \(\times\) \(\sigma_{\text{peak}}^{\text{stim}}\) for Er\(^{3+}\) in 50SiO\(_2\)-50PbF\(_2\) glass is close to those of tellurite and bismuth glasses, and more than those of silicate, phosphate and germane glasses.

3.4 Lifetime of \(5\text{I}_{3/2}\) level of Er\(^{3+}\)

The lifetime of \(5\text{I}_{3/2}\) level of Er\(^{3+}\) is also an important parameter for optical amplifier. A critical factor in the success of Er\(^{3+}\)-doped fiber amplifier in optical communications is the long lifetime of the metastable state that permits the required high population inversions to be obtained under steady-state conditions using modest pump powers.\(^{32}\) \textbf{Figure 9} shows the compositional dependence of the lifetime of \(5\text{I}_{3/2}\) level of Er\(^{3+}\) in 50SiO\(_2\)-\((50-x)\) PbO-xPbF\(_2\) (x = 0, 10, 20, 30, 40, and 50 mol\%) glasses.

4. Conclusions

The present oxyfluoride silicate glasses were prepared and analyzed. Er\(^{3+}\)-doped 50SiO\(_2\)-50PbF\(_2\) glass showed broad emission spectra of 1.55 \(\mu\)m with a large stimulated emission cross-section, long lifetimes of \(5\text{I}_{3/2}\) level of Er\(^{3+}\) and good thermal stability. The gain bandwidth properties of Er\(^{3+}\)-doped 50SiO\(_2\)-50PbF\(_2\) glass was evaluated by FWHM \(\times\) \(\sigma_{\text{peak}}^{\text{stim}}\) product, and the FWHM \(\times\) \(\sigma_{\text{peak}}^{\text{stim}}\) value of Er\(^{3+}\)-doped 50SiO\(_2\)-50PbF\(_2\) glass is close to those of tellurite glasses and bismuth glasses (554), is larger than those of silicate glasses phosphates and germane glasses. The large stimulated emission cross-section of Er\(^{3+}\)-doped 50SiO\(_2\)-50PbF\(_2\) glass results from the large refractive index of the glass host. The broad and flat emission of Er\(^{3+}\) around 1.55 \(\mu\)m can be used as host material for potential broadband optical amplifier in WDM network system.

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References


