www.czasopisma.pan.pl PAN www.journals.pan.pl

Opto-Electronics Review 25 (2017) 238–241

Contents lists available at ScienceDirect

Opto-Electronics Review

journal homepage: http://www.journals.elsevier.com/opto-electronics review

Erbium-doped lead silicate glass for near-infrared emission and temperature-dependent up-conversion applications

W.A. Pisarski [a,*], J. Pisarska [a], R. Lisiecki [b], W. Ryba-Romanowski [b]

[a] University of Silesia, Institute of Chemistry, Szkolna 9, 40-007 Katowice, Poland
[b] Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna 2, 50-422 Wrocław, Poland

ARTICLE INFO

Article history:
Received 16 January 2017
Accepted 23 June 2017
Available online 3 August 2017

Keywords:
Lead silicate glasses
Er^{3+} ions
Near-infrared emission: up-conversion process

ABSTRACT

Erbium-doped lead silicate glass has been investigated for near-infrared emission and up-conversion applications. Near-infrared emission due to $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} is relatively broad (70.5 nm) and long-lived (3.7 ms). Also, up-conversion luminescence spectra of Er^{3+} ions in lead silicate glass have been examined as a function of temperature. The relative intensities of luminescence bands corresponding to $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions of Er^{3+} were determined with temperature. The fluorescence intensity ratio and temperature sensitivity were calculated. The maximum sensitivity for Er^{3+} doped lead silicate glass is close to $26.4 \times 10^{-4}\ K^{-1}$ at T = 590 K.

1. Introduction

Lead silicate glasses have received great attention in the past due to their good chemical and physical properties, such as high stability against crystallization, ease of preparation, thermal conductivity and heat capacity. Furthermore, PbO-SiO_2 systems exhibit a wide glass formation composition range up to 90 mol% PbO and they contain extraordinarily large amounts of free volume (voids), which cannot be found in conventional binary silicate glasses. For that reason, PbO-SiO_2 glasses are classified as a "binary network-former glass" with large amounts of free volume [1]. Also, lead silicate glasses belong to materials emitting light in a wide spectral region under UV–vis or NIR laser excitation. The advantage of these glass systems are large transparency from UV to NIR spectral ranges and quite easy incorporation of Er^{3+} [2–5], Nd^{3+} [6–8], Eu^{3+} [9], Pr^{3+} [10] and other rare earth ions [11] into glass host matrices. Transition metal ions as the optically active ions are incorporated [12,13], as well.

In this work, erbium-doped lead silicate glass belonging to the family of heavy metal glasses HMG [14–17] has been investigated for near-infrared emission and up-conversion applications. In particular, the up-conversion luminescence spectra of Er^{3+} ions in lead silicate glass have been examined with temperature. A special attention has been paid to Er^{3+} doped lead silicate glass to optical temperature sensor applications. Recently, the up-conversion luminescence processes of Er^{3+} ions in lead silicate glass were presented and discussed in details [2–4]. However, the up-conversion luminescence spectra of Er^{3+} ions in lead silicate glass varying with temperature were not specifically examined. The previously published work suggests that the thermometry range, relying on the fluorescence intensity ratio method, is excessively extended due to the high vitreous transition temperature in Er^{3+}/Yb^{3+} co-doped lead-free silicate glass [18].

2. Experimental

Glass with general formula 45PbO-45SiO_2-9Ga_2O_3-1Er_2O_3, in mol%, were prepared by mixing and melting appropriate amounts of metal oxides of high purity (99.99%, Aldrich Chemical Co.). A homogeneous mixture was heated in a protective atmosphere of dried argon. Mixed reagents were melted for 0.5 h at 1100 °C.

Near-infrared emission spectrum was measured using a Continuum Model Surelite I optical parametric oscillator pumped by a third harmonic of a Nd:YAG laser. Up-conversion luminescence has been excited with diode laser at 980 nm. Luminescence was dispersed by a 1-m double grating monochromator and detected with a photomultiplier with S-20 spectral response. Emission spectra were collected using a Stanford SRS 250 boxcar integrator with accuracy of ±0.2 nm. Luminescence decay curve was recorded and stored by a Tektronix TDS 3052 oscilloscope with accuracy of ±2 μs.

3. Results and discussion

3.1. Near-infrared emission

The previously published works for Tm^{3+} [19,20] and Ho^{3+} [21,22] in lead silicate glasses and fibers suggest their near-infrared

* Corresponding author.
E-mail address: wojciech.pisarski@us.edu.pl (W.A. Pisarski).

http://dx.doi.org/10.1016/j.opelre.2017.06.011
1896-3757/

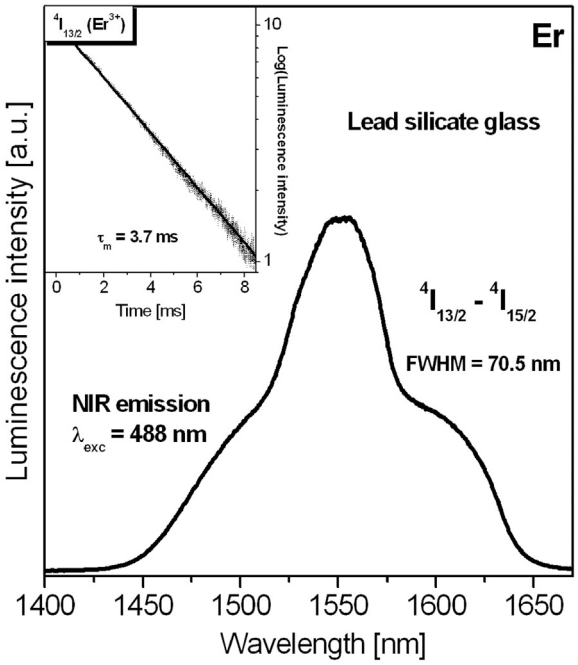

Fig. 1. Near-infrared emission of Er^{3+} ions in lead silicate glass. Inset shows decay curve for the $^4I_{13/2}$ state of Er^{3+}.

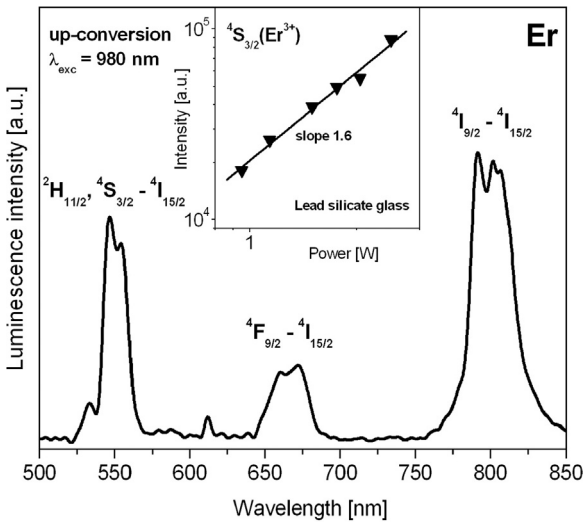

Fig. 2. Up-conversion luminescence spectrum of Er^{3+} ions in lead silicate glass. Inset shows the log–log dependence of up-conversion luminescence intensities on the excitation power.

laser application at 2000 nm. Here, the experimental results for Er^{3+} ions in lead silicate glass are presented and discussed in relation to potential applications at third telecommunication window.

Figure 1 presents near-infrared emission spectrum which was recorded for Er^{3+} ions in lead silicate glass. The spectrum was measured under excitation of $^4F_{7/2}$ state by 488 nm laser line. In many cases, erbium doped materials are efficiently pumped by commercially available laser sources using a 488 nm line [23], because the absorption band of the Er^{3+}:$^4I_{15/2} \rightarrow {}^4I_{11/2}$ transition around 980 nm characterize relatively weak ground state absorption. NIR emission band at about 1550 nm corresponds to $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+}. The spectral linewidth $\Delta\lambda$ defined as full width in half maximum (FWHM) was determined. The value of FWHM for $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} is nearly close to 70.5 nm, which is demanded for tunable solid-state lasers and broadband optical amplifiers. The inset of Fig. 1 shows luminescence decay from the $^4I_{13/2}$ state of Er^{3+} in lead silicate glass. The luminescence lifetime calculated by fitting the decay curve is also an important spectroscopic parameter for broadband optical amplifiers. The relatively long lifetime of the $^4I_{13/2}$ state required for the high population inversion is the critical factor in the success of erbium-doped fiber amplifiers (EDFA) in the optical communications. Luminescence decay analysis for lead silicate glass indicates that the $^4I_{13/2}$ measured lifetime of Er^{3+} is close to 3.7 ms and its experimental value is significantly longer in comparison to erbium-doped lead borate glasses studied earlier by us for near-infrared broadband optical amplifiers [24].

3.2. Temperature-dependent up-conversion process

Figure 2 presents up-conversion luminescence spectrum of Er^{3+} ions in lead silicate glass. The inset shows the log–log dependence of luminescence intensity on the excitation power. The spectra were measured under 980 nm diode-laser excitation. The observed luminescence bands at about 550 nm, 670 nm and 800 nm correspond to $^2H_{11/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$, $^4F_{9/2} \rightarrow {}^4I_{15/2}$ and $^4I_{9/2} \rightarrow {}^4I_{15/2}$ transitions of Er^{3+}, respectively. Two dominant 2-photon mechanisms are involved in the up-conversion process, namely the excited state absorption ESA and the energy transfer up-conversion ETU [25]. The $^4I_{11/2}$ (Er^{3+}) level is directly excited by 980 nm line. In the ESA process, the Er^{3+} ions ($^4I_{11/2}$ state) absorb photons and are then excited to $^4F_{7/2}$ state. In the ETU process, two excited Er^{3+} ions ($^4I_{11/2}$ state) interact with each other. One of them is de-excited to $^4I_{15/2}$ ground state, whereas the other is promoted to $^4F_{7/2}$ state. Both the ESA and ETU processes populate the $^4F_{7/2}$ state which transfers energy very fast to $^4S_{3/2}$ state by a non-radiative multiphonon process. The excited state absorption mechanism ESA leads to a fast increase of the up-conversion luminescence, whereas the energy transfer mechanism ETU is expected to show a relatively slow increase after the laser pulse. Further investigations clearly indicate that glasses singly doped with Er^{3+} ions present usually a rapid increase of the up-conversion luminescence during the laser pulse. Based on experimental results published recently [26], the observed up-conversion luminescence processes are mainly due to excited state absorption processes (ESA). In particular, these processes are dominant, where activator concentration is relatively low. Finally, the up-conversion luminescence spectrum due to $^2H_{11/2}$,$^4S_{3/2} \rightarrow {}^4I_{15/2}$ (green), $^4F_{9/2} \rightarrow {}^4I_{15/2}$ (red) and/or $^4I_{9/2} \rightarrow {}^4I_{15/2}$ (NIR) transitions of Er^{3+} are observed. The mechanism of up-conversion process was determined from the log–log dependence of luminescence intensity on the excitation power using the following relation:

$$I_{UPC} \sim P^n{}_{pump}, \tag{1}$$

where: I_{UPC} denotes the up-conversion integrated luminescence intensity, P – the laser power and n – number of photons. The slope of 1.6 for the $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} in lead silicate glass indicates that 2-photon mechanism was involved in the up-conversion process. It was schematized on the energy level diagram (Fig. 3).

Further experimental studies indicate that the up-conversion luminescence spectra of rare earths in glasses are changed drastically with temperature [27]. Figure 4 shows up-conversion luminescence spectra of Er^{3+} ions in lead silicate glass as a function of temperature. The spectra were recorded in the 500–580 nm spectral ranges under 980 nm excitation by cw laser-diode. In this spectral region two green luminescence bands are observed which correspond to $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ thermally coupled transitions of Er^{3+}. Their relative emission band intensities were determined with temperature.

Table 1
Maximum sensitivity S_{MAX} for Er^{3+} doped lead silicate glass and other silicate based glass host matrices.

Rare earth	Glass host	S_{MAX} ($\times 10^{-4}$ K^{-1})	T (K)	Temperature range (K)	Excitation λ (νμ)	Ref.
Er^{3+}	PbO-SiO_2-Ga_2O_3	26	590	300–650	980	[a]
Er^{3+}	SiO_2-B_2O_3-Na_2O	23	296	296–673	978	[29]
Er^{3+}/Yb^{3+}	SiO_2-BaF_2-ZnF_2	27	513	250–650	980	[30]
Er^{3+}/Yb^{3+}	SiO_2-B_2O_3-Na_2O-BaO	31	550	300–700	970	[18]
Er^{3+}/Yb^{3+}	SiO_2-B_2O_3-Na_2O	33	296	296–723	978	[31]

[a] This work.

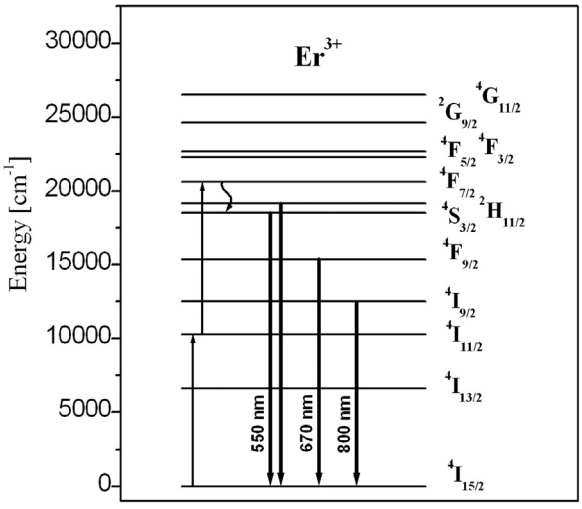

Fig. 3. Energy level diagram of Er^{3+}. All transitions are also indicated.

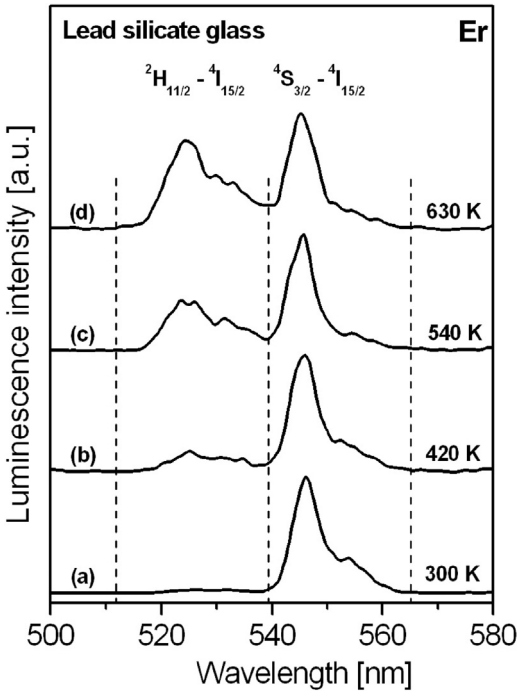

Fig. 4. Influence of temperature on up-conversion luminescence of Er^{3+} ions in lead silicate glass.

Fluorescence Intensity Ratio R (or FIR) from each thermally coupled $^2H_{11/2}$ and $^4S_{3/2}$ levels to the $^4I_{15/2}$ ground state can be expressed by the following equation:

$$R = \frac{I_H}{I_S} = C\exp\left(-\frac{\Delta E}{kT}\right) \quad (2)$$

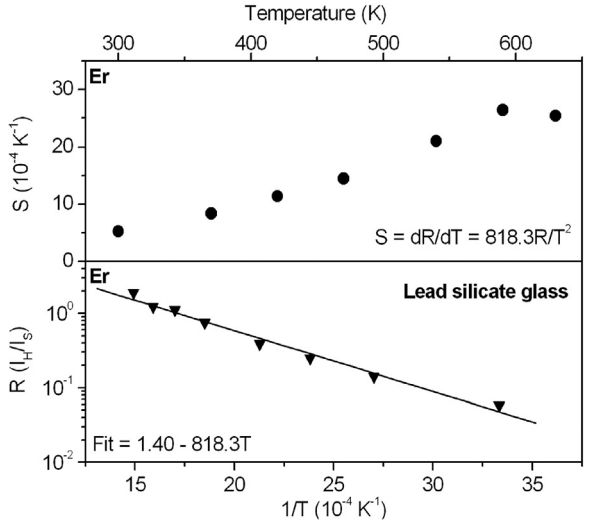

Fig. 5. Fluorescence intensity ratio R and temperature sensitivity S for Er^{3+} doped lead silicate glass.

where I_H and I_S are the integrated luminescence intensities of the transitions of $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$, ΔE – energy gap between $^2H_{11/2}$ and $^4S_{3/2}$ levels, k – Boltzmann constant. The pre-exponential constant C is given by:

$$C = \frac{g_H \sigma_H \omega_H}{g_S \sigma_S \omega_S}, \quad (3)$$

where g, σ, ω are the degeneracy, the emission cross-section, the angular frequency of fluorescence transitions from the $^2H_{11/2}$ and $^4S_{3/2}$ levels to the $^4I_{15/2}$ level, respectively.

The rate of R varies with temperature and it is usually defined as temperature sensitivity S:

$$S = \frac{dR}{dT} = R\left(\frac{\Delta E}{kT^2}\right). \quad (4)$$

The fluorescence intensity ratio R and sensitivity S varying with temperature are presented in Fig. 5. For erbium-doped lead silicate glass, the maximum sensitivity is equal to 26.4×10^{-4} K^{-1} at T = 590 K and its value is higher in comparison to PbO-GeO_2-Ga_2O_3 glass containing Er^{3+} ions [28]. On the other hand, the maximum sensitivity is similar to that one obtained for silicate based glasses containing Er^{3+} and Er^{3+}/Yb^{3+} ions [18,29–31]. The results are summarized in Table 1.

4. Conclusions

Erbium-doped lead silicate glass has been investigated for near-infrared emission and temperature dependent up-conversion applications. Near-infrared emission corresponding to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ions is relatively broad (70.5 nm) and long-lived (3.7 ms). Up-conversion luminescence spectra of Er^{3+} ions in lead silicate glass have been examined for temperature sensing. In the 500–580 nm spectral ranges, two green luminescence bands are observed, which correspond to transi-

tions originating from thermally coupled $^2H_{11/2}$ and $^4S_{3/2}$ excited states to $^4I_{15/2}$ ground state of Er^{3+}. The log–log dependence of luminescence intensity on the excitation power confirms 2-photon mechanism of up-conversion process. The relative luminescence band intensities of $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions of Er^{3+} were determined with temperature. Temperature sensitivity was analyzed based on the fluorescence intensity ratio R from each thermally coupled $^2H_{11/2}$ and $^4S_{3/2}$ levels to the $^4I_{15/2}$ ground state of Er^{3+}. The maximum sensitivity is due to $26.4 \times 10^{-4}\,K^{-1}$ at T = 590 K, which indicates that erbium-doped lead silicate glass is promising for optical temperature sensors.

Novelty statement

In this work, Er^{3+}-doped lead silicate glass belonging to heavy metal glass family has been studied for NIR emission and up-conversion applications. In particular, the up-conversion luminescence spectra of Er^{3+} have been examined with temperature. A special attention has been paid for Er^{3+} doped lead silicate glass to optical temperature sensor applications. Temperature-dependent up-conversion luminescence spectra of Er^{3+} ions in lead silicate glass were not specifically examined.

Acknowledgement

The National Science Centre (Poland) supported this work under research project 2014/13/B/ST7/01729.

References

[1] S. Kohara, H. Ohno, M. Takata, T. Usuki, H. Morita, K. Suzuya, J. Akola, L. Pusztai, Lead silicate glasses: binary network-former glasses with large amounts of free volume, Phys. Rev. B 82 (2010) 134209.
[2] J.A. Capobianco, G. Prevost, P.P. Proulx, P. Kabro, M. Bettinelli, Upconversion properties of Er^{3+} doped lead silicate glasses, Opt. Mater. 6 (1996) 175–184.
[3] B. Karmakar, R.N. Dwivedi, FT-IRRS, UV-Vis-NIR absorption and green upconversion in Er^{3+} doped lead silicate glass, J. Non-Cryst. Solids 342 (2004) 132–139.
[4] S. Xu, G. Wang, S. Dai, J. Zhang, L. Hu, Z. Jiang, Infrared to visible upconversion in Er^{3+}-doped lead oxyfluorosilicate glasses, J. Lumin. 109 (2004) 187–192.
[5] N.O. Dantas, Fanyao Qu, J.T. Arantes Jr., Experimental study of absorption and luminescence properties of Er^{3+} in lead silicate glass, J. Alloys Compd. 344 (2002) 316–319.
[6] E.O. Serqueira, N.O. Dantas, A.F.M. Monte, M.J.V. Bell, Judd Ofelt calculation of quantum efficiencies and branching ratios of Nd^{3+} doped glasses, J. Non-Cryst. Solids 352 (2006) 3628–3632.
[7] K. Zou, H. Guo, M. Lu, W. Li, Ch. Hou, W. Wei, J. He, B. Peng, B. Xiangli, Broad-spectrum and long-lifetime emissions of Nd^{3+} ions in lead fluorosilicate glass, Opt. Express 17 (2009) 10001–10009.
[8] M. Bettinelli, A. Speghini, M.G. Brik, Spectroscopic studies of emission and absorption properties of $38PbO\text{-}62SiO_2$:Nd^{3+} glass, Opt. Mater. 32 (2010) 1592–1596.
[9] D. Zhao, X. Qiao, X. Fen, M. Wang, Local vibration around rare earth ions in SiO_2-PbF_2 glass and glass ceramics using Eu^{3+} probe, Physica B 395 (2007) 10–15.
[10] K. Bhargavi, V. Sudarsan, M.G. Brik, M. Sundara Rao, Y. Gandhi, P. Nageswara Rao, N. Veeraiah, Influence of Al declustering on the photoluminescent properties of Pr^{3+} ions in PbO-SiO_2 glasses, J. Non-Cryst. Solids 362 (2013) 201–206.
[11] L. Żur, J. Janek, M. Sołtys, J. Pisarska, W.A. Pisarski, Spectroscopic properties of Eu^{3+}, Dy^{3+} and Tb^{3+} ions in lead silicate glasses obtained by conventional high-temperature melt-quenching technique, Phys. Scr. T157 (2013) 014035.
[12] F. Qu, N.O. Dantas, Energy transfer in Cr^{3+}/Nd^{3+}-codoped lead silicate glasses, Physica B 327 (2003) 79–87.
[13] T.G.V.M. Rao, A. Rupesh Kumar, M. Rami Reddy, Spectroscopic studies of tungsten ions in PbO-PbF_2-SiO_2 glasses, J. Non-Cryst. Solids 358 (2012) 25–29.
[14] J. Pisarska, W.A. Pisarski, Synthesis and properties of multicomponent lead fluoroborate glasses containing rare earth ions, J. Optoelectron. Adv. Mater. 7 (2005) 2667–2669.
[15] W.A. Pisarski, L. Żur, J. Pisarska, Optical transitions of Eu^{3+} and Dy^{3+} ions in lead phosphate glasses, Opt. Lett. 36 (2011) 990–992.
[16] W.A. Pisarski, Ł. Grobelny, J. Pisarska, R. Lisiecki, W. Ryba-Romanowski, Spectroscopic properties of Yb^{3+} and Er^{3+} ions in heavy metal glasses, J. Alloys Compd. 509 (2011) 8088–8092.
[17] L. Żur, M. Sołtys, J. Pisarska, W.A. Pisarski, Absorption and luminescence properties of terbium ions in heavy metal glasses, J. Alloys Compd. 578 (2013) 512–516.
[18] S. Zhou, C. Li, Z. Liu, S. Li, C. Song, Thermal effect on up-conversion in Er^{3+}/Yb^{3+} co-doped silicate glass, Opt. Mater. 30 (2007) 513–516.
[19] X. Liu, X. Wang, L. Wang, P. Kuan, M. Li, W. Li, X. Fan, K. Li, L. Hu, D. Chen, Realization of 2 μm laser output in Tm^{3+}-doped lead silicate double cladding fiber, Mater. Lett. 125 (2014) 12–14.
[20] G. Tang, T. Zhu, W. Liu, W. Lin, T. Qiao, M. Sun, D. Chen, Q. Qian, Z. Yang, Tm^{3+} doped lead silicate glass single mode fibers for 2.0 μm laser applications, Opt. Mater. Express 6 (2016) 2147–2157.
[21] X. Liu, F. Huang, S. Gao, X. Wang, L. Hu, D. Chen, Compositional investigation of ~2.0 luminescence of Ho^{3+}-doped lead silicate glass, Mater. Res. Bull. 71 (2015) 11–15.
[22] X. Liu, P. Kuan, D. Li, S. Gao, X. Wang, L. Zhang, L. Hu, D. Chen, Heavily Ho^{3+}-doped lead silicate glass fiber for ~2 μm fiber lasers, Opt. Mater. Express 6 (2016) 1093–1098.
[23] E. Cattaruzza, M. Back, G. Battaglin, E. Trave, Unexpected behavior of the 1.54 μm luminescence in Er-doped silica films, J. Non-Cryst. Solids 401 (2014) 186–190.
[24] W.A. Pisarski, J. Pisarska, R. Lisiecki, Ł. Grobelny, G. Dominiak-Dzik, W. Ryba-Romanowski, Erbium-doped oxide and oxyhalide lead borate glasses for near-infrared broadband optical amplifiers, Chem. Phys. Lett. 472 (2009) 217–219.
[25] F. Auzel, Upconversion and anti-stokes processes with f and d ions in solids, Chem. Rev. 104 (2004) 139–174.
[26] A. de Pablos-Martín, J. Méndez-Ramos, J. del-Castillo, A. Durán, V.D. Rodríguez, M.J. Pascual, Crystallization and up-conversion luminescence properties of Er^{3+}/Yb^{3+}-doped $NaYF_4$-based nano-glass-ceramics, J. Eur. Ceram. Soc. 35 (2015) 1831–1840.
[27] M. Kochanowicz, D. Dorosz, J. Zmojda, J. Dorosz, P. Miluski, Influence of temperature on upconversion luminescence in tellurite glass co-doped with Yb^{3+}/Er^{3+} and Yb^{3+}/Tm^{3+}, J. Lumin. 151 (2014) 155–160.
[28] W.A. Pisarski, J. Pisarska, R. Lisiecki, W. Ryba-Romanowski, Sensitive optical temperature sensor based on up-conversion luminescence spectra of Er^{3+} ions in PbO-Ga_2O_3-XO_2 (X = Ge, Si) glasses, Opt. Mater. 59 (2016) 87–90.
[29] Ch. Li, B. Dong, Ch. Ming, M. Lei, Application to temperature sensor based on green up-conversion of Er^{3+} doped silicate glass, Sensors 7 (2007) 2652–2659.
[30] L. Feng, B. Lai, J. Wang, G. Du, Q. Su, Spectroscopic properties of Er^{3+} in a oxyfluoride glass and upconverted and temperature sensor behavior of Er^{3+}-Yb^{3+}-codoped oxyfluoride glass, J. Lumin. 130 (2010) 2418–2423.
[31] Ch. Li, B. Dong, S. Li, Ch. Song, Er^{3+}-Yb^{3+} co-doped silicate glass for optical temperature sensor, Chem. Phys. Lett. 443 (2007) 426–429.