Frequency Upconversion Fluorescence Emission of Er^{3+}-Doped Oxychloride Germanate Glass *

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Frequency upconversion fluorescence property of Er^{3+}-doped oxychloride germanate glass is investigated. Intense green and red emissions centred at 525, 546, and 657 nm, corresponding to the transitions $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$, and $^4F_{9/2} \rightarrow {}^4I_{15/2}$, respectively, were simultaneously observed at room temperature. The quadratic dependence of the 525, 546, and 657 nm emissions on excitation power indicates that a two-photon absorption process occurs under 975 nm laser diode (LD) excitation. The Raman spectrum investigation indicates that oxychloride germanate glass has the maximum phonon energy at $\sim 805\,cm^{-1}$. The thermal stability of this oxychloride germanate glass is evaluated by differential scanning calorimetry, and thermal stability factor ΔT ($\Delta T = T_x - T_g$) is 187° C. Intense upconversion luminescence and good thermal stability indicate that Er^{3+}-doped oxychloride germanate glass is a promising upconversion laser material.

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Rare-earth doped (RED) optical glasses are important materials for colour display, optical data storage, optoelectronics, medical diagnostics, sensor, and undersea optical communication.[1−6] Optical properties of trivalent lanthanide ions such as Er^{3+}, Tm^{3+}, and Nd^{3+} in glasses have been extensively studied to develop upconversion visible or ultraviolet lasers that can be operated at room temperature.[4−6] Among the trivalent lanthanide ions, Er^{3+} ion is most studied, and the upconversion process of this ion in various kinds of host materials has been investigated.[7] Host materials for Er^{3+} ions play an important role in obtaining high-efficient upconversion signal, since glass host with low phonon energy can reduce the multiphonon relaxation (MPR) and thus achieves strong upconversion luminescence. Though fluoride glasses have been studied due to low phonon energies, oxide glasses are more appropriate for practical applications due to their high chemical durability and thermal stability. Among oxide glasses, lead germanate glasses combine high mechanical strength, high chemical durability, and better temperature stability, which make them promising materials for technological applications such as new lasing materials, upconversion phosphors, and optical waveguides.[8] As is known, glasses based on mixed oxide-halide systems combine the good optical properties of halide glasses (a broad range of optical transmittance and low optical losses) with the better chemical and thermal stability of oxide glasses.[8] Thus it is expected that oxychloride germanate should bring together the interesting properties of the two systems. In this Letter, the upconversion fluorescence, structural and thermal stability properties of the sample are investigated. Intense upconversion fluorescence bands centred at around 525, 546, and 657 nm were observed, and the possible upconversion mechanisms were discussed and estimated.

The glass used in this work was synthesized by conventional melting and quenching method. The starting materials are reagent-grade $PbCl_2$, PbO, BaO, ZnO, K_2O and high-purity GeO_2 (> 99.999%). The glass sample studied has the following composition: (mol%) $55GeO_2$-25(BaO+ZnO+K_2O)-20$PbCl_2$-1Er_2O_3 (GPC). Undoped GPC glass was also prepared. About 20 g batches of the well-mixed raw materials was melted at 1300°C for 30 min in covered aluminium oxide crucible in an electronic furnace with O_2 atmosphere. When the melting was completed, the liquid was cast into a stainless steel plate. The obtained glass was annealed for several hours at the glass transition temperatures (417°C) before cooling it to room temperature at a rate of 20°C/h, and then was cut and polished carefully in order to meet the requirements for optical measurements. The UV-Vis/NIR absorption spectrum was recorded between 350 and 1700 nm by a Perkin Elmer Lambda 900 spectrophotometer. The upconversion luminescence spectrum was obtained with a TRIAX550 spectrofluorimeter upon excitation of 975 nm LD with the maximum power of 2 W. The Raman spectrum was recorded on an FT-Raman spectrophotometer (Nicolet MODULE) within the range of 100–1000 cm^{-1}. The glass transi-

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tion temperature T_g and the crystallization onset temperature T_x were determined by differential scanning calorimetry at a heating rate of 10°C/min. All the measurements were performed at room temperature.

Figure 1 shows the absorption spectrum consists of ten absorption bands centered at 1532, 977, 800, 653, 547, 521, 488, 451, 409, 379 nm, corresponding to the absorptions from the ground state $^4I_{15/2}$ to the excited states $^4I_{13/2}$, $^4I_{11/2}$, $^4I_{9/2}$, $^4F_{9/2}$, $^4S_{3/2}$, $^2H_{11/2}$, $^4F_{7/2}$, $^4F_{3/2,5/2}$, $^2H_{9/2}$, and $^4G_{11/2}$, respectively. Many researchers have applied the Judd-Ofelt theory to determine the important spectroscopic and laser parameters of RED glasses and crystals, and the calculation procedure was provided in some papers.[9,10] The Judd-Ofelt intensity parameters Ω_t (t = 2, 4, 6) in Er^{3+}-doped GPC glass, were found to be $\Omega_2 = 4.05 \times 10^{-20}\,cm^2$, $\Omega_4 = 1.18 \times 10^{-20}\,cm^2$, and $\Omega_6 = 0.69 \times 10^{-20}\,cm^2$. Previous studies reveals that Ω_2 parameter is indicative of the amount of the covalent bond and strongly dependent on the local environments of Er^{3+} ion sites, while the Ω_6 parameter is related to the viscosity and the rigidity of the glass host or the overlap integrals of the $4f$ and $5d$ orbits.[11] For comparison, we also listed the Ω_t values of other glasses in Table 1.[12] Compared with fluoride, phosphate and bismuthate glasses, the investigated glass has larger Ω_2 parameter, indicating that they are more covalent than fluoride, phosphate and bismuthate glasses.

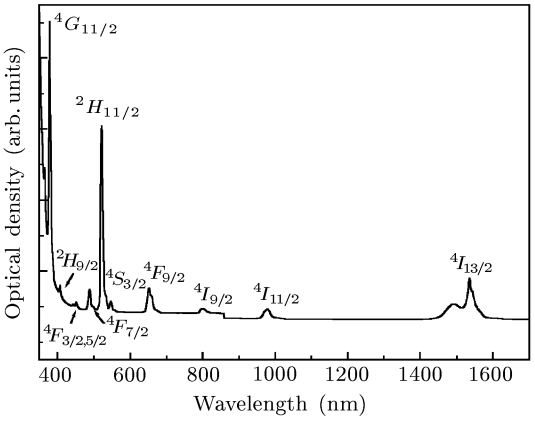


Fig. 1. Absorption spectrum of 1 mol% Er^{3+}-doped GPC glass.

Table 1. Comparisons of parameters Ω_t (t = 2, 4, 6) in GPF glass and other glasses.

Glass	Ω_2	Ω_4	Ω_6
Fluorophosphate[12]	2.90	1.63	1.26
Germanate[12]	4.81	1.41	0.48
Silicate[12]	4.23	1.04	0.61
Aluminate[12]	5.60	1.60	0.61
Fluoride[12]	2.90	1.27	1.11
Phosphate[12]	3.89	1.01	0.55
Tellurite[12]	5.05	1.45	1.22
Bismuth[12]	3.86	1.52	1.17
GPC	4.05	1.18	0.69

Figure 2 shows the room temperature upconversion spectrum of Er^{3+} doped GPC glass when the incident light's power density was 400 mW/cm^2. The observed emissions correspond to transitions of Er^{3+} ions from excited states to the ground state. Intense green and red emission bands centred at around 525, 546, and 657 nm wavelength are attributed to the $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$, and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions, respectively. The emission intensities are normalized with respect to the peak intensity at 546 nm. Three possible mechanisms have been proposed to explain the frequency upconversion phenomena of rare earth ions, namely excited state absorption (ESA), energy transfer upconversion (ET), and photon avalanche upconversion processes. It was suggested that the dominant mechanisms are ESA and ET for green and red emission under 975 nm LD excitation.[2,5] In frequency upconversion process, the upconversion emission intensity I_{up} increases in proportion to the nth power of infrared (IR) excitation intensity I_{IR}, that is, $I_{up} \propto I_{IR}^n$, where n is the number of IR photons absorbed per visible photon emitted.[12] A plot of $\log I_{up}$ vs $\log I_{IR}$ yields a straight line with slope n. Figure 3 shows such a plot for the 525, 546, and 657 nm emissions in Er^{3+} doped GPC glass under 975 nm excitation. Values of 1.80, 1.75 and 1.85 were obtained for n corresponding to the 525, 546, and 657 nm emission bands, respectively. The results indicate that a two-photon process populates $^4S_{3/2}$, $^2H_{11/2}$ and $^4F_{9/2}$ levels. According to the energy matching conditions and quadratic dependence on excitation power, the possible upconversion mechanisms for the emission bands are discussed based on the simplified energy levels of Er^{3+} presented in Fig. 4. For the green emissions, in the first step, the $^4I_{11/2}$ level is directly excited at 975 nm. The second step involves the excitation processes based on the long-lived $^4I_{11/2}$ level as follows: ET, $^4I_{11/2}$ (Er^{3+}) + $^4I_{11/2}$ (Er^{3+}) $\rightarrow$ $^4F_{7/2}$ (Er^{3+}) + $^4I_{15/2}$ (Er^{3+}); ESA, $^4I_{11/2}$(Er^{3+}) + a photon $\rightarrow$ $^4F_{7/2}$(Er^{3+}). The populated Er^{3+} $^4F_{7/2}$ level then relaxes rapidly and nonradiatively to the next lower levels $^2H_{11/2}$ and $^4S_{3/2}$ resulting from the small energy gap between them. Er^{3+} ion at the $^2H_{11/2}$ state can also decay to the $^4S_{3/2}$ state due to multiphonon relaxation process. The estimated energy gap between the $^2H_{11/2}$ state and the next lower state $^4S_{3/2}$ is $\sim$800 cm^{-1}.[12] Thus, multiphonon relaxation rate is very large and the 525 nm emission intensity is reduced. The above processes then produces the two $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ green emissions centred at 525 and 546 nm, respectively. The red emission at 657 nm is originated from the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition and the population of $^4F_{9/2}$ is based on the processes as follows: $^4I_{13/2}$ + $^4I_{11/2}$ $\rightarrow$ $^4I_{15/2}$ + $^4F_{9/2}$ (ET). The $^4I_{13/2}$ level is populated owing to the nonradiative re-

laxation from the upper $^4I_{11/2}$ level. If we use the absorption bands in the spectrum presented in Fig. 1 as the average energy of the state, the $^4I_{13/2}$ state has energy of ~1532 nm and the $^4F_{9/2}$ state has energy of 653 nm leading to an energy gap of 879 nm between the $^4I_{13/2}$ and $^4F_{9/2}$ states. Therefore, the process, $^4I_{13/2}$ + a photon → $^4F_{9/2}$, may also occur by a strongly non-resonant process. In addition, the nonradiative process from the $^4S_{3/2}$ state, which is populated by means of the process described previously, to the $^4F_{9/2}$ level also contributes to the red emission.

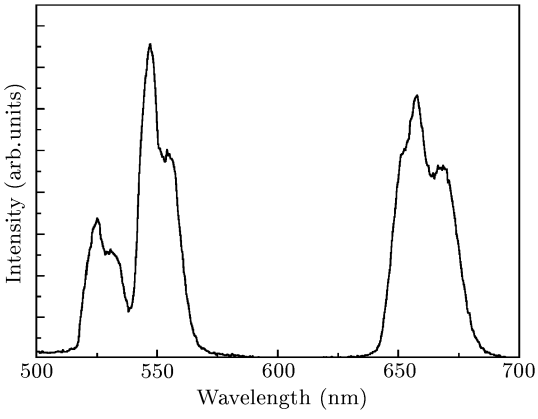


Fig. 2. Upconversion fluorescence spectra of GPC glass under 975 nm LD excitation.

Figure 5 shows the Raman spectrum of GPC glass. A least-squares fit was made for the Raman spectrum, assuming a Gaussian shape for each Raman band. In general, the low frequency Raman band is neither expected to be Gaussian-like, nor even symmetric, but on a first approximation, the low frequency features were also assumed to be Gaussian.[13] Then the Raman spectrum is developed through a deconvolution using Gaussian distribution and five bands appear at around 120, 191, 411, 530, and 805 cm^{-1}. The Raman spectrum of GPC glass shows only one high-frequency band around 805 cm^{-1}, and it has been well understood and is assigned to Ge–O stretching vibration of the four-fold coordinated $[GeO_4]$.[14] The strong 411 cm^{-1} band could be attributed to the Ge–O–Pb bridging vibrations,[15,16] while the 530 cm^{-1} band is from the Ge–O–Ge stretching vibration.[14–18] The information on Pb^{2+} ions can be deduced from the 120 cm^{-1} band assigned to Pb–Cl stretching vibration. Lead-chloride enters glass as an intermediate between a network former and a network modifier, increases the number of nonbridging oxygens and weakens the glass network. As a result, the Ge–O stretching band shifts to 805 cm^{-1}, which is much smaller than that of the pure GeO_2 glass that has a maximum phonon band around 865 cm^{-1}.[19] Then we can deduce that $PbCl_2$ has an important influence on the formation

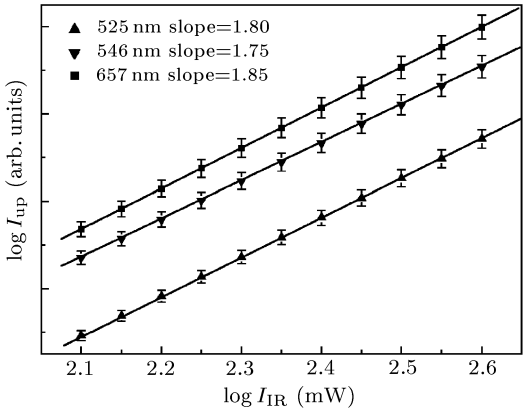


Fig. 3. Dependence of upconversion fluorescence intensity on excitation power under 975 nm LD excitation for GPC glass.

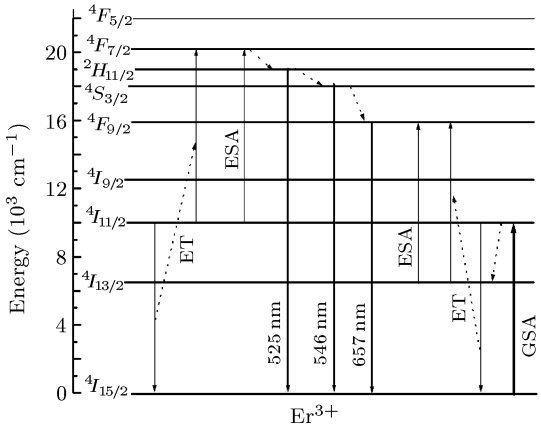


Fig. 4. Simplified energy level diagram of Er^{3+} and possible transition pathways in oxyfluoride germanate glass.

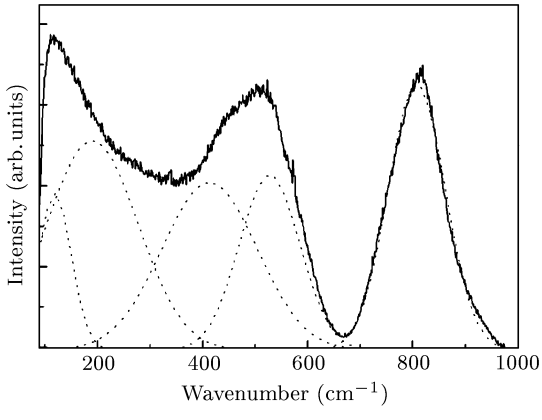


Fig. 5. Peak-deconvolution of FT-Raman spectrum of GPC glass.

of the glass network. Addition of $PbCl_2$ into germanate glass results in a lowering of the maximum phonon energy, which is lower than those of phosphate: 1100 cm^{-1}, silicate: 1000 cm^{-1}, germanate:

$900\,\mathrm{cm}^{-1}$.[19,20] Therefore, it can be deduced that the oxychloride germanate glass is better candidates for upconversion luminescence of Er^{3+} ions.

Figure 6 shows a DTA curve of the GPC glass. The thermal stability factor, ΔT ($\Delta T = T_x - T_g$), has been frequently used as a rough estimate of the glass thermal stability. To achieve a large working range of temperature during sample fibre drawing, it is desirable for a glass host to have ΔT as large as possible.[2,5] The ΔT value of this novel oxychloride germanate glass, 187°C, is much larger than that of R_2O–ZnO–TeO_2 glass,[2,5] indicating that this novel oxychloride germanate glass is much preferable for preform fabrication and crystal-free fibre drawing.

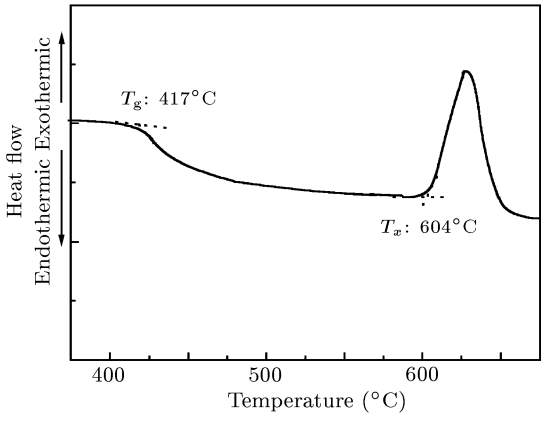


Fig. 6. Differential thermal analysis of GPC glass.

In conclusion, we have studied the upconversion fluorescence, structural and thermal stability properties of the oxychloride germanate glass. Intense infrared-to-visible upconversion fluorescence in oxychloride germanate glass has been observed under continuous wave excitation at 975 nm at room temperature. The intense 525, 546, and 657 nm upconversion fluorescence emissions, corresponding to the $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$, and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions, respectively, are due to two-photon absorption processes. The Raman spectrum investigation indicates that $PbCl_2$ plays an important role in the formation of glass network, and has an important influence on the upconversion luminescence of Er^{3+} ions. This novel oxychloride germanate glass with intense upconversion fluorescence and good thermal stability can be used as potential host material for upconversion lasers.

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