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## **Tm<sup>3+</sup>-doped lead silicate glass sensitized by Er<sup>3+</sup> for efficient ~2μm mid-infrared laser material**

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### **Abstract**

Er<sup>3+</sup>/Tm<sup>3+</sup> co-doped lead silicate glasses with low phonon (953 cm<sup>-1</sup>) and good thermal stability were synthesized. The ~2μm mid-infrared emission resulting from the <sup>3</sup>F<sub>4</sub> → <sup>3</sup>H<sub>6</sub> transition of Tm<sup>3+</sup> sensitized by Er<sup>3+</sup> has been observed by 808 nm LD pumping. The optimal luminescence intensity was obtained in the sample with 1Tm<sub>2</sub>O<sub>3</sub>/2.5Er<sub>2</sub>O<sub>3</sub> co-doped. Moreover, the energy transfer mechanism from Er<sup>3+</sup> to Tm<sup>3+</sup> ion was analyzed. Absorption and emission cross section have been calculated. The calculated maximum emission cross section of Tm<sup>3+</sup> is 2.689×10<sup>-21</sup> cm<sup>2</sup> at 1863 nm. Microparameters of energy transfer between Er<sup>3+</sup> and Tm<sup>3+</sup> ions have also been analyzed. These results ensure that the prepared Er<sup>3+</sup>/Tm<sup>3+</sup> co-doped lead silicate glasses have excellent spectroscopic properties in mid-infrared region and provide a beneficial guide for mid-infrared laser material.

**Keywords:** Er<sup>3+</sup>/Tm<sup>3+</sup> codoped; lead silicate; 2μm emission; energy transfer;

### **Introduction**

High-power, robust and efficient laser, especially around ~2μm band, has attracted a great deal of attention for a variety tasks such as spectroscopy and materials processing. They have been needed for applications in precision medical laser surgery, eye-safe atmospheric sensing and optical pumping sources [1-3]. The transitions of Tm<sup>3+</sup>: <sup>3</sup>F<sub>4</sub> → <sup>3</sup>H<sub>6</sub> and Ho<sup>3+</sup>: <sup>5</sup>I<sub>7</sub> → <sup>5</sup>I<sub>8</sub> have a corresponding peak emission wavelength around 2μm, respectively. Among the rare-earth ions, they are well-known for providing ~2μm emissions in fiber. Ho<sup>3+</sup> ions whose radiative transition <sup>5</sup>I<sub>7</sub> → <sup>5</sup>I<sub>8</sub> is

characterized by a broad emission band, high emission cross-section and a relatively long lifetime. However,  $\text{Ho}^{3+}$  ions doped fiber laser has been limited because of the lack of an efficient, common commercial and high-power excitation source for  $\text{Ho}^{3+}$  ions [4]. It cannot be pumped directly by a readily available commercial high-power 808 or 980 nm laser diode (LD) [5].  $\text{Tm}^{3+}$  is considered particularly appropriated to generate  $2\mu\text{m}$  laser, because it can be excited with commercial LD pump sources emitting at  $0.79\mu\text{m}$  [6]. Moreover, Cross-relaxation ('two-for-one' excitation) between neighboring  $\text{Tm}^{3+}$  ions is especially resonant in silicate glass and can nearly double the slope efficiency [7]. So it has been considered as the ideal candidate to generate a near  $2\mu\text{m}$  luminescent center which exhibits high-power and high efficiency characteristics. And its output has a wide spectrum of laser gain tuning from at least  $1.86\mu\text{m}$  to around  $2.09\mu\text{m}$  [6]. In order to get a powerful and efficient near  $2\mu\text{m}$  emission from  $\text{Tm}^{3+}$ ,  $\text{Er}^{3+}$  is introduced to sensitize  $\text{Tm}^{3+}$ . It can lead a strong absorption of pump energy.

It has to be noted here that the choice of the glass matrix for production of the active fiber's core, have crucial impact on the spectroscopic properties of the fiber laser. The key issue in construction of new active optical fibers is elaboration of low phonon and thermally stable oxide glass [8]. It is common knowledge that the silicate glasses are marked by robust mechanical resistance and good thermal stability, and phosphate glasses are recognized for their excellent capability for dissolving rare earth elements stemming from the presence of numerous non-bridge oxygen atoms in their structure. But high phonon energy ( $1000$  to  $1200\text{ cm}^{-1}$ ) of silicate or phosphate glasses imply relatively high probability of non-radiative transition and strongly limits PAET (phonon assisted energy transfer) between active dopants [4, 9]. Among the glassy materials, low phonon energy glass systems are fluoride [10], tellurite [11] and bismuth-germanate [12] glass, which phonon vibrations are in the range of  $300$ - $750\text{ cm}^{-1}$ . Unfortunately, poor mechanical properties and low thermal stability make it difficult to use these glasses in optical fibers practical applications. These problems can be overcome by adding lead oxide into silicate glasses, which have attracted a considerable interest for their combination of high thermal stability, low phonon energies ( $\sim 950\text{ cm}^{-1}$ ) [13]. These make lead silicate glasses promising material for the development of optical fibers. Here we performed a composition of lead silicate glasses doped with  $\text{Er}^{3+}$  and  $\text{Tm}^{3+}$  ions to study luminescent properties of  $\sim 2\mu\text{m}$  spectral range.

## 1. Experiments

### 2.1. Glass Syntheses

The lead silicate glasses were prepared according to the following of molar compositions:  $56\text{SiO}_2\text{-}30\text{PbO}\text{-}13(\text{AlF}_3\text{+Na}_2\text{O+BaO+Sb}_2\text{O}_3)\text{-}1\text{Tm}_2\text{O}_3\text{-}x\text{Er}_2\text{O}_3$  (where  $x = 0, 0.5, 1.0, 2.0, 2.5,$  and  $3.0$ ) by melt quenching method. They were denoted as 1T-0E, 1T-0.5E, 1T-1E, 1T-2E, 1T-2.5E, 1T-3E, respectively. The homogenized set pure materials was melted in a platinum crucible in an electric furnace in  $T=1350^\circ\text{C}$  for 50 minutes. Then the molten glass was poured out onto a brass plate and then annealed in air atmosphere at  $500^\circ\text{C}$  for 4 h. The annealed samples were finally cut and were polished with the dimensions of  $10 \times 10 \times 1.2 \text{ mm}^3$  for determining spectral properties.

### 2.2. Measurements

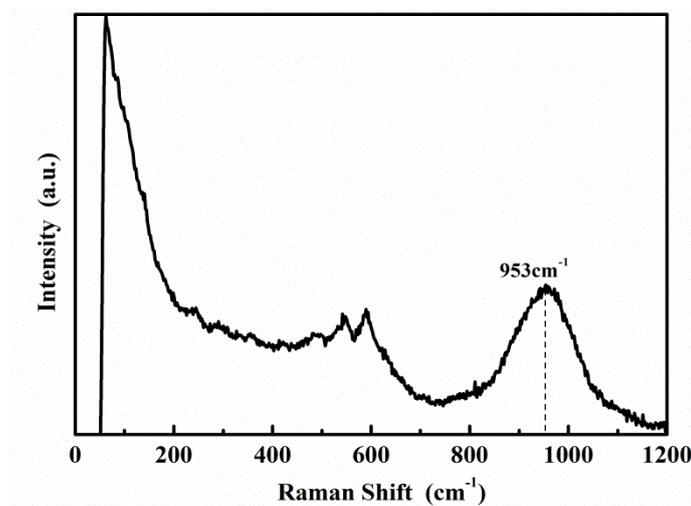
DSC (differential scanning calorimeter) measurement was performed with 10K/min using the NETZSCH DTA 404 PC differential scanning calorimeter. The glass density was measured by using Archimedes' liquid-immersion method in distilled water. The refractive index was measured by the prism minimum deviation method at three wavelengths, 633, 1311 and 1539 nm. Raman studies were carried out using a Raman spectrometer (Renishaw inVia). Excitation wavelength of 532 nm was used. Absorption spectra measurements within the range from 300 to 2100 nm were taken using PerkinElmer Lambda 900 UV/VIS/NIR double beam spectrophotometer (Waltham, MA). Fluorescence spectra of the samples were measured by a computer controlled FLS980 Spectrometer (Edinburgh Instruments) with an 808nm laser diode. TDS 3012C type Digital Phosphor Oscilloscope (100MHz, 1.25GS/S) was used to measure and display the lifetime decay curves.

## 3. Results and discussion

### 3.1 Raman Spectrum

From literature it's known that the highest frequency phonon can be determined from Raman spectrum [14]. Figure 1 presents the Raman spectrum of the prepared lead silicate glass in the range from 0 to  $1200 \text{ cm}^{-1}$ . It is clear seen that the maximum phonon energy of the lattice merely reaches to  $953 \text{ cm}^{-1}$ . It's well known that low phonon energy profitably reduces multi-phonon relaxation for  $\text{RE}^{3+}$  excited states and thus impacts the energy transfer (ET) process [10]. So relatively low maximum phonon energy of the fabricated glasses enables to efficient  $\text{Er}^{3+} \rightarrow \text{Tm}^{3+}$  energy transfer. Besides, the lead silicate network is depolymerized with the PbO doped,

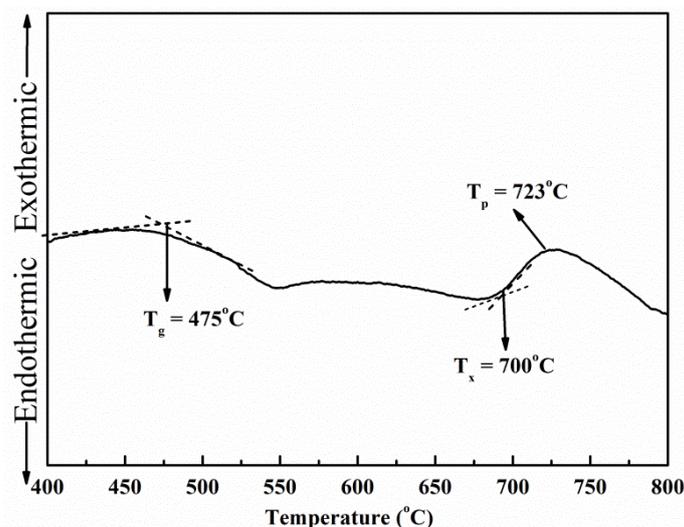
which is favorable to improve the solubility of  $RE^{3+}$  ions. The results indicate the manufactured lead silicate glass is a promising material for the development of optical fibers.



**Fig.1.** Raman spectrum of the lead silicate glass.

### 3.2 Thermal stability

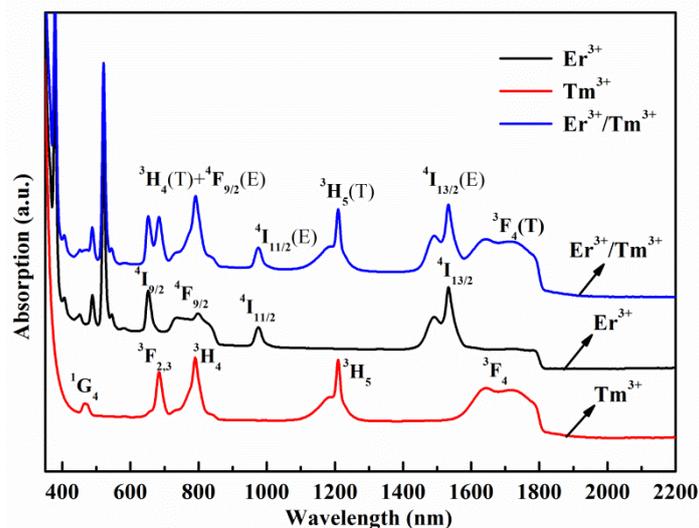
The DSC measurement of the sample is shown in Fig.2. The values of  $T_g$ ,  $T_x$ , and  $T_p$  are  $510^\circ\text{C}$ ,  $700^\circ\text{C}$ , and  $723^\circ\text{C}$ , respectively. It exhibits much higher  $T_g$  than tellurite ( $460^\circ\text{C}$ ) [15] and fluorophosphate glasses ( $463^\circ\text{C}$ ) [16]. Glass fiber with a higher  $T_g$  is beneficial to resist the thermal damage and can be pumped by high power lasers [17]. The glass criterion,  $\Delta T = T_x - T_g$ , is often used for evaluating the glass forming ability.  $\Delta T$  should be more than  $120^\circ\text{C}$  to minimize probability of crystallization during the drawing process [18]. In this glass, the  $\Delta T$  is  $190^\circ\text{C}$ , higher than that in  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-BaO-BaF}_2\text{-La}_2\text{O}_3$  system [19], but smaller than that in  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-R}_2\text{O}$  [18]. Hence, this lead silicate glass with good thermal stability might be selected as promising laser materials.



**Fig.2.** The DSC curve of the matrix.

### 3.3 Absorption spectra and Judd-Ofelt analysis

Figure 3 presents absorbance spectra of 1mol%  $\text{Tm}_2\text{O}_3$  singly doped, 0.5mol%  $\text{Er}_2\text{O}_3$  singly doped as well as 1mol%  $\text{Tm}_2\text{O}_3$ -0.5mol%  $\text{Er}_2\text{O}_3$  co-doped sample. In the range from 350 to 2200 nm, five absorption bands of  $\text{Tm}^{3+}$  ions at 1724, 1210, 792, 683 and 470 nm corresponding to transitions from the ground state  $^3\text{H}_6$  to the higher located energy levels  $^3\text{F}_4$ ,  $^3\text{H}_5$ ,  $^3\text{H}_4$ ,  $^3\text{F}_{2,3}$ , and  $^1\text{G}_4$ , respectively. By the same token, for  $\text{Er}^{3+}$  ions, four absorption bands at 1536, 976, 799, and 654nm corresponding to transitions from the ground state  $^4\text{I}_{15/2}$  to the higher levels  $^4\text{I}_{13/2}$ ,  $^4\text{I}_{11/2}$ ,  $^4\text{I}_{9/2}$ , and  $^4\text{F}_{9/2}$ . Above characteristic absorption bands are labeled in figure 3. The absorption band around 980nm and 808nm can be observed in the  $\text{Er}^{3+}/\text{Tm}^{3+}$  co-doped sample and thereby this glass can be efficiently pumped by 980 nm or 808 nm LD. It is worth noting that the intense absorption band near 790 nm in  $\text{Er}^{3+}/\text{Tm}^{3+}$  co-doped sample due to the  $\text{Tm}^{3+}:^3\text{H}_6 \rightarrow ^3\text{H}_4$  and  $\text{Er}^{3+}:^4\text{I}_{15/2} \rightarrow ^4\text{I}_{9/2}$ . Not only  $\text{Tm}^{3+}$  ( $^3\text{H}_4$ ) but also  $\text{Er}^{3+}$  ( $^4\text{I}_{9/2}$ ) are excited when samples are pumped by 808 nm LD. It can lead an intense absorption of pump energy. Here, we use 808 nm LD as the pumping sources.



**Fig.3.** Absorption spectra of  $\text{Tm}^{3+}$  singly doped,  $\text{Er}^{3+}$  singly doped and  $\text{Er}^{3+}/\text{Tm}^{3+}$  co-doped lead silicate glasses.

### 3.4 Luminescence properties and energy transfer

The luminescence spectra of  $\text{Tm}^{3+}$  via energy transfer from  $\text{Er}^{3+}$  ions in 1400-2200nm spectral range were presented in Fig.4. The insert is the lifetime of  $\text{Tm}^{3+}$ . So we can calculate spontaneous radiative transition probability (A). The result is 1.73852. Fig.4 clearly illustrates the dependence of the emission intensity at the wavelength around 2 $\mu\text{m}$  on the concentration of  $\text{Er}^{3+}$  ions (Here the concentration of  $\text{Tm}^{3+}$  ions remain 1mol%). The glass doped exclusively with 1mol%  $\text{Tm}^{3+}$  ions is characterized by the strong luminescence (the red line) with the peak at the wavelength 1840nm originated from  $\text{Tm}^{3+}: {}^3\text{F}_4 \rightarrow {}^3\text{H}_6$  transition. As for  $\text{Er}^{3+}/\text{Tm}^{3+}$ , it is noticed that increasing of  $\text{Er}_2\text{O}_3$  content leads to strong increasing of luminescence at 1840 nm originated from  ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$  transition which indicates effective  $\text{Er}^{3+} \rightarrow \text{Tm}^{3+}$  energy transfer. Obtained enhanced luminescence at the wavelength of 1840nm was possible due to the phonon assisted energy transfer (PAET) between  $\text{Er}^{3+}$  and  $\text{Tm}^{3+}$  ions. Moreover, after this concentration is exceed 2.5mol%, a decrease in the emission intensity takes place, possibly as a result of diffusion transitions of the donor-donor type or concentration quenching [20]. The mechanism of energy transfer between  $\text{Er}^{3+}$  and  $\text{Tm}^{3+}$  ions is presented in Fig.5.

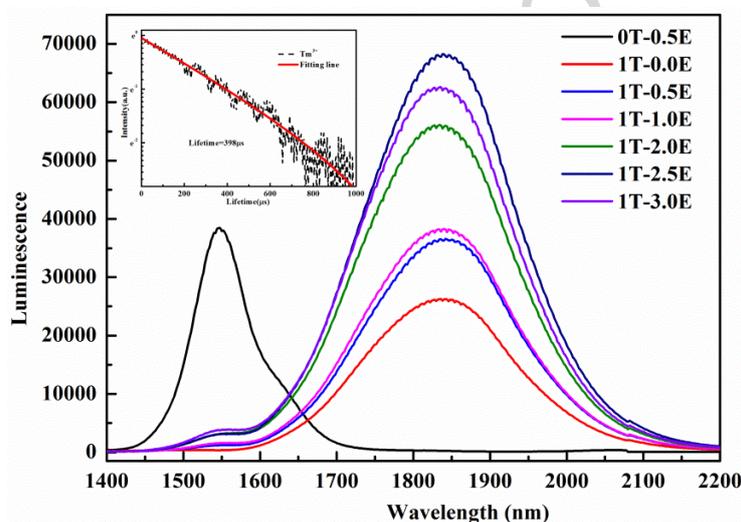
(1) Firstly, pumping glasses with the 808nm laser radiation, and by ground state absorption (GSA), the ions in the  $\text{Tm}^{3+}$ : the ground state  ${}^3\text{H}_6$  level jump to a higher  ${}^3\text{H}_4$  level, at the same time,  $\text{Er}^{3+}$  are excited from the ground state  ${}^4\text{I}_{15/2}$  to the excited state  ${}^4\text{I}_{9/2}$  level.

(2) When ions are stimulated, the energy transfer (ET1) from the  $\text{Tm}^{3+}: {}^3\text{H}_4$  state to  $\text{Er}^{3+}: {}^4\text{I}_{9/2}$  state may occur. For  $\text{Er}^{3+}$  ions, majority of ions in  ${}^4\text{I}_{9/2}$  rapidly return to the

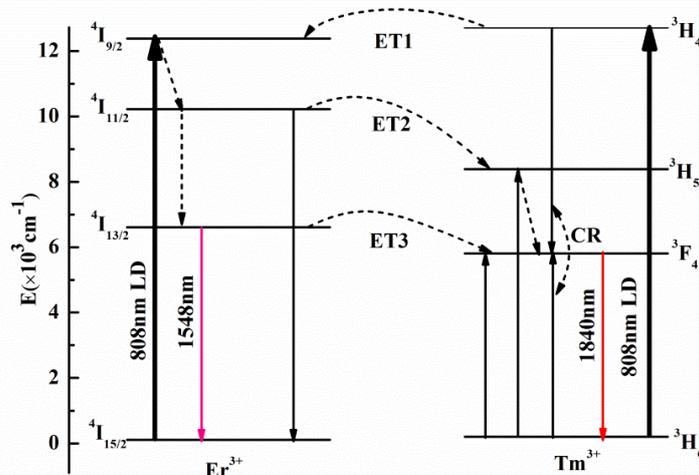
lower  ${}^4I_{11/2}$  level and populated via multi-phonon relaxation (or non-radiative transition). The ions in  ${}^4I_{11/2}$  are divided into two parts, a part of the ions relax non-radiatively to the  ${}^4I_{13/2}$ ,  ${}^4I_{15/2}$  level respectively and another part transfer energy to the  ${}^3H_5$  level of  $Tm^{3+}$  through ET2.

(3) Later, for ions existing in  $Er^{3+}: {}^4I_{13/2}$  level, one part of the ions relaxes their energy to the ground state  ${}^4I_{15/2}$ , generating near infrared 1545nm emission. And the rest can transfer its energy to the  ${}^3F_4$  state of  $Tm^{3+}$  via ET3.

(4) At last, the ions on the  $Tm^{3+}: {}^3F_4$  state can be populated through ET3, the nonradiative relaxation of the  $Tm^{3+}: {}^3H_5$  state, and cross-relaxation ('two-for-one' excitation) between neighboring  $Tm^{3+}$  ion. Then the emission at 1840 nm corresponding to the  ${}^3F_4 \rightarrow {}^3H_6$  transition was also measured.



**Fig. 4** Emission spectra of the obtained glasses doped with  $Er^{3+}$  as well as  $Er^{3+}$  and  $Tm^{3+}$  ions excited by 808nm LD; the insert is the lifetime of  $Tm^{3+}$ .



**Fig. 5** The energy transfer diagrams of  $Er^{3+}/Tm^{3+}$  co-doped lead silicate glass pumped by 808nm LD.

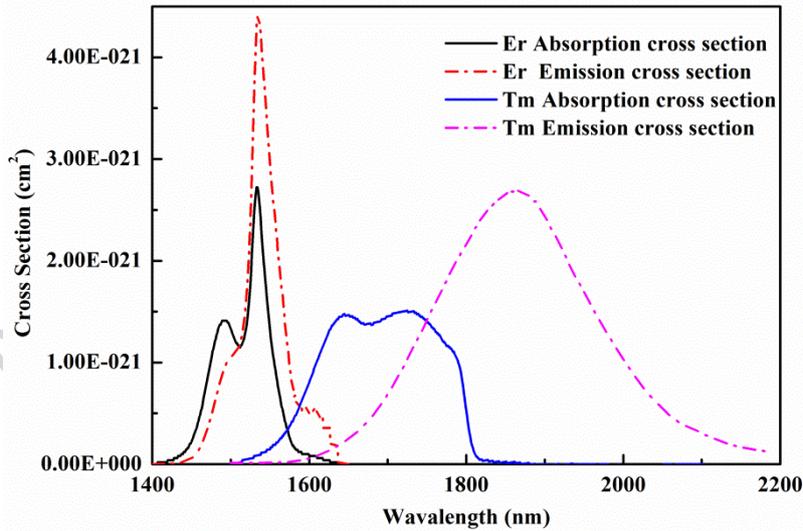
According to the above measured absorption spectra, the absorption cross section ( $\sigma_{abs}(\lambda)$ ) can be expressed as Beer–Lambert equation [21]:

$$\sigma_{abs}(\lambda) = \frac{2.303 \log(I_0(\lambda)/I(\lambda))}{Nl} \quad (1)$$

$I_0(\lambda)$  and  $I(\lambda)$  denote the incident optical intensity, the optical intensity throughout the glass, respectively,  $N$  is the density of rare-earth ion (ions/cm<sup>3</sup>) and  $l$  is the thickness (cm) of polished glass. According to the above measured emission spectra, the emission cross section ( $\sigma_{em}(\lambda)$ ) can be calculated by Füchtbauer-Ladenburg equation [22]

$$\sigma_{em}(\lambda) = \frac{\lambda^4 A_{rad}}{8\pi cn^2} \times \frac{\lambda I(\lambda)}{\int \lambda I(\lambda) d\lambda} \quad (2)$$

where  $\lambda$  is the wavelength,  $A_{rad}$  is the radiative transition probability ( $A_{rad} = 2512 \text{ s}^{-1}$ ),  $c$  is the speed of light in vacuum,  $n$  is refractive index of the prepared glass ( $n=1.73852$ ),  $I(\lambda)$  is the fluorescence intensity, and  $\int \lambda I(\lambda) d\lambda$  denotes the integral area. Figure 6 shows the calculated absorption and emission cross section. Obviously, it can be seen the overlap between the emission cross section of  $\text{Er}^{3+}$  and the absorption section of  $\text{Tm}^{3+}$  large indicating the existence of efficient energy transfer from  $\text{Er}^{3+}$  to  $\text{Tm}^{3+}$ . The calculated maximum  $\sigma_{em}(\lambda)$  is  $2.689 \times 10^{-21} \text{ cm}^2$  at 1863 nm. For a laser medium, it is generally desirable to ensure that the high stimulated emission cross section is extremely useful to provide high gain in fiber.



**Fig.6.** Absorption and emission cross section of  $\text{Er}^{3+}$  and  $\text{Tm}^{3+}$  in lead silicate glass.

### 3.5 Microparameters of energy transfer between $\text{Er}^{3+}$ and $\text{Tm}^{3+}$ ions

Förster and Dexter developed a method for estimating the microscopic probability rate of phonon-assisted energy transfer between  $\text{RE}^{3+}$  ions in solids. To further

determine the probability rate of energy transfer between donor (D) and acceptor (A) ions of the matrix, the relevant energy transfer microparameters can be expressed as the following equation [23-25]:

$$W_{D-A} = \left(\frac{2\pi}{\hbar}\right) |H_{DA}|^2 S_{DA}^N \quad (3)$$

where  $|H_{DA}|$  is the matrix element of the perturbation Hamilton between initial and final states in the energy transfer process, N is the total phonons in the whole energy transfer process ( $N=m+k$ ). And  $S_{DA}^N$  denote the overlap integral between the m-phonon emission line shape of ion donor (m-phonon emission sideband) and the k-phonon absorption line shape of ion acceptor (k-phonon absorption sideband). It is well known that phonons play an important role in these processes. The multiphonon processes should be involved in the energy-transfer process between ions in which excitation energies of the two ions have a large mismatch in the absence of vibrational transition. The emission cross section ( $\sigma_{em}$ ) of D ( $\text{Er}^{3+}$ ) with m-phonon emission and absorption cross section ( $\sigma_{abs}$ ) of A ( $\text{Tm}^{3+}$ ) with k-phonon absorption can be expressed as

$$\sigma_{e(m\text{-phonons})}^D = \sigma_e^D(\lambda_m^+) \approx \frac{S_0^m e^{-S_0}}{m!} (\bar{n} + 1)^m \sigma_{e(\text{expt})}^D (E - m\hbar\omega_0) \quad (4)$$

$$\sigma_{a(k\text{-phonons})}^A = \sigma_a^A(\lambda_k^-) \approx \frac{S_0^k e^{-S_0}}{k!} (\bar{n})^k \sigma_{a(\text{expt})}^A (E + k\hbar\omega_0) \quad (5)$$

Here  $S_0$  denote the Huang-Rhys factor and  $\bar{n} = 1/(e^{\hbar\omega_0/kT} - 1)$  is the average occupancy of phonon mode at temperature T (Here is room temperature).  $\lambda_m^+ = 1/(\frac{1}{\lambda} - m\hbar\omega_0)$  and  $\lambda_k^- = 1/(\frac{1}{\lambda} + k\hbar\omega_0)$  are the wavelengths of D (Here is  $\text{Er}^{3+}$ ) with m-phonon emission and A (Here is  $\text{Tm}^{3+}$ ) with k-phonon absorption, respectively. For the case of small k-phonon annihilation process and just focusing on the m-phonon creation process, by this consideration, the microscopic probability rate based on the evaluation of the overlap integral between the absorption and emission cross sections can be obtained using the following equations:

coefficients of the direct transfer (D→A):

$$C_{D-A} = \frac{6cg_{low}^D}{(2\pi)^4 n^2 g_{up}^D} \sum_{N=0}^{\infty} \sum_{k=0}^N P_{(N-k)}^+ P_k^- P_k^+ \int \sigma_e^D(\lambda_N^+) \sigma_a^A(\lambda) d\lambda \quad (6)$$

coefficients of back transfer (A→D)

$$C_{A-D} = \frac{6cg_{low}^A}{(2\pi)^4 n^2 g_{up}^A} \sum_{N=0}^{\infty} \sum_{k=0}^N P_{(N-k)}^- P_k^- P_k^+ \int \sigma_e^A(\lambda_N^-) \sigma_a^D(\lambda) d\lambda \quad (7)$$

where

$$P_{(N-k)}^+ \cong \exp[-(2\bar{n} + 1)S_0] \frac{S_0^{(N-k)}}{(N-k)!} (\bar{n} + 1)^{N-k} \quad (8)$$

$$P_k^- \cong \exp[-2\bar{n}S_0] \frac{S_0^k}{k!} (\bar{n})^k \quad (9)$$

The  $g_{\text{low}}^D$  ( $g_{\text{low}}^A$ ) and  $g_{\text{up}}^D$  ( $g_{\text{up}}^A$ ) are the degeneracies of the respective lower and upper levels of the donor (acceptor), respectively.  $P_{(N-k)}^+$  is the probability of (N-k) phonon emission by the donor and  $P_k^-$  denotes the probability of k phonon absorption by the acceptor. The signal (+) was used to specify the phonon creation probability and (-) for the phonon annihilation. Using the Eq.(3)-(9), the energy transfer properties between  $\text{Er}^{3+}$  and  $\text{Tm}^{3+}$  ions have been calculated. The obtained energy transfer values are given in Table I. The result shows that the direct ( $\text{Er}^{3+} \rightarrow \text{Tm}^{3+}$ ) transfer needs the assistance of 1 (54.5%), 2 (45.4%), and 3 (0.0693%) phonon emissions while the respective back transfer needs the assistance of 1 (37.6%), 2(13.5%), 3(52%) and 4 (0.03%) phonon absorptions (or annihilations). We observed a multiphonon mechanism dominated by the one-phonon creation 54.5%. It's clearly shows that effective energy exchange takes place between  $\text{Er}^{3+}$  and  $\text{Tm}^{3+}$  ions. In general, back transfer is always less probable than direct-transfer process [24]. It was seen for the case of  $\text{Er}^{3+} \rightarrow \text{Tm}^{3+}$  transfer, the back transfer probability is <0.05% of the direct process. What's more, the energy transfer coefficient of  $\text{Er}^{3+} \rightarrow \text{Er}^{3+}$  transition is the largest because compared with the phonon assisted energy transfer processes, this process is resonant.

**Table I** Energy transfer parameters between  $\text{Er}^{3+}$  and  $\text{Tm}^{3+}$  in lead silicate.

Energy transfer	N(number of phonons) (% phonon assisted)				Coefficient ( $10^{-40}$ $\text{cm}^6/\text{s}$ )
$\text{Er}^{3+} (^2F_{5/2}) \rightarrow \text{Er}^{3+} (^2F_{7/2})$ (resonant)	0		1		47.8
	47.4		0.218		
$\text{Er}^{3+} (^4I_{13/2}) \rightarrow \text{Tm}^{3+} (^3F_4)$ (Nonresonant Direct transfer)	1	2	3		38.8
	54.5	45.4	0.0693		
$\text{Tm}^{3+} (^3F_4) \rightarrow \text{Er}^{3+} (^4I_{13/2})$ (Nonresonant Back transfer)	1	2	3	4	0.018
	37.6	13.5	52	0.03	

#### 4. Conclusions

To summarize, an elaborated description of the luminescent properties of fabricated lead silicate glasses co-doped with  $\text{Er}^{3+}/\text{Tm}^{3+}$  ions have been studied in the article. The Raman spectrum, thermal stability, absorption and emission cross section have been calculated and analyzed. Results indicated that  $\text{Tm}^{3+}$  in the prepared glasses had low Raman spectrum ( $953\text{cm}^{-1}$ ), superior thermo-mechanical stability ( $T_g=475^\circ\text{C}$ ,  $\Delta T$

=225°C) large emission cross section ( $2.689 \times 10^{-21} \text{ cm}^2$ ). Process of the strong increasing of luminescence at 1840nm occurs as a result of the phonon-assisted energy transfer from erbium ions. So microparameters of energy transfer properties between  $\text{Er}^{3+}$  and  $\text{Tm}^{3+}$  ions have also been calculated. It's clearly shows that the back transfer probability is <0.05% of the direct process. It contributes to obtain the enhanced  $\sim 2\mu\text{m}$  emission of  $\text{Tm}^{3+}$  from  $\text{Er}^{3+}$ . The experimental results suggested that lead silicate co-doped with  $\text{Er}^{3+}/\text{Tm}^{3+}$  is good active material construction sources of radiation working in the  $2\mu\text{m}$  spectral range.

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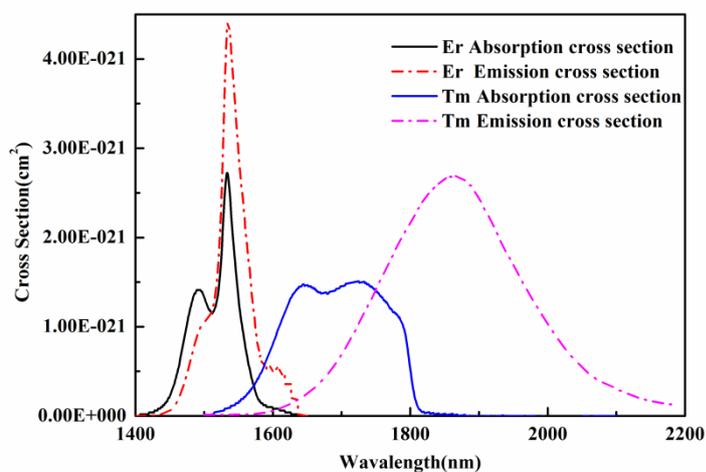
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*Opt. Mater.*, 60 (2016), pp. 252-257.

## Graphical Abstract



It can be seen the overlap between the emission cross section of Er<sup>3+</sup> and the absorption section of Tm<sup>3+</sup> large indicating the existence of efficient energy transfer from Er<sup>3+</sup> to Tm<sup>3+</sup>. The calculated maximum emission cross section of Ho<sup>3+</sup> is  $2.689 \times 10^{-21}$  cm<sup>2</sup> at 1863 nm. This suggests that the lead silicate glass is excellent mid-infrared laser material.

### Highlights

1. The phonon energy of the matrix is  $953\text{ cm}^{-1}$ .
2. The efficient energy transfer from  $\text{Er}^{3+}$  to  $\text{Tm}^{3+}$  has been analyzed.
3. Intense  $2\mu\text{m}$  emission has been obtained in  $\text{Er}^{3+}/\text{Tm}^{3+}$  codoped lead glass
4. Microparameters of energy transfer between  $\text{Er}^{3+}$  and  $\text{Tm}^{3+}$  ions have been calculated. The back transfer probability is  $<0.05\%$  of the direct process.

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