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Optical properties and upconversion fluorescence in Er³⁺-doped ZZA glass

X. Zhang^{a,*}, K. Pita^a, S. Buddhudu^a, E. Daran^b, Y.L. Lam^a, X.R. Liu^c

^a Photonics Research Group, Division of Microelectronics, School of Electrical and Electronic Engineering,
Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore

^b Laboratoire d'Analyse et d'Architecture des Systemes du CNRS, 31077 Toulouse Cedex 4, France

^c Laboratory of Excited State Processes, Chinese Academy of Sciences, Changchun 130021, China

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Abstract

We report the optical properties and upconversion emissions from the Er³⁺ ions in a ZrF₄-based glass system ZrF₄-ZnF₂-AlF₃. Judd–Ofelt intensity parameters (Ω_t) with $t = 2, 4, 6$ were obtained by analyzing the room temperature absorption spectrum. Upon 800 nm laser excitation, upconversion fluorescence was observed in blue, green and red regions at both 25 and 300 K. The main mechanism appears to be energy transfer among Er³⁺ ions in excited states. The green and red emissions result from a two-step process while the blue one is owing to a three-step energy transfer process.

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1. Introduction

Rare earth doped fluoride glasses have attracted more attention in recent years due to their potential applications as short wavelength laser sources, optical amplifiers for telecommunication and optical waveguide devices in the infrared region. Due to the lower phonon energy, infrared or red radiation induced upconversion processes have been widely observed in fluoride glasses doped with

different rare earth ions [1,2]. Upconversion laser emission has been already demonstrated with Er³⁺, Ho³⁺, Tm³⁺, Pr³⁺ and Nd³⁺ doped fluoride glass fibers [2]. In order to search for chemically stable and more efficient upconversion materials, different glass compositions have been investigated based on fluorozirconate [3–5], fluoroaluminate [6–8], fluoroindate [9–11] glasses and so on. The most efficient material is still the ZrF₄-based system known as ZBLAN, which was first reported by Poutain et al. in 1975 [12]. However, its low chemical durability, low mechanical strength and low glass transition temperature have caused serious problems for its practical applications.

Qiu et al. have reported a new ZrF₄-based glass system ZrF₄-ZnF₂-AlF₃ and labeled as ZZA (or ZZnA) [13]. According to their results, this system

* Corresponding author. Present address: Chemical Process Center, Gintic Institute of Manufacturing Technology, 71, Nanyang Drive, Singapore 638075. Tel.: +65-7938494; fax: +65-7924967.

E-mail address: zhangx@gintic.gov.sg (X. Zhang).

showed several important advantages compared to the ZBLAN system including high chemical stability, high mechanical strength and excellent glass forming characteristics. However, for the best of our knowledge, the behaviors of rare earth ions in this glass have not been studied yet. It is therefore necessary to investigate the optical properties of rare earth ions in this glass system. In this paper, we report the infrared laser induced upconversion properties of Er^{3+} doped ZZA glass with excitation in the 800 nm range from a Ti:sapphire laser.

2. Experimental

For the preparation of the glass samples, high purity anhydrous fluorides ZnF_2 , AlF_3 , BaF_2 , YF_3 and ErF_3 were used as starting materials. ZrF_4 component was obtained from the fluorination of ZrO_2 with NH_4HF_2 at 300–400 for 5–10 h. The raw materials were mixed with 10–20% of NH_4HF_2 in order to transfer the residual oxides into fluorides. The well-mixed batches were put in an alumina crucible heated to about 350 °C for 30 min to 1 h for fluorination and then melted at about 900 °C for 30 min in N_2 atmosphere. The melt was poured onto a preheated brass mould and pressed with a stainless plate. The glass obtained was post-annealed at 500 °C for 30 min. The typical glass composition was 20ZrF_4 – 30ZnF_2 – 25AlF_3 – 10BaF_2 – 14YF_3 – 1ErF_3 .

Absorption spectra in the range of 200–1100 nm for the glass samples were measured by using a HP 8453 spectrophotometer. Upconversion measurements were performed by using a cw tunable Ti:sapphire laser. The excitation wavelength can be tuned from 750–900 nm. The samples were fixed in a cryostat circulated by liquid helium to obtain a working temperature ranging from 25 K to RT. The detail of the experimental procedure was reported previously [14].

3. Results and discussion

Fig. 1 shows the room temperature absorption spectra for Er^{3+} ZZA glass samples. The main absorption lines are assigned in the spectra. The

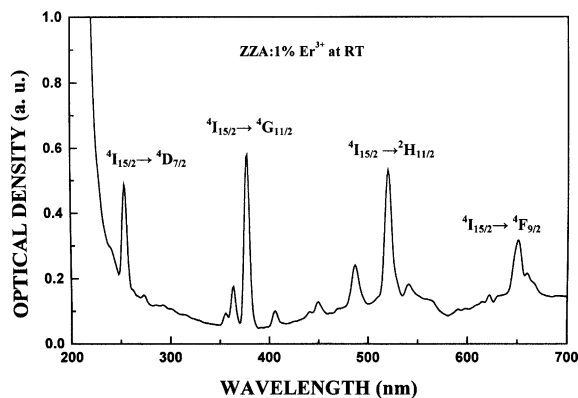


Fig. 1. Room temperature absorption spectrum of ZZA:1% Er^{3+} .

intense absorption lines are due to ${}^4\text{I}_{15/2} \rightarrow {}^2\text{H}_{11/2}$ (520 nm), ${}^4\text{I}_{15/2} \rightarrow {}^4\text{G}_{11/2}$ (380 nm) and ${}^4\text{I}_{15/2} \rightarrow {}^4\text{D}_{7/2}$ (255 nm).

According to the absorption spectrum shown in Fig. 1, the oscillator strength of each absorption band can be calculated using the equation:

$$P = \frac{mc^2n^2}{\pi e^2N\chi} \int k(v)dv \quad (1)$$

where N is the number of activator ions in a unit volume, m and c are mass and charge of the electron, n is the refractive index of the sample, χ is the term for the effective field at a well-located center in a medium of isotropic refractive index n and is given by $\chi_{\text{ED}} = n(n^2 + 2)^2/9$ for electric dipole transitions and $\chi_{\text{MD}} = n^3$ for magnetic dipole transitions. $\int k(v)dv$ is the integrated absorption coefficient, and the value for each absorption transition can be calculated from the absorption spectrum.

In the Judd–Ofelt treatment [15,16], the line strength S for a given transition of average energy ν (in cm^{-1}), can be expressed by the oscillator strength as follow:

$$S = \frac{3h(2J+1)}{8\pi^2mc\nu} P \quad (2)$$

In our work, since there is no allowed magnetic dipole transitions, only the electric dipole transitions were taken into account and therefore, $S = S_{\text{ED}}$ and $P = P_{\text{ED}}$. The electric dipole line strength S_{ED} between an initial J manifold $| (S, L)J \rangle$ and a final J' manifold $| (S', L')J' \rangle$ is obtained by

$$S_{ED}[(S, L)J; (S', L')J'] = \sum_{t=2,4,6} \Omega_{(t)} | \langle (S, L)J || U^{(t)} || (S', L')J' \rangle |^2 \quad (3)$$

where the terms $||U^{(t)}||$ are the reduced matrix elements of the unit tensor operators, which are insensitive to the host lattice and are calculated by some researchers before. [17] $\Omega_{(t)}$ ($t = 2, 4, 6$) are Judd–Ofelt intensity parameters which contain the effects of the crystal field terms, radial integrals of an electron, and so on. The $\Omega_{(t)}$ parameters can be determined from a least-squares fit to the values of measured S_{ED} using Eq. (3).

The fitted $\Omega_{(t)}$ parameters are given in Table 1. We show also the results for Er^{3+} doped ZBLAN and aluminate glasses [18] for comparison. The $\Omega_{(2)}$ values for the three kind glasses are aluminate > ZZA > ZBLAN indicating that the covalence of ZZA is higher than that of ZBLAN but lower than that of aluminate. Usually, the degree of covalence has a close relation with the chemical stability of a glass. This evidence indicates that ZZA glass possesses a superior chemical stability over the ZBLAN glass, which is in consistent with the previously reported results on glass chemistry study [13]. Measured and calculated oscillator

Table 1
Intensity parameters, $\Omega_{(t)}$ (10^{-20} cm^2), of Er^{3+} in aluminate, ZZA and ZBLAN glasses

Glass	$\Omega_{(2)}$	$\Omega_{(4)}$	$\Omega_{(6)}$
Aluminate [18]	5.60	1.60	0.61
ZZA	3.08	1.78	0.20
ZBLAN [18]	2.91	1.27	1.11

Table 2
Experimental and calculated oscillator strengths for ZZA:Er glass

Transitions	Energy (cm^{-1})	$P_{\text{exp}} (\times 10^6)$	$P_{\text{cal}} (\times 10^6)$	$\Delta P (\times 10^6)$
${}^4\text{I}_{15/2} \rightarrow {}^4\text{I}_{11/2}$	10286	0.50	0.16	-0.34
${}^4\text{F}_{9/2}$	15373	1.05	1.74	0.69
${}^2\text{H}_{11/2}$	19230	5.04	5.13	0.09
${}^4\text{F}_{7/2}$	20551	0.91	1.07	0.16
${}^4\text{F}_{5/2} + {}^4\text{F}_{3/2}$	22247	0.43	0.27	-0.26
${}^2\text{H}_{9/2}$	24630	0.67	0.21	-0.46
${}^4\text{G}_{11/2}$	26490	9.17	9.10	-0.07
${}^4\text{G}_{9/2}$	27472	1.90	1.51	-0.49
${}^4\text{D}_{7/2}$	39370	9.79	8.56	-1.23

rms deviation

6.7×10^{-7}

strengths are given in Table 2. The rms is about 6.7×10^{-7} , which shows a good fitting.

Upon excitation into the ${}^4\text{I}_{15/2} \rightarrow {}^4\text{I}_{11/2}$ transition with a Ti:sapphire laser at about 800 nm, Er^{3+} -doped ZZA glass sample shows mainly three upconversion emissions at 25 K. Fig. 2 shows the blue and green emission spectra from ${}^2\text{H}_{9/2} \rightarrow {}^4\text{I}_{15/2}$ and ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$ transitions. The green emission is the most intense upconversion emission observed. Another emission band was observed between 650 and 670 nm arising from ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$ transition. At room temperature, a weak band due to ${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2}$ transition has been also detected between 515 and 535 nm, which is about 1/5 of the intensity for the ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$ band. At low temperature the green emission band is about two times stronger than the room temperature band (Fig. 2).

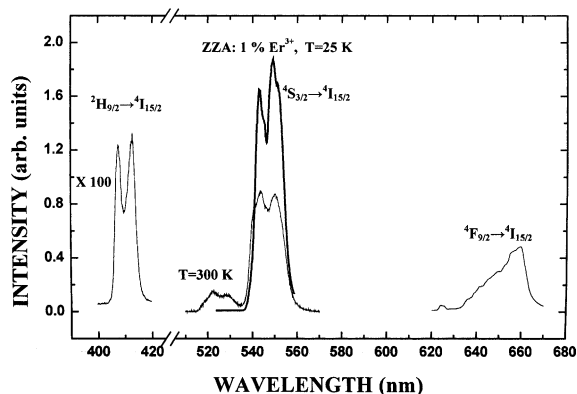


Fig. 2. Blue, green and red upconversion spectra for ZZA:1% Er^{3+} with 800 nm excitation obtained at 25 K and room temperature (for green emission).

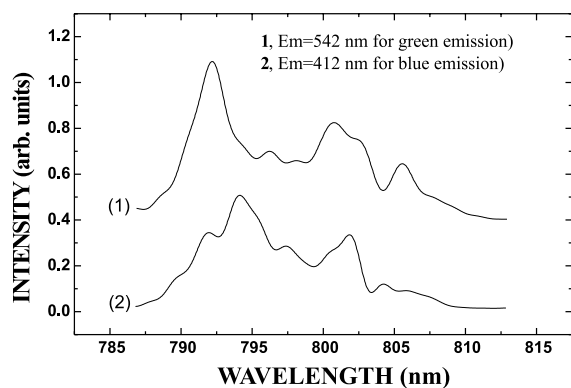


Fig. 3. Excitation spectra for the blue and green upconversion emissions at 25 K.

The 25 K excitation spectra for green and blue emissions are slightly different. Both spectra are registered in the same range while the band shapes are different (Fig. 3). This is due to the different excitation processes: a two-step process for the green emission while a three-step process for the blue one (see below).

Fig. 4 shows the evolution of emission intensities on laser power by monitoring the emission peaks at 412, 551 and 660 nm. According to the slopes of the fitted straight lines in log–log plot, a three-photon upconversion process is assigned to the blue emission from $^2H_{9/2}$ level, while a two-photon process is responsible for the green and red upconversions from $^4S_{3/2}$ and $^4F_{9/2}$ levels.

The luminescence lifetime of $Er^{3+} \ ^4S_{3/2}$ is about 0.35 ms in ZZA under 380 nm UV light excitation. However, under upconversion condition with 800 nm laser excitation, the measured lifetime for the same level is about 1 ms. This result rules out the sequential excitation mechanism for the observed upconversion, because the emitting level would keep its intrinsic lifetime under the two-step excitation process. Since other recognized upconversion mechanisms such as photon avalanche, cooperative excitation and luminescence have no sense with this work, the predominant upconversion mechanism should be the energy transfer between different excited states. The proposed upconversion process is shown in Fig. 5.

Firstly, the 800 nm excitation raises the Er^{3+} ion to the $^4I_{9/2}$ state. With a fast multiphonon relax-

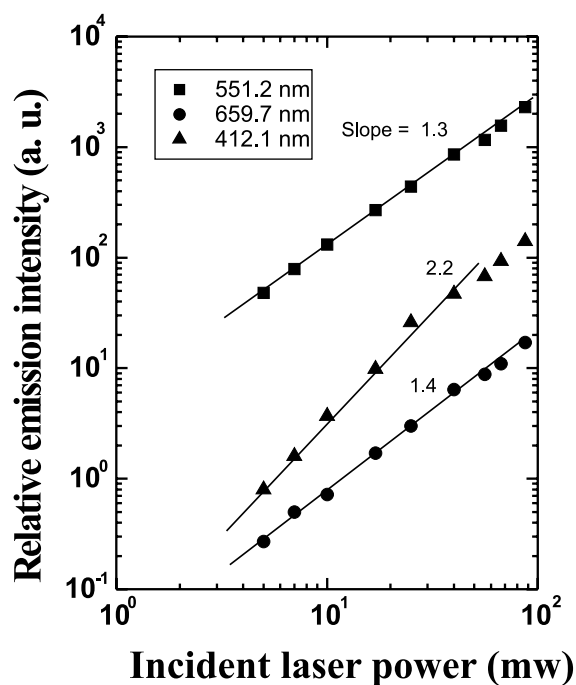


Fig. 4. Log–log plots for different upconversion emissions as a function of incident laser powers for ZZA:1% Er^{3+} .

ation, the excited ions decay to the lower-lying $^4I_{11/2}$ level. This level usually has a lifetime of several milliseconds in glass hosts. Then the first energy transfer takes place between two adjacent excited Er^{3+} ions in $^4I_{11/2}$ state inducing that one ion re-excites to a higher energy level ($^4F_{7/2}$) and the other de-excites to the ground state. In the third step, a second energy transfer process between ions in $^4I_{11/2}$ and $^4S_{3/2}$ states excites the Er^{3+} ions to even higher level to populate the $^2H_{9/2}$ level. Due to the three-photon process, the blue emission is relatively weak compare to the green and red ones.

In summary, the Er^{3+} ion shows efficient green upconversion in ZZA glass both at 25 K and at room temperature. Judd–Ofelt analysis shows that the covalence of ZZA glass is higher than ZBLAN glass resulting in an increase of the chemical stability. The predominant upconversion mechanisms are energy transfer between excited Er^{3+} ions: a two-step energy transfer process for green and red upconversions and a three-step process for blue emission.

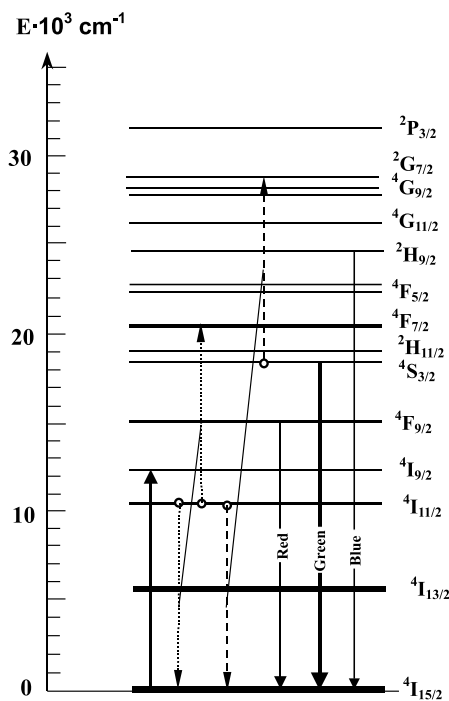


Fig. 5. Schematic upconversion mechanisms under 800 nm excitation proposed for Er^{3+} -doped ZZA glass.

Acknowledgements

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