

## 1.5 $\mu\text{m}$ Amplification and Upconversion Emission of $\text{Er}^{3+}$ Doped Tellurite Glasses for Laser Applications

S. Arunkumar, K. Marimuthu\*

Department of Physics, Gandhigram Rural Institute–Deemed University, Gandhigram – 624 302, India

\*Corresponding author: mari\_ram2000@yahoo.com

### Abstract

In the present investigations, a series of  $\text{Er}^{3+}$  doped glasses with the composition  $30\text{TeO}_2 + (30-x) \text{Bi}_2\text{O}_3 + 20\text{ZnO} + 20\text{CdO} + x\text{Er}_2\text{O}_3$  ( $x = 0.05, 0.1, 0.5, 1$  and  $3$  wt%) were prepared by melt-quenching technique and characterized through FTIR, Raman, optical absorption, emission and decay curve measurements. Optical absorption spectra have been analyzed using Judd–Ofelt theory to interpret the local environment of the  $\text{Er}^{3+}$  ion site. In order to elucidate the potential application of  $\text{Er}^{3+}$  ions in the prepared glasses the radiative properties were calculated for the  $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$  and  $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$  emission transitions. The absorption and emission cross-section for the  $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$  transition at  $1.5 \mu\text{m}$  were calculated using McCumber theory and compared with the results obtained from JO theory. The decay curves of the  $^4\text{I}_{13/2}$  level have been measured and the fall in lifetime value with the increase in  $\text{Er}^{3+}$  ion concentration can be attributed to the cross-relaxation between  $\text{Er}^{3+}$  ion to the free OH-radical. The upconversion emission spectra were recorded at  $980 \text{ nm}$  excitation and their energy transfer mechanism through ground state absorption and various excited state absorption are discussed.

**Keywords:** Nephelauxetic effect, Judd-Ofelt theory, Gain Bandwidth, Upconversion emission, Lifetime.

### 1. Introduction

The spectroscopic and laser properties of RE ions are strongly affected by the local symmetry structure at the RE vicinity as well as the distribution of doping

ions in the glass matrix [1]. The development of the new luminescent materials with appropriate composition doped with  $\text{RE}^{3+}$  ions is of interest for understanding the electronic excitation and relaxation phenomena RE ions in the chosen glass matrices. Heavy metal oxide (HMO) glasses are more suitable due to its high refractive index, low phonon energy and good chemical durability that help to improve the quantum efficiencies of the matrix [2,3]. Recent year, glasses containing HMO ( $\text{Bi}_2\text{O}_3$ ,  $\text{TeO}_2$ ,  $\text{ZnO}$ ,  $\text{CdO}$ ) have attracted attention for excellent infrared transmission due its higher refractive index since the stimulated emission cross-sections and gain bandwidths are proportional to refractive index [4]. The combination of favourable chemical and physical properties of heavy metal oxide glasses containing moderately high RE doping levels increases their applicability in laser active medium [5]. Among the trivalent RE ions, the erbium ion ( $\text{Er}^{3+}$ ) has been extensively studied because of its ability to emit light within the near-ultraviolet to the near-infrared range upon excitation with infrared light in a number of hosts [6,7].  $\text{Er}^{3+}$  ions doped glasses have been received much attention due to the  $1.5\mu\text{m}$  emission from the  $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$  transition of  $\text{Er}^{3+}$  ions is eye safe and located in the optical third communication window where the losses are minimum [8,9]. The present work presents a detailed investigation of the optical characteristics of  $\text{Er}^{3+}$  doped HMO:tellurite glasses.

### 2. Experimental

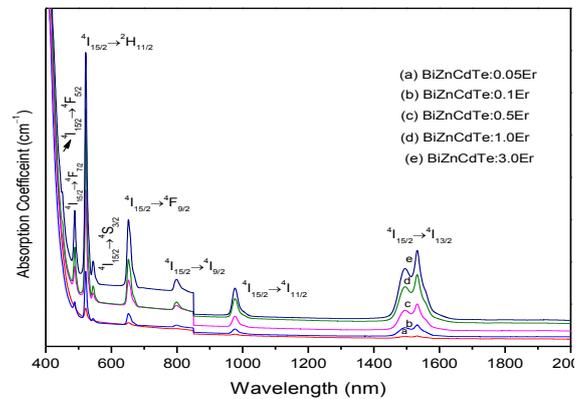
$\text{Er}^{3+}$  ions doped glasses were a composition of  $30\text{TeO}_2 + (30-x)\text{Bi}_2\text{O}_3 + 20\text{ZnO} + 20\text{CdO} + x\text{Er}_2\text{O}_3$  ( $x = 0.05,$

0.1, 0.5, 1 and 3 wt%) prepared prepared by conventional melt quenching technique [10]. All the starting materials were purer than 99.9%. Batches of 15 g were weighed and taken into porcelain crucible melted at 900°C for 45 minutes in electric furnace. The homogenous melt were poured onto a well polished preheated brass mold followed by annealing at 300°C for 12 hours and then allowed to reach room temperature gradually to remove the thermal strain and air bubbles. Finally the glasses were polished on both sides with dimensions of 2.5×1.5×0.4cm<sup>3</sup> before further optical investigations. The absorption spectral measurements were made using CARY 500, UV-Vis-NIR spectrophotometer in the wavelength range 400–1900 nm with a spectral resolution of ±1.0 nm. NIR luminescence spectra were recorded using EG&G Princeton Applied Research model 5210 spectrophotometer with a spectral resolution of ±0.5 nm. The decay curves corresponding to the <sup>4</sup>I<sub>13/2</sub>→<sup>4</sup>I<sub>15/2</sub> transition were recorded by exciting the samples with a 10 ns pulsed optical parametric oscillator (OPO) pumped by a Nd-YAG laser (EKSPLA NT342/3/UVE) and the signal from the extended PMT was acquired by a digital oscilloscope (LeCroy wavesurfer 424). All these measurements were carried out at room temperature.

### 3. Nephelauxetic effect

Figure 1 shows the absorption spectra of the present Er<sup>3+</sup> doped glasses. The absorption spectra exhibit various electronic transitions such as <sup>4</sup>I<sub>13/2</sub> (6531), <sup>4</sup>I<sub>11/2</sub> (10266), <sup>4</sup>I<sub>9/2</sub> (12481), <sup>4</sup>F<sub>9/2</sub> (15311), <sup>4</sup>S<sub>3/2</sub> (18345), <sup>2</sup>H<sub>11/2</sub> (19256), <sup>4</sup>F<sub>7/2</sub> (20474), <sup>4</sup>F<sub>5/2</sub> (22111), and <sup>4</sup>F<sub>3/2</sub> (22567) (in cm<sup>-1</sup>) from the <sup>4</sup>I<sub>15/2</sub> ground state. Due to the nephelauxetic effect the absorption band position of the Er<sup>3+</sup> ion shift towards the higher energy side which indicates that the Er–O bond is of ionic in nature in the prepared glasses. From the optical absorption spectra, Nephelauxetic ratios and

bonding parameter values have been calculated to study the nature of the Dy<sup>3+</sup>-ligand bond in the prepared glasses. The δ values are found to be 0.016, 0.052, 0.089, 0.057 and 0.036 for the prepared BiZnCdTe:xEr<sup>3+</sup> glasses. The positive magnitude of the δ values indicate the covalency of the Er–O bond and the covalency of the Er–O bond is found to increase with increase in Er<sup>3+</sup> ion content upto 0.5 wt% and after that, the covalency decreases due to the nephelauxetic effect.



**Figure 1.** Absorption spectra of the Er<sup>3+</sup> doped BiZnCdTe:xEr glasses

### 4. JO intensity parameter and covalency

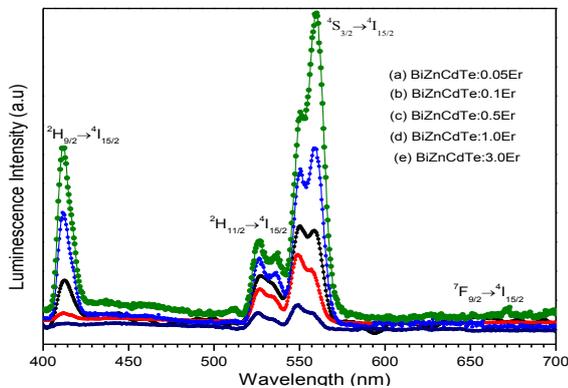
Judd-Ofelt theory have been used to analyses the absorption spectral intensities based on the assumption that the average energy difference between the 4f levels is much larger than the energy spread of the excited configuration. Oscillator strength of the transition expresses the probability of radiative transitions between a given pair of J multiplets. The  $f_{exp}$  and  $f_{cal}$  values of the <sup>2</sup>H<sub>11/2</sub> hypersensitive transition are found to be higher than the reported Er<sup>3+</sup> doped [4-7] glasses. The JO intensity parameters ( $\Omega_2$ ,  $\Omega_4$  and  $\Omega_6$ ) gives information about the local field symmetry around the RE ion site and the nature of the bond between RE ions with its surrounding ligands. The values of  $\Omega_2$  is very sensitive to the local environment of the RE ions and often gives information about the

symmetry of the coordination structure, polarizability of ligands and the nature of the RE–O bonding in the ligand field [1]. The  $\Omega_4$  parameters is related to the bulk properties and  $\Omega_6$  is inversely related to the rigidity of the medium and also affected by the vibronic transitions of the RE ions. The JO intensity parameters of the present  $\text{Er}^{3+}$  doped glasses are presented in table 1 along with the reported  $\text{Er}^{3+}$  doped glasses [3-4]. The observed  $\Omega_2 > \Omega_6 > \Omega_4$  trend represents a change in the surrounding ligand field environment do not show any symmetry inversion symmetry around the cation. Among the prepared glasses, 0.5wt% glass exhibits higher spectroscopic quality factor ( $\Omega_4/\Omega_6 = 1.70$ ) value and is found to be higher than the reported [1-6] glasses thus suggests its potential for various photonic applications.

**Table 1.** Judd-Ofelt ( $\times 10^{-20} \text{cm}^2$ ) parameters of  $\text{Er}^{3+}$  doped  $\text{BiZnCdTe:xEr}$  glasses

Glass codes	$\Omega_2$	$\Omega_4$	$\Omega_6$	$\Omega_4/\Omega_6$
BiZnCdTe:0.05Er	9.32	3.12	2.35	1.33
BiZnCdTe:0.1Er	9.67	3.87	2.54	1.52
BiZnCdTe:0.5Er	10.45	4.30	2.51	1.70
BiZnCdTe:1.0Er	9.41	3.33	2.06	1.61
BiZnCdTe:02.0Er	8.93	3.45	2.35	1.47
Bismuthborate [1]	4.44	1.17	1.64	0.71
oxyfluoride [3]	8.57	2.05	2.60	0.79
Lead-telluroborate	5.69	0.31	1.74	0.18

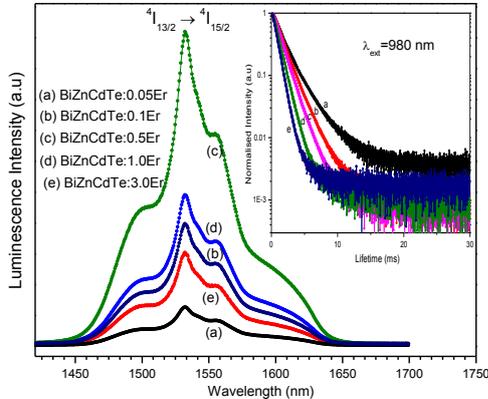
### 5. Down conversion emission spectra



**Figure 2.** Downconversion emission spectra of  $\text{Er}^{3+}$  doped  $\text{BiZnCdTe:xEr}$  glass

Figure 2 shows the emission spectra of the prepared  $\text{Er}^{3+}$  doped glasses under 485 nm excitation. The emission spectra exhibit intense  $^2\text{H}_{9/2} \rightarrow ^4\text{I}_{15/2}$  and  $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ ,  $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$  and weak  $^7\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$  emission transitions corresponding to the band positions at 409, 528, 557 and 654 nm respectively. It is observed from figure 2 that the intensity of the emission bands increases up to 0.5 wt%  $\text{Er}_2\text{O}_3$  content and after that quenching occurs and the role of energy transfer is studied with lifetime analysis. The quenching of emission intensities with increase of  $\text{Er}^{3+}$  ion concentration is due to the increase of non-radiative energy transfer [2]. Cross-relaxation is a important quenching center caused by migration of the excitation energy among the  $\text{Er}^{3+}$  ions through the resonant energy transfer between two  $\text{Er}^{3+} - \text{Er}^3$  [5-9]. The possible cross-relaxation channels are ( $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{11/2}; ^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2}$ ), ( $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{9/2}; ^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2}$ ) which reason for the luminescence quenching. The radiative parameters of the prepared glasses have been calculated. The stimulated emission cross-section value is found to be maximum for  $^4\text{S}_{3/2}$  level for all the prepared glasses. The stimulated emission cross-section and the radiative lifetime values for the  $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$  transition are found to be 22.54, 25.15, 31.73, 28.16, 26.67 ( $\times 10^{-21} \text{cm}^2$ ) and 0.22, 0.15, 0.11, 0.17, 0.18 ( $\mu\text{s}$ ) corresponding to 0.05, 0.1, 0.5, 1 and 3 wt% content of  $\text{Er}^{3+}$  ions, respectively. The higher value of the stimulated emission cross-section is favorable for achieving low threshold and high gain to obtain CW laser action. Among the prepared glasses,  $\text{BiZnCdTe:0.5Er}$  glass possesses higher stimulated emission cross-section and branching ratio values and is suggested for suitable green laser applications.

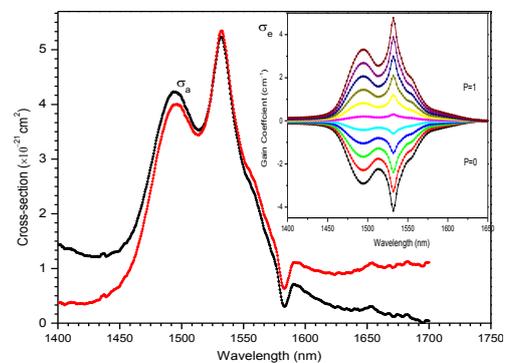
## 6. Optical Amplification at 1.5 $\mu\text{m}$



**Figure 3.** NIR Emission and decay curve of  $^4I_{13/2} \rightarrow ^4I_{15/2}$  level of  $\text{Er}^{3+}$  ions in prepared glasses

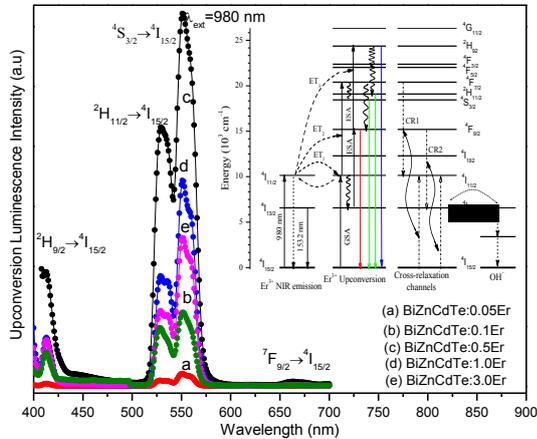
Figure 3 shows the NIR emission spectra exciting at 980 nm corresponding to the  $^4I_{13/2} \rightarrow ^4I_{15/2}$  transition of the  $\text{Er}^{3+}$  ions. The full width at half maximum (FWHM) is an important parameter for laser action and the FWHM values are found to be 85, 91, 96, 93 and 88 nm corresponding to 0.05, 0.1, 0.5, 1 and 3 wt% content of  $\text{Er}^{3+}$  ions, respectively. It clearly indicates that, higher FWHM values of the broad emission bands are suitable for tunable laser medium and it could be used as a potential candidate for compact and efficient eye safe NIR lasers. The decay curves of the  $^4I_{13/2}$  excited level of the  $\text{Er}^{3+}$  ions were recorded and presented in inset of figure 3. The calculated and experimental lifetime of the  $^4I_{13/2}$  level is found to be 2.57, 2.34, 2.11, 1.97, 1.81 and 2.29, 1.99, 1.63, 1.34 0.98ms corresponding to the prepared 0.05, 0.1, 0.5, 1 and 3 wt% content of  $\text{Er}^{3+}$  containing glasses, respectively. The quantum efficiency is an important parameter which is defined as ratio of the number of photons generated in radiative transition to the number of photons absorbed [3]. The quantum efficiency values are found to be 89, 85, 77, 68 and 54 for the prepared  $\text{Er}^{3+}$  doped  $\text{BiZnCdTe}:\text{xEr}$  glasses, respectively.

The absorption and emission cross-section values for the  $^4I_{13/2} \rightarrow ^4I_{15/2}$  transition of the  $\text{Er}^{3+}$  ions in the prepared glasses are calculated using McCumber theory. The measured  $\sigma_a$  and  $\sigma_e$  values of the  $\text{BiZnCdTe}:\text{0.5Er}$  glass is shown in figure 4 and values are 5.24, 5.33 ( $\times 10^{-21} \text{ cm}^2$ ) which comparably higher than the reported  $\text{Er}^{3+}$  doped glasses [6,8,9]. The  $\sigma_a$   $\sigma_e$  values are found to decrease with the increase in  $\text{Er}^{3+}$  ion content. The gain coefficient were derived from the  $\sigma_a$   $\sigma_e$  values using expression  $G=N[P\sigma_e(\lambda)-(1-p)\sigma_a(\lambda)]$ , where P is the population inversion (0 to 1) and N is the total concentration (in ions/ $\text{cm}^3$ ) of the  $\text{Er}^{3+}$  ions. From the measured absorption and emission cross-section values as a function of wavelength the gain coefficient for the 0.5wt%Er content glass have been calculated for the various P (0.1, 0.2, 0.4, 0.6, 0.8 and 1.0) values and the results are presented in inset of figure 4. It is clearly observed that, the zero-shift in the peak values of the gain coefficient for various P values and the zero gain coefficient were observed for P=0.4 due to the fact that ground state and excited states are equally populated [4,5]. The gain coefficient of 0.5wt%  $\text{Er}^{3+}$  containing glass is found to be 0.52  $\text{cm}^{-1}$  and is closer to the reported  $\text{Er}^{3+}$  glasses [6,7,8] which indicates the prepared  $\text{BiZnCdTe}:\text{0.5Er}$  glass is more suitable for designing the  $\text{Er}^{3+}$ -doped broad-band optical amplifiers.



**Figure 4.** The  $\sigma_a$ ,  $\sigma_e$  and Gain coefficient (inset) of  $^4I_{13/2} \rightarrow ^4I_{15/2}$  level of  $\text{Er}^{3+}$  in  $\text{BiZnCdTe}:\text{0.5Er}$  glass.

## 7. Upconversion Emission spectra



**Figure 5.** Upconversion emission through GSA, ESA and possible energy transfer of quenching mechanism of  $Er^{3+}$  ions in prepared glasses.

Figure 5 shows the upconversion emission spectra of prepared glasses at 980 nm excitation and their possible energy transfer mechanism through ground state absorption and various excited state absorption are shown in the inset of figure 5. The upconversion emission spectra exhibit  ${}^2H_{9/2} \rightarrow {}^4I_{15/2}$ ,  ${}^2H_{11/2} \rightarrow {}^4I_{15/2}$ ,  ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$  emission transitions. For the green emission,  $Er^{3+}$  ions are excited from the ground state to the  ${}^4I_{11/2}$  state through GSA and further promoted to the  ${}^4F_{7/2}$  state through ESA and then  $Er^{3+}$  ion relaxes to the various excited states ( ${}^4S_{3/2}$ ,  ${}^2H_{11/2}$  and  ${}^2H_{9/2}$ ) through the energy transfer, multiphonon relaxation and cross relaxation process taking place between two  $Er^{3+}$  levels through the following energy transfer mechanism [9]. The  ${}^4I_{11/2}$  level is directly excited at 980 nm and the excitation processes based on the long-lived  ${}^4I_{11/2}$  excited level follows through the energy transfer (ET)  $I_{11/2} + 4I_{11/2} \rightarrow 4F_{7/2} + 4I_{15/2}$  and excited state absorption (ESA)  ${}^4I_{11/2} + h\nu \rightarrow 4F_{7/2}$  mechanism. The populated  ${}^4F_{7/2}$  level may relax non-radiatively to the next lower levels  ${}^2H_{11/2}$  and  ${}^4S_{3/2}$  separated by a small energy gap ( $721 \text{ cm}^{-1}$ ) responsible for green emission. The  ${}^2H_{11/2}$  state can non-radiatively decay to the  ${}^4S_{3/2}$  state due to the multiphonon relaxation process

because of the fact that, the 535 nm emission band possess lower intensity than the 555 nm emission band due to the higher multiphonon relaxation rate [8]. Thus the  ${}^2H_{11/2} \rightarrow {}^4I_{15/2}$  and  ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$  two radiative transitions correspond to the green emission. The energy transfer mechanism for the red emission which originates from the  ${}^4F_{9/2} \rightarrow {}^4I_{15/2}$  transition and the population of  ${}^4F_{9/2}$  state follows as: ESA:  ${}^4I_{13/2} + h\nu \rightarrow {}^4I_{9/2}$  and ET between  $Er^{3+}$  ions:  ${}^4I_{13/2} + {}^4I_{11/2} \rightarrow {}^4F_{9/2} + {}^4I_{15/2}$ . The  ${}^4I_{13/2}$  level is populated due to the non-radiative relaxation from the upper  ${}^4I_{11/2}$  level. The radiative transition from the  ${}^4F_{9/2}$  level to the  ${}^4I_{15/2}$  level contributes to the red emission [6].

## 8. Conclusion

Concentration dependent optical absorption and emission properties of  $Er^{3+}$  doped HMO glasses have been studied and reported. The bonding parameter studies reveal the covalent nature of the metal-ligand bond in the title glasses and the covalency decrease beyond 0.5wt% content of  $Er^{3+}$  ions. The JO intensity parameters follows the trend as  $\Omega_2 > \Omega_4 > \Omega_6$  uniformly for all the prepared glasses and the higher  $\Omega_2$  values indicate the presence of higher asymmetry around the  $Er^{3+}$  ion site. Among the prepared glasses, BiZnCdTe:0.5 glass possess higher  $A$ ,  $\beta$ ,  $\sigma_a$ ,  $\sigma_e$  and  $\eta$  values for  ${}^4S_{3/2}$  emission transition suggesting its suitability for green laser applications and the higher values of these parameters for  ${}^4I_{13/2}$  transition is suitable for higher gain optical amplifiers.

## 9. Acknowledgement

One of the authors Dr. S. Arunkumar is grateful to the University Grants Commission (UGC), for the award of the Postdoctoral Research Fellowship (No. F/31-1/2017/PDFSS-2017-18-TAM-15016).



**International Journal of  
Scientific Research in Science and Technology (IJSRST)**

**Print ISSN : 2395-6011, Online ISSN : 2395-602X**

**International Conference on Advanced Materials**

Held on 14, 15 December 2017, Organized by Department of Physics,  
St. Joseph's College, Trichy, Tamilnadu, India



**10. References**

- [1] Y.H. Liu, Y.J. Chen, Y.F. Lin, Z.D. Luo, Y.D. Huang, *Opt. Mat.* 30 (2008) 1883–1888.
- [2] C.R. Kesavulu, V.B. Sreedhar, C.K. Jayasankar, K Jang, D Shin, S Soo Yi, *Mat. Res. Bull.* 51 (2014) 336–344.
- [3] K. Selvaraju, K. Marimuthu, *J. Lumin.* 132, 1171–1178 (2012).
- [4] M.V. Vijaya Kumar, K. Rama Gopal, R.R. Reddy, G.V. Lokeswara Reddy, B.C. Jamalaihah, *J. Lumin.* 142 (2013) 128–134
- [5] A.A Reddy, S. Surendra Babu, G. Vijaya Prakash, *Opt. Comm.* 285 (2012) 5364–5367
- [6] B.C. Jamalaihah, T. Suhasini, L.R Moorthy, K.J. Reddy, I. Kim, D Yoo, K Jang, *Opt. Mater.* 34 (2012) 861–867.
- [7] D. Ramachari, L. Rama Moorthy, C.K. Jayasankar, *Opt. Mater.* 36 (2014) 823–828.
- [8] K. Selvaraju, N. Vijaya, K. Marimuthu, and V. Lavin, *Phys. Status Solidi A* 210, No. 3, 607–615 (2013).
- [9] J Coelho, J Azevedo, G Hungerford, N.S. Hussain, *Opt. Mater.* 33 (2011) 1167–1173.