

Visible green upconversion luminescence of $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Li}^{+}$ co-doped CaWO_4 particles

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Abstract

The upconversion (UC) luminescence of $\text{Li}^{+}/\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped CaWO_4 phosphors is investigated in detail. Single crystallized $\text{CaWO}_4:\text{Li}^{+}/\text{Er}^{3+}/\text{Yb}^{3+}$ phosphor can be obtained, co-doped up to 25.0/5.0/20.0 mol% ($\text{Li}^{+}/\text{Er}^{3+}/\text{Yb}^{3+}$) by solid-state reaction. Under 980 nm excitation, $\text{CaWO}_4:\text{Li}^{+}/\text{Er}^{3+}/\text{Yb}^{3+}$ phosphor exhibited strong green UC emissions visible to the naked eye at 530 and 550 nm induced by the intra-4f transitions of Er^{3+} ($^2\text{H}_{11/2}, ^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$). The optimum doping concentrations of $\text{Yb}^{3+}/\text{Li}^{+}$ for the highest UC luminescence were verified to be 10/15 mol%, and a possible UC mechanism that depends on the pumping power is discussed in detail.

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1. Introduction

Over the past several decades, upconversion (UC) luminescence in rare earth (RE) ions doped phosphor materials has been extensively studied since its discovery in the 1960s [1]. Potential applications include solar cells, novel display technologies and, more recently, biophysics. The UC phosphors could indeed be used as probes for imaging of individual molecules in biological cells [2]. Moreover, fluorescence imaging using near infrared (NIR) excitation is expected to have a major impact in biomedical imaging [3]. The application of UC phosphor is also being considered in the photovoltaic industry to develop high-efficiency solar cells [4].

Both of the above applications require, however, the development of more efficient and highly stable UC phosphors with low excitation density thresholds. Up to now, most of the RE doped UC phosphors have been halides such as NaYF_4 [5]. However, they have very poor physicochemical stabilities, which make their applications difficult in industrial fields. Therefore, it is important to

search for stable oxide host materials with high UC efficiency.

Tungstate represents an important family of oxide materials that can be applied in various fields, such as photoluminescence, microwave, optical fibers, and scintillating materials [6]. Among them, calcium tungstate (CaWO_4) has high density (6.1 g/cm^3), high irradiation damage resistance and relatively low photon threshold energy compared to the other oxide materials [7]. The W^{6+} ions in CaWO_4 matrices have strong polarization because of their large electric charge and small radius; this strong polarization consequently decreases symmetries and enhances the Stark energy splitting of the RE ion in the crystal field [8]. In this work, $\text{Li}^{+}/\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped CaWO_4 UC phosphors ($\text{CaWO}_4:\text{Li}^{+}/\text{Er}^{3+}/\text{Yb}^{3+}$) were synthesized with various Yb^{3+} concentrations by solid-state reaction. Their structural and UC luminescent properties were investigated, and effects of Yb^{3+} concentrations on UC luminescence were discussed according to the UC mechanism.

2. Experimental

$\text{CaWO}_4:\text{Li}^{+}/\text{Er}^{3+}/\text{Yb}^{3+}$ UC phosphor samples were prepared by the traditional solid-state reaction method. The starting materials were CaCO_3 (Kojundo Chemical,

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99.99%), WO_3 (Kojundo Chemical, 99.99%), Li_2CO_3 (Kojundo Chemical, 99.99%), Er_2O_3 (Shinetsu Chemical 99.99%) and Yb_2O_3 (Shinetsu Chemical 99.99%). The molar ratios of the cations were as follows: $(1-2x-2y)\text{-Ca}^{2+} + x\text{Yb}^{3+} + y\text{Er}^{3+} + (x+y)\text{Li}^+ + \text{W}^{6+}$, $x=0.000, 0.050, 0.100, 0.150, 0.200$ and $y=0.050$. In this work, the Er^{3+} concentration was fixed at 5.0 mol% [9] to investigate the effects of Yb^{3+} concentration ranging from 0 to 20 mol% on UC luminescence. The charge discrepancy of Ca^{2+} with Er^{3+} and Yb^{3+} could be compensated by Li^+ co-doping. Based on the above chemical formula, the starting powders with the designed stoichiometric quantities were ball-milled for 2 h, and then were calcined at 800 °C for 2 h in air. The crystalline phases of the synthesized samples were identified by X-ray powder diffraction (XRD), operating at 40 kV using $\text{Cu-K}\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$). The UC luminescence spectra were recorded using a spectrophotometer at room temperature. A 980 nm laser diode with maximum 100 mW output was used as the excitation source. The pumping power dependence of UC emission was calculated using irradiation power from 20 to 110 mW (SPEX, 1404p, France).

3. Results and discussion

Fig. 1(a) shows phase identification of the $\text{CaWO}_4\text{:Li}^+/\text{Er}^{3+}/\text{Yb}^{3+}$ samples with various $\text{Li}^+/\text{Yb}^{3+}$ concentrations calcined at 1000 °C for 2 h. The prominent peaks corresponded well to the scheelite-type CaWO_4 phase (JCPDS # 41-1431) at all $\text{Li}^+/\text{Yb}^{3+}$ concentrations. No impurities or secondary phases could be identified from the XRD patterns in the limit of XRD resolution, thus suggesting that single crystallized $\text{CaWO}_4\text{:Li}^+/\text{Er}^{3+}/\text{Yb}^{3+}$ with various $\text{Li}^+/\text{Yb}^{3+}$ concentrations up to 25.0/20.0 mol% can be obtained by solid-state reaction. Based on the effective ionic radii of the cations with different coordination numbers (CN) [10] and large charge difference between Ca^{2+} ion and W^{6+} ion, it can be expected that Li^+ , Er^{3+} and Yb^{3+} [$r(\text{Li}^+)=0.92 \text{ \AA}$, $r(\text{Er}^{3+})=1.004 \text{ \AA}$, $r(\text{Yb}^{3+})=0.985 \text{ \AA}$, when $\text{CN}=8$] are preferably substituted into the Ca^{2+} sites [$r(\text{Ca}^{2+})=1.12 \text{ \AA}$, when $\text{CN}=8$] instead of the W^{6+} sites [$r(\text{W}^{6+})=0.66 \text{ \AA}$, when $\text{CN}=4$]. Note, that when the Ca^{2+} ions are substituted by the Li^+ , Er^{3+} or Yb^{3+} ions with a smaller ionic radius than that of Ca^{2+} , the corresponding lattice constant becomes smaller. In Fig. 1(b), the (1 1 2) and (1 0 3) diffraction peaks shift to higher 2θ angle, indicating the decrease of the lattice constants when $\text{Li}^+/\text{Yb}^{3+}$ ions are substituted into the Ca^{2+} ion sites.

Fig. 2 shows the UC luminescence spectra of the prepared $\text{CaWO}_4\text{:Li}^+/\text{Er}^{3+}/\text{Yb}^{3+}$ phosphors with various $\text{Li}^+/\text{Yb}^{3+}$ concentrations from 0.50/0.00 to 25.0/20.0 mol% under 980 nm laser excitation. The UC luminescence spectra consist of three regions: (1) intense green emission between 515 and 540 nm assigned to $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ transitions (G_1), (2) green emission between 540 nm and

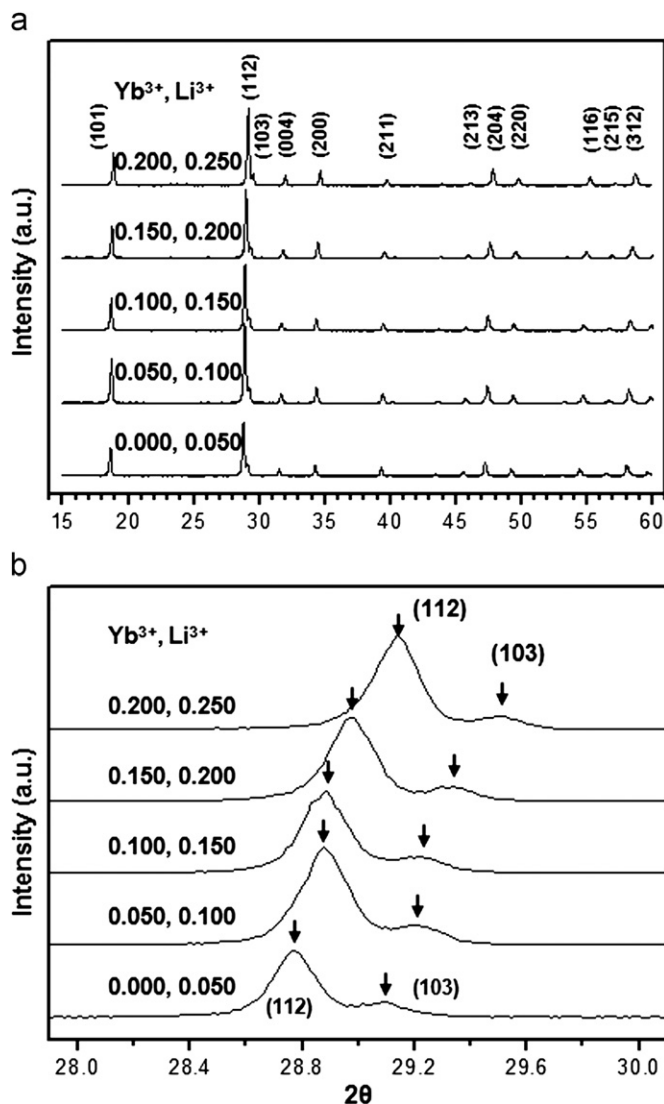


Fig. 1. (a) XRD patterns of $\text{CaWO}_4\text{:Li}^+/\text{Er}^{3+}/\text{Yb}^{3+}$ samples with various $\text{Li}^+/\text{Yb}^{3+}$ concentrations calcined at 1000 °C for 2 h and (b) Enlarged XRD patterns near $2\theta=29^\circ$ for (112) and (103) peaks.

560 nm assigned to $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transitions (G_2) and (3) the relatively weak red emission between 650 and 680 nm assigned to $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transitions of Er^{3+} ions [11].

The intensity of the UC emission was enhanced by the doping of the sensitizer Yb^{3+} . When the Yb^{3+} ions are doped, green emissions increase because the Yb^{3+} ions absorb light of 980 nm wavelength, effectively. The relative integral intensities of the G_1 and G_2 increase approximately 12 and 7 times, respectively, when the Yb^{3+} concentration is 10.0 mol%. These results show that the Yb^{3+} ion plays a role in the energy transfer process [12,13]. The intensities of green UC emission (G_1) increased with increasing $\text{Li}^+/\text{Yb}^{3+}$ concentration and maximized in the 15.0/10.0 mol% sample. Thus, we confirmed that optimum $\text{Li}^+/\text{Yb}^{3+}$ doping concentration for strongest green emission was 15.0/10.0 mol% with Er^{3+}

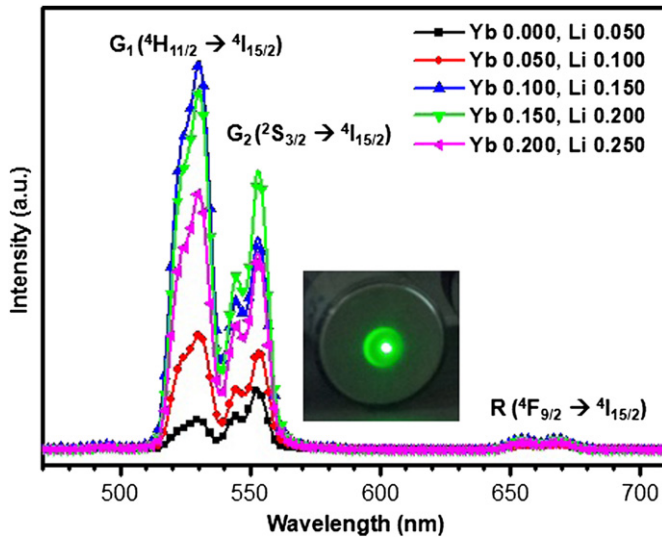


Fig. 2. UC luminescence spectra of $\text{CaWO}_4:\text{Li}^+/\text{Er}^{3+}/\text{Yb}^{3+}$ samples with $\text{Li}^+/\text{Yb}^{3+}$ concentrations excited at 980 nm. The inset photograph shows strong green emission for the sample with $\text{Li}^+/\text{Yb}^{3+}$ concentration of 25.0/20.0 mol%, as observed by the naked eye, excited by a 980 nm laser diode.

doping concentration fixed at 5.0 mol%. The 15.0/5.0/10.0 mol% ($\text{Li}^+/\text{Er}^{3+}/\text{Yb}^{3+}$) co-doped CaWO_4 sample emitted the strongest green light visible by the naked eye when excited by a 980 nm laser diode of 100 mW, as shown in the inset of Fig. 2. The green emission ratio (G_1/G_2) was almost unchanged, which indicated that the populating probability of Er^{3+} from $^4\text{F}_{7/2}$ to $^2\text{H}_{11/2}$ or $^4\text{S}_{3/2}$ levels remained stable with increase of Yb^{3+} concentration.

Fig. 3(a) shows the green and red UC luminescence intensities of the 25.0/5.0/20.0 mol% ($\text{Li}^+/\text{Er}^{3+}/\text{Yb}^{3+}$) co-doped CaWO_4 sample plotted on a logarithmic scale as a function of pump power. In UC processes, the UC emission intensity I_{UC} is proportional to the n value of the irradiation pumping power P , that is $I_{\text{UC}} \propto P^n$, where n is the number of pumping photons required to produce UC emission, I_{UC} is the luminescence intensity, and P is the laser pumping power [14]. The calculated n values were 1.63, 1.71, 1.61, and 1.72 for green emissions at 530 and 550 nm and for red emissions at 656 and 670 nm, respectively. These results indicated that a two-photon UC process was assigned to the green and red emissions in the $\text{Li}^+/\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped CaWO_4 .

The UC emission mechanism and population processes for the green ($^4\text{H}_{11/2}$, $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$) and red ($^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$) UC luminescence in $\text{CaWO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ system are illustrated in Fig. 4. Under the excitation of 980 nm, Er^{3+} and Yb^{3+} ions are initially excited from the ground state to the excited state through the ground state absorptions (GSA) process ($\text{Er}^{3+}: ^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2}$, $\text{Yb}^{3+}: ^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$) and the energy transfer upconversion (ETU) process of $^2\text{F}_{5/2}(\text{Yb}^{3+}) + ^4\text{I}_{15/2}(\text{Er}^{3+}) \rightarrow ^2\text{F}_{7/2}(\text{Yb}^{3+}) + ^4\text{I}_{11/2}(\text{Er}^{3+})$ which are responsible for the population at $^4\text{I}_{11/2}$ level in Er^{3+} . For the green emissions, the energy transition from $^4\text{I}_{11/2}$

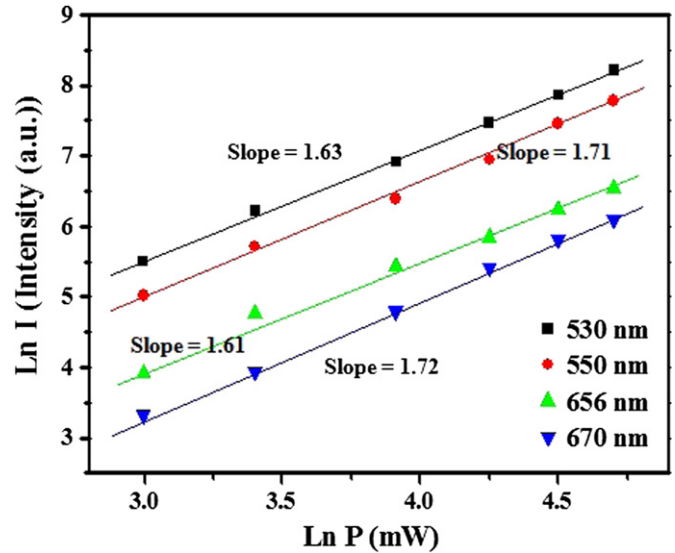


Fig. 3. Pumping power dependence of UC emission of 25.0/5.0/20.0 mol% ($\text{Li}^+/\text{Er}^{3+}/\text{Yb}^{3+}$) co-doped CaWO_4 sample under working currents from 20 to 110 mW at 530, 550, 655 and 670 nm.

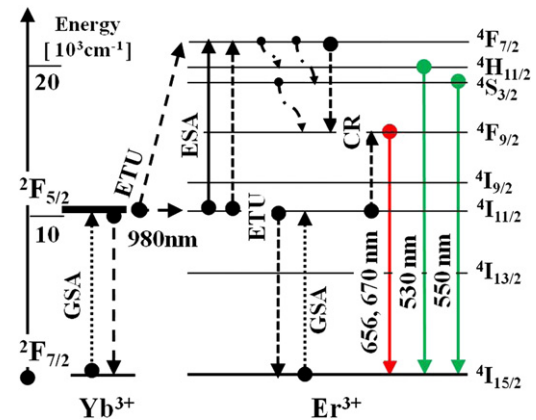


Fig. 4. A simplified energy level diagram of Er^{3+} with Yb^{3+} ions and the dominant UC mechanisms in the $\text{CaWO}_4:\text{Li}^+/\text{Er}^{3+}/\text{Yb}^{3+}$ phosphor.

level to $^4\text{F}_{7/2}$ level of Er^{3+} is involved in three possible processes as follows [11,15]:

- (1) ESA (excited state absorption): $^4\text{I}_{11/2}(\text{Er}^{3+}) + \text{a photon (980 nm)} \rightarrow ^4\text{F}_{7/2}$
- (2) ETU: $^2\text{F}_{5/2}(\text{Yb}^{3+}) + ^4\text{I}_{11/2}(\text{Er}^{3+}) \rightarrow ^2\text{F}_{7/2}(\text{Yb}^{3+}) + ^4\text{F}_{7/2}(\text{Er}^{3+})$
- (3) ETU: $^4\text{I}_{11/2}(\text{Er}^{3+}) + ^4\text{I}_{11/2}(\text{Er}^{3+}) \rightarrow ^4\text{F}_{7/2}(\text{Er}^{3+}) + ^4\text{I}_{15/2}(\text{Er}^{3+})$

These three possible processes can populate the $^4\text{F}_{7/2}$ level from the $^4\text{I}_{11/2}$ level in Er^{3+} , and then $^4\text{F}_{7/2}$ level relaxes rapidly and non-radiatively to the next lower levels at $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ in Er^{3+} . As a result, above mentioned processes can produce the green emissions in the spectral lines near 530 and 550 nm. The UC emission is dominated

by strong green emission at 530 nm ($^4I_{11/2} \rightarrow ^4I_{15/2}$) and 550 nm ($^4S_{3/2} \rightarrow ^4I_{15/2}$). For the red emission, on the other hand, $^4F_{9/2}$ level is generated by non-radiative relaxation from $^4S_{3/2}$ to $^4F_{9/2}$ level and cross relaxation (CR) $^4F_{7/2} + ^4I_{11/2} \rightarrow ^4F_{9/2} + ^4F_{9/2}$ transition [16,17]. Finally, $^4F_{9/2}$ level relaxes radiatively to the ground state at $^4I_{15/2}$ level and releases red emission at 656 and 670 nm.

4. Conclusion

In summary, $\text{CaWO}_4\text{:Li}^+/\text{Er}^{3+}/\text{Yb}^{3+}$ phosphor was synthesized, co-doped up to 25.0/5.0/20.0 mol% ($\text{Li}^+/\text{Er}^{3+}/\text{Yb}^{3+}$), by solid-state reaction. Under 980 nm excitation, $\text{CaWO}_4\text{:Li}^+/\text{Er}^{3+}/\text{Yb}^{3+}$ phosphors exhibited bright green UC luminescence visible to naked eyes at 530 and 550 nm. The optimum doping concentration of Yb^{3+} for highest green UC luminescence was 10.0 mol%. A two-photon process was responsible for both green and red UC emissions. It is concluded that $\text{CaWO}_4\text{:Li}^+/\text{Er}^{3+}/\text{Yb}^{3+}$ phosphors can be a promising candidate for meeting the requirements of biomedical or solar cell applications.

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References

- [1] N. Bloembergen, Solid state infrared quantum counters, *Physical Review Letters* 2 (1959) 84–85.
- [2] F. Wang, X. Liu, Recent advances in the chemistry of lanthanide-doped upconversion nanocrystals, *Chemical Society Reviews* 38 (2009) 976–989.
- [3] Z. Liu, R. Peng, Inorganic nanomaterials for tumor angiogenesis imaging, *European Journal of Nuclear Medicine and Molecular Imaging* 37 (2010) S147–S163.
- [4] B.S. Richards, A. Shalav, Enhancing the near-infrared spectral response of silicon optoelectronic devices via up-conversion, *IEEE Transactions on Electron Devices* 54 (2007) 2679–2684.
- [5] J.C. Boyer, F. Vetrone, L.A. Cuccia, J.A. Capobianco, Synthesis of colloidal upconverting NaYF_4 nanocrystals doped with Er^{3+} , Yb^{3+} and Tm^{3+} , Yb^{3+} via thermal decomposition of lanthanide trifluoroacetate precursors, *Journal of the American Chemical Society* 128 (2006) 7444–7445.
- [6] J.H. Ryu, G.S. Park, K.M. Kim, J.-W. Yoon, K.B. Shim, Synthesis of CaWO_4 nanocolloidal suspension via pulsed laser ablation and its optical properties, *Applied Physics A* 88 (2007) 731–736.
- [7] M.J. Treadaway, R.C. Powell, Luminescence of calcium tungstate crystals, *The Journal of Chemical Physics* 61 (1974) 4003–4011.
- [8] L.F. Johnson, G.D. Boyd, K. Nassau, R.R. Soden, Continuous operation of a solid-state optical maser, *Physical Review* 126 (1963) 1406–1409.
- [9] D.-H. Kim, J.H. Ryu, J.H. Chung, K.B. Shim, S.-Y. Cho, Green upconversion luminescence of $\text{Li}^+/\text{Er}^{3+}/\text{Yb}^{3+}$ tridoped CaWO_4 and effects of Er^{3+} concentration, *Journal of the Electrochemical Society* 158 (2011) J345–J348.
- [10] R.D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, *Acta Crystallographica A* 32 (1976) 751–767.
- [11] F. Auzel, Upconversion and anti-stokes processes with f and d ions in solids, *Chemical Reviews* 104 (2004) 139–173.
- [12] H.X. Yang, H. Lin, L. Lin, Y.Y. Zhang, B. Zhai, E.Y.B. Pun, Powerful visible upconversion fluorescence of Er^{3+} in novel bismuth gallate glasses compared with in common tellurite glasses, *Journal of Alloys and Compounds* 453 (2008) 493–498.
- [13] Y. Bai, Y. Wang, G. Peng, W. Zhang, Y. Wang, K. Yang, X. Zhang, Y. Song, Enhanced white light emission in $\text{Er}/\text{Tm}/\text{Yb}/\text{Li}$ codoped Y_2O_3 nanocrystals, *Optics Communications* 282 (2009) 1922–1924.
- [14] C. Ming, F. Song, J. Hou, Y. Yu, G. Zhang, H. Yu, T. Sun, J. Tian, Single color upconversion emission in $\text{Ho}^{3+}/\text{Yb}^{3+}$ and $\text{Tm}^{3+}/\text{Yb}^{3+}$ doped $\text{P}_2\text{O}_5\text{--MgO}_2\text{--Sb}_2\text{O}_3\text{--MnO}_2\text{--AgO}$ glasses, *Optics Communications* 284 (2011) 3304–3307.
- [15] R.H. Page, K.I. Schaffers, P.A. Waide, J.B. Tassano, S.A. Payne, W.F. Krupke, Upconversion-pumped luminescence efficiency of rare-earth doped hosts sensitized with trivalent ytterbium, *Journal of the Optical Society of America B. Optical physics* 15 (1998) 996–1008.
- [16] V. Singh, V.K. Rai, K.A. Shamery, J. Nordmann, M. Haase, NIR to visible upconversion in $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped CaYAl_3O_7 phosphor obtained by solution combustion process, *Journal of Luminescence* 131 (2011) 2679–2682.
- [17] Q. Sun, X. Chen, Z. Liu, F. Wang, Z. Jiang, C. Wang, Enhancement of the upconversion luminescence intensity in Er^{3+} doped BaTiO_3 nanocrystals by co-doping with Li^+ ions, *Journal of Alloys and Compounds* 509 (2011) 5336–5340.