

Effect of change in CaO concentration on spectroscopic properties of Tm³⁺ ions in phosphate glasses

TALAM SATYANARAYANA^a, TILAK MUKHERJEE^b, GUNNAM NAGARJUNA^c

^aDepartment of Electronics and Instrumentation Engineering, Lakireddy Bali Reddy College of Engineering (Autonomous), Mylavaram – 521 230, Andhra Pradesh, India,

^bDepartment of Electronics and Communication Engineering, Lakireddy Bali Reddy College of Engineering (Autonomous), Mylavaram – 521 230, Andhra Pradesh, India,

^cDepartment of Chemistry, S.R.R. & C.V.R. Govt. College, Vijayawada -520004, Krishna, Andhra Pradesh., India.

Glasses of particular composition 50 P₂O₅-(25-x) CaO-22 Na₂O-3 K₂O: x Tm₂O₃ (0.2 ≤ x ≤ 1.0 mol %) were prepared using conventional melt quenching. The samples were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The characterization studies reveal that the samples have amorphous nature. Further, spectroscopic investigations viz., optical absorption and fluorescence for all samples have been carried out in visible and NIR regions at room temperature. The absorption spectra has exhibited six bands and corresponding transitions have assigned. Similarly, the emission spectra has exhibited six bands in visible region when excited at 456 nm; two bands in NIR region excited at 698 nm. The reasons for variations in intensities and spectral positions of all bands have been discussed in detail with increase in concentration of thulium ions in addition to their structural changes.

(Received July 29, 2015; accepted September 29, 2016)

Keywords: Tm³⁺ glasses; X-ray diffraction; Luminescence, Optical properties

1. Introduction

The reason for selecting investigation on glass materials is that they are comparatively cheap, relatively easier to produce and mainly, they can be synthesized in a wide range of compositions based on required optical properties. It is also observed that glass has become vital material for modern optoelectronic field. Isotropic properties of glasses help us a lot in making broadband amplifiers in such a way by providing required degree of irregular state around rare earth ion, in turn causing broadening of luminescence band.

There has been growing demand for glassy lasers in view of their frequent use in various optoelectronic devices and high density optical storage systems. In addition, investigation on spectroscopic properties of rare earth doped phosphate and silicate based glasses with different network modifiers has gained momentum due to their potential applications in science and technology. Conventional silicate glasses with high content of SiO₂ permit only very small amounts of rare earth ions due to clustering problem and they also possess tendency to crystallization during optical fiber drawing [1]. The clustering problem of silicate glasses does not allow them to be suitable hosts for rare earth ions as clustering causes concentration quenching luminescence that resulting from cross relaxation of neighbouring ions. The selection of appropriate hosts for rare earth ions is very important as optical properties are strongly depending on glassy hosts. The crystal field potential is one of the key parameter that provides information about splitting of energy levels of 4f electrons and also radiative transitions among them. In

order to understand luminescence properties, it is highly essential to know the relation between optical properties and surrounding atomic arrangement for rare earth ions along with nature of chemical bonding between rare earth ions and their ligands [2]. Phosphate based glasses are found to be prominent candidates to act as suitable host materials for various rare-earth metal ions viz., Tm³⁺, Pr³⁺, Sm³⁺ etc. These glasses possess unique physical properties, viz., high thermal expansion coefficients, low melting temperature, softening temperature and high ultra-violet and far-infrared transmission [3-5] in comparison with conventional borosilicate glasses. More specifically, phosphate oxide based glasses have better physical and chemical properties, such as mechanical strength, chemical durability and thermal stability than that of fluoride glasses [6]. It has been observed that the high phonon energy of phosphate glass has a negative effect on the luminescence efficiency compared to fluoride, tellurite, silicate glasses. This, however, is counter-balanced by the large dopant concentrations and wide absorption cross-section of the Tm³⁺ ions. Phosphate glasses also exhibit a very high solubility for rare earth ions. This feature permits the introduction of large concentrations of active ions into relatively small volumes resulting in smaller laser devices with high energy storage capabilities. These high dopant concentrations also result in very rapid and efficient energy transfer between rare earth ions.

Intensive investigations being carried out on Tm³⁺ ions in various host glasses due to the facts that these ions give infrared emission around 2 μm and their up-conversion capability from infrared to visible light [7-9]. Quite recently, Jiani et. al [10] have reported luminescence

of thulium ions in bismuth germinate glasses after addition of Ag nanoparticles.

Glasses doped with Tm^{3+} ions are found to be potential hosts of visible and near infrared lasers for optical reading and sensing applications. The ability of Tm^{3+} ion in emitting different wavelengths ranging from near infrared to ultraviolet makes the host glasses suitable for variety of applications viz., S-band (1460–1530 nm) amplification (TDFAs) in optical telecommunication ($^3\text{H}_4 \rightarrow ^3\text{F}_4$ transition), high density storage devices ($^1\text{D}_2 \rightarrow ^3\text{F}_4$ transition, 450 nm), medicine ($^3\text{F}_4 \rightarrow ^3\text{H}_6$ transition, range of 1.8–1.9 μm) and remote sensing [11–13].

Very recently, we have carried out spectroscopic properties for Tm^{3+} ions in $(50-x) \text{P}_2\text{O}_5$ -27CaO-20Na₂O-3K₂O: $x\text{Tm}_2\text{O}_3$ ($0.5 \leq x \leq 2.0$ mol %), where thulium ions introduced by reducing phosphorous pentoxide [14]. In the present investigation, we have synthesized $50 \text{P}_2\text{O}_5$ -(25-x) CaO-22 Na₂O-3 K₂O: $x \text{Tm}_2\text{O}_3$ ($0.2 \leq x \leq 1.0$ mol %) replacing calcium oxide with Tm_2O_3 along with few more compositional changes. The aim of the present work is to characterize the glass samples by XRD & SEM; to explore the optical absorption and the fluorescence spectra of Tm^{3+} ions with increasing dopant in calcium phosphate glasses. Further, the study is intended to discuss the changes in luminescence features.

2. Experimental methods

For the present study, a particular glass composition $50 \text{P}_2\text{O}_5$ -(25-x) CaO-22 Na₂O-3 K₂O: $x \text{Tm}_2\text{O}_3$ ($0.2 \leq x \leq 1.0$ mol %) is chosen. The details of the composition and corresponding nomenclature are given below.

CT₂: $50 \text{P}_2\text{O}_5$ -24.8 CaO-22 Na₂O- 3 K₂O: 0.2 Tm_2O_3

CT₄: $50 \text{P}_2\text{O}_5$ -24.6 CaO-22 Na₂O- 3 K₂O: 0.4 Tm_2O_3

CT₆: $50 \text{P}_2\text{O}_5$ -24.4 CaO-22 Na₂O- 3 K₂O: 0.6 Tm_2O_3

CT₈: $50 \text{P}_2\text{O}_5$ -24.2 CaO-22 Na₂O- 3 K₂O: 0.8 Tm_2O_3

CT₁₀: $50 \text{P}_2\text{O}_5$ -24 CaO-22 Na₂O- 3 K₂O: 1.0 Tm_2O_3

Phosphorous pentoxide (P_2O_5) was added in the form of ammonium dihydrogen orthophosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) whereas sodium, potassium, and calcium were introduced in the form of their respective anhydrous carbonates. But Tm_2O_3 was added directly as available. All the raw materials of chemicals were of analytical grade and used without further purification. All reagents were thoroughly mixed in an agate mortar and melted in a platinum crucible in the temperature range of 1300 to 1500 °C in a PID temperature controlled furnace for about half an hour. The resultant melts were rotated several times 30 min apart to achieve homogeneity. The homogeneous resultant bubble

free melts were cast into preheated stainless steel moulds of the required dimensions. The prepared samples were directly transferred to a regulated muffle furnace at 480 °C for annealing. After 1 h, the muffle furnace was left to cool to room temperature at a rate of 30 °C/h⁻¹. The samples prepared were ground and optical polished to the dimensions of 2 cm × 2 cm × 0.2 cm. The amorphous nature of samples was identified using Rigaku D/Max ULTIMA III X-ray diffractometer with CuK_α radiation. Scanning electron microscopy studies were also carried out on these samples to observe the crystallinity using HITACHI S-3400N Scanning Electron Microscope. The density d of the bulk samples was determined to an accuracy of (± 0.0001) by the standard principle of Archimedes' using *o*-xylene (99.99% pure) as the buoyant liquid. Ultraviolet, visible and NIR absorption spectra were recorded for perfectly polished glass samples with a spectral resolution of 0.1 at room temperature in the spectral wavelength range covering 300–1100 nm using JASCO Model V-670 UV–vis-NIR spectrophotometer. The luminescence spectra of the glass samples were recorded at room temperature on a Photon Technology International (PTI) fluorescence spectrophotometer.

3. Results and discussion

It is very important to calculate physical parameters that provide information about structural changes in the glasses with increase in the dopant concentration. From the measured values of the density and average molecular weight M of the samples, various other physical properties such as thulium ion concentration N_i , mean thulium ion separation r_i and polaron radius r_p [15] are calculated and presented in Table 1. Significant increase in thulium ion concentration along with slight increase in density 'd' with increase in dopant Tm_2O_3 has been observed. The replacement of CaO with massive Tm_2O_3 might be the reason for such increasing trend of ion concentration and density of glass samples.

X-ray diffraction spectra of P_2O_5 -CaO-Na₂O-K₂O: Tm_2O_3 glasses are shown in Fig. 1. XRD patterns of all samples have indicated the absence of sharp peaks confirming that the prepared glass samples were of amorphous in nature. The glassy phase is well structured such that there are no voids and breakages.

Scanning electron microscopy (SEM) pictures for some of the P_2O_5 -CaO- Na₂O-K₂O: Tm_2O_3 glasses are presented in Fig. 2. These pictures clearly indicate that prepared glasses do not contain any crystal grains confirming amorphous nature to them. Thus, it supports the result of above XRD patterns.

Table 1: Physical parameters of P_2O_5 -CaO- Na_2O - K_2O : Tm_2O_3 glasses.

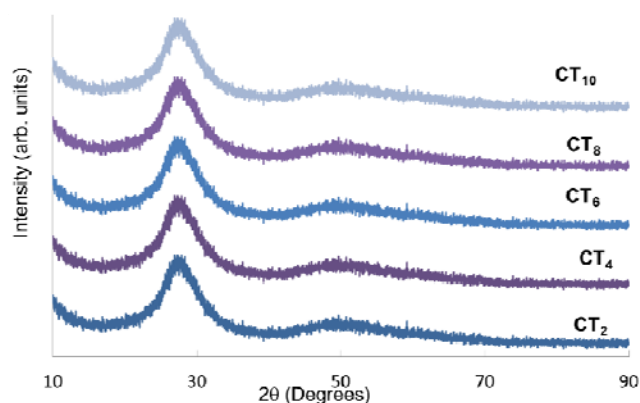
Glass sample	Avg. Mol. Wt. (g/mol)	Density (g/cm ³)	Conc. of Tm^{3+} ions N_i ($10^{21}/cm^3$)	Inter ionic distance of Tm^{3+} ions r_i (Å°)	Polaron radius r_p (Å°)
CT ₂	173.1	6.901	4.80	0.59	0.24
CT ₄	173.7	7.032	9.75	0.47	0.19
CT ₆	174.5	7.163	14.84	0.41	0.16
CT ₈	175.1	7.295	20.07	0.37	0.14
CT ₁₀	175.7	7.426	25.45	0.34	0.13

The prepared glass samples are mixtures of glass network former (P_2O_5), intermediate oxides and modifiers (CaO, Na_2O & K_2O). Phosphorous pentoxide is one of the strong glass network formers and possesses PO_4 tetrahedron network structure. With bridging oxygens, PO_4 tetrahedrons forming chains through covalent bonding. Whereas neighboring phosphate chains are linked together by cross bonding between the metal cation and two non-bridging oxygen atoms of each PO_4 tetrahedron. In general, the P-O-P bond between PO_4 tetrahedra is much stronger than the cross bond between chains via the metal cations. CaO acts as modifier that may enter the phosphate glass network by breaking P-O-P bonds and introduce bonding defects. Na_2O & K_2O are considered to be incipient glass network formers and those not readily form the glass but they can form glass in the presence of the modifier oxides like CaO [16].

In the present typical composition, alkali oxides act as incipient glass network modifiers and produce more number of non-bridging oxygens (NBO's) causing glass devitrification by reducing viscosity of phosphate glasses. Glass network modification results from addition of alkali oxides would create suitable phosphate host environment for Tm^{3+} ions. It also has been observed that as concentration of thulium ions increased, the more number of NBO's created, causing loosely packed structure so that Tm^{3+} ions will have strong chemical bonding with surrounding ligand ions which in turn alters luminescence properties.

The presence of alkali oxides Na_2O and K_2O in the causes loosely packed glass structures due to more number of non-bridging oxygens. Due to structural modifications, resultant glass structures become less ionic and it also reduces ionic character of ion-host ligands. Thus presence of alkali ions confirming the decrease of ligand field strength that causing variations in intensities and spectral

positions of emission bands. As there are no significant changes in positions of bands, the constant percentages of alkali oxides throughout the series of glass samples could also be the one of the reasons.

Fig. 1 XRD patterns of P_2O_5 -CaO- Na_2O - K_2O : Tm_2O_3 glasses.

Normally, the effect of intermediate oxides like CaO is less on spectral positions of emission bands in comparison with alkali oxides due to the fact that they have limited role in glass structure modifications. In general, structural modifications resulting by addition of modifier oxides producing non-bridging oxygens there by making opened glass structure. The physical properties of glass samples may changes in accordance with the structural modifications. The glass structure has become looser which also been confirmed form density increase with conc. of thulium oxide, since the Tm^{3+} ions enters phosphate network at the expense of systematic phosphorous structural units.

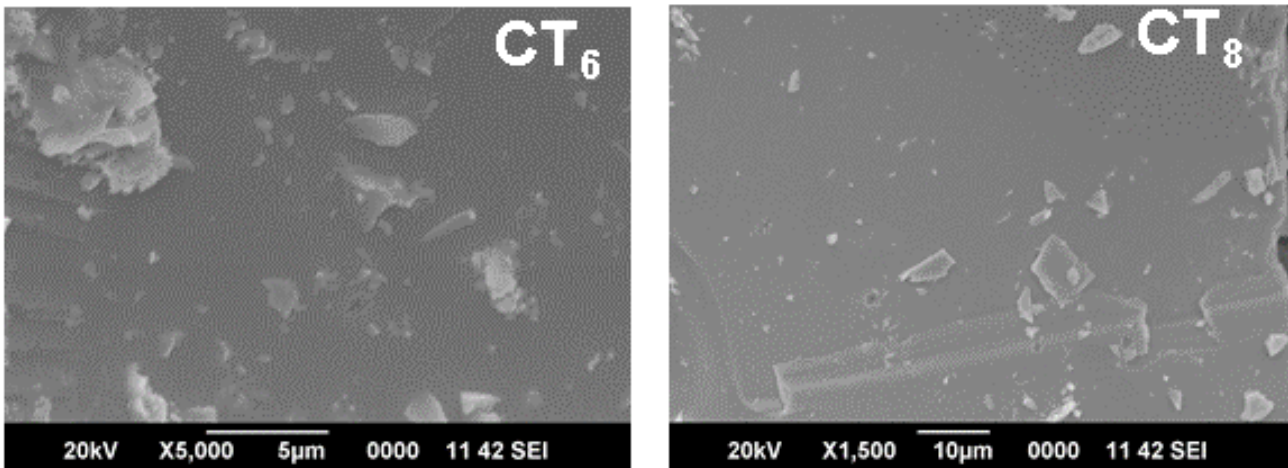
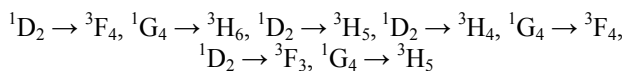


Fig. 2 SEM pictures for some of P_2O_5 -CaO- Na_2O - K_2O : Tm_2O_3 glasses recorded at different magnifications.

The spectroscopic properties of rare earth doped glasses predominantly depend on the nature of dipole-dipole interactions occurred. Fig. 3 represents the optical absorption spectra of P_2O_5 -CaO- Na_2O - K_2O : Tm_2O_3 glasses recorded at room temperature in the wavelength range 300-2100 nm. The spectrum of glass sample CT₄ has exhibited six (06) well known absorption bands peaking at 456, 663, 702, 796, 1215 and 1675 nm corresponding to the transitions from 3H_6 (the ground state of Tm^{3+} ion) \rightarrow 1G_4 , 3F_2 , 3F_3 , 3F_4 , 3H_5 and 3H_4 respectively [8, 17,18]. A small kink observed at 460 nm is shown as inset of the Fig. 3 for prompt observation. The sharper peak observed for the absorption band corresponding to the transition $^3H_6 \rightarrow ^3H_5$ is might be due to magnetic dipole interaction. Out of all the transitions, $^3H_6 \rightarrow ^1G_4$ is used for recording emission spectra in visible region whereas $^3H_6 \rightarrow ^3F_3$ transition for NIR region. From the spectra, it is clear that the peak widths and positions of absorption bands of all glass samples have shown no appreciable change as thulium concentrations increased. Thus it allows us to conclude that the variation in the positions of absorption bands is independent of glass composition.

Fig. 4 shows emission spectra in visible and NIR regions for P_2O_5 -CaO- Na_2O - K_2O glasses doped with different amounts of Tm^{3+} ions pumped at 456 nm ($^3H_6 \rightarrow ^1G_4$ transition) and 698 nm ($^3H_6 \rightarrow ^3F_3$ transition) respectively. The emission spectra of all samples in visible region have exhibited six bands in increasing wavelength order associated to following transitions:



Out of all the transitions, $^1G_4 \rightarrow ^3H_6$ and $^1D_2 \rightarrow ^3H_5$ transitions are found to be more sharp and intense. From the spectra, it is also observed that intensities of emission bands in visible and NIR regions increased monotonically at the beginning with respect to increase in the concentration of Tm_2O_3 .

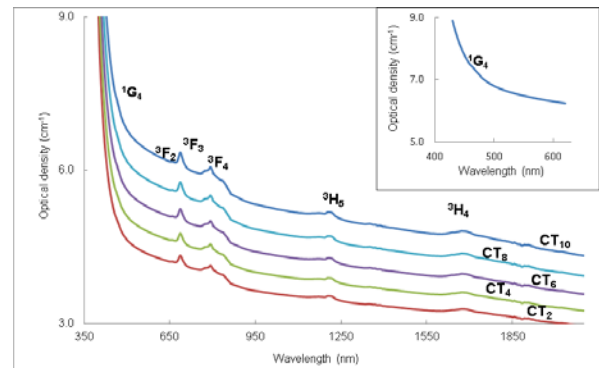


Fig. 3. A comparison plot of optical absorption spectra of P_2O_5 -CaO- Na_2O - K_2O : Tm_2O_3 glasses (all the transitions are from the ground state 3H_6). Inset shows the small kink observed at about 460 nm associated to $^3H_6 \rightarrow ^1G_4$ in all samples.

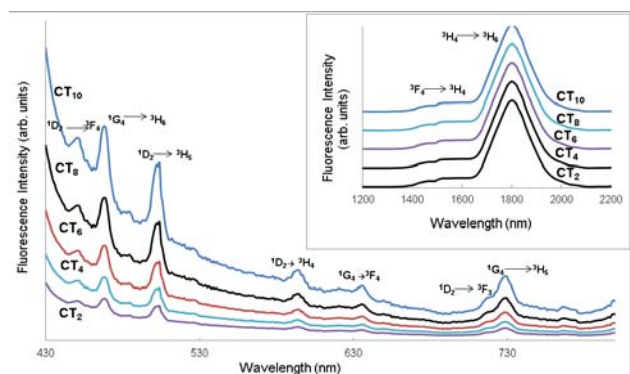


Fig. 4. Emission spectra of P_2O_5 -CaO- Na_2O - K_2O glasses doped with different concentrations of Tm_2O_3 ($\lambda_{exc} = 410$ nm). Inset shows the emission spectra in NIR region for all samples excited at 698 nm.

Similarly, the emission spectra of all samples in NIR region (Inset of Fig. 4) have exhibited two bands; one prominent, intense band associated to $^3H_4 \rightarrow ^3H_6$ along with small kink corresponding to the transition $^3F_4 \rightarrow ^3H_4$. The intensity of small kink is decreased with increase in the concentration of Tm_2O_3 , whereas the intensity of sharp

band increases continuously with Tm₂O₃ content. The reason for such variations could be due to typical cross relaxation mechanism among composite oxides [9].

4. Conclusion

We prepared glasses of particular composition P₂O₅-CaO-Na₂O-K₂O: Tm₂O₃ by fusing a mixture of their respective reagent grade powders in a platinum crucible at 850 °C for 40 min. The characterization properties XRD and SEM were carried out to analyse the morphology of the samples. Further, the spectroscopic properties were investigated by measuring the absorption and fluorescence in visible & NIR regions at room temperature. Characterization studies confirms the amorphous nature and no signs of crystallinity. The absorption spectra has exhibited six prominent bands. The peak widths and positions of all absorption bands corresponding to all glass samples have shown no appreciable change with increase in thulium concentration. Thus it allows us to conclude that the variation in the positions of absorption bands is almost independent of glass composition. The emission spectra of all glass samples have shown six bands in visible and two bands in NIR region. All emission bands in visible region are found to be more sharp and intense. Among two bands in NIR region, the intensity of small kink is decreased with increase in the concentration of Tm₂O₃, whereas the intensity of sharp band increases continuously with Tm₂O₃ content. These glasses would be more useful in making designs optical fiber communication systems and laser fibers due to their significant infrared emission.

Acknowledgements

One of the authors, Dr. T. Satyanarayana, is highly thankful to SERB-DST & UGC, Govt. of India for the financial assistance to carry out this work.

References

- [1] M. J. Dejneka, *J. Non-Crystalline Solids* **239**, 149 (1998).
- [2] Hiroyuki Inoue, Kohei Soga, Akio Makishima, *J. Non-Crystalline Solids* **331**, 58 (2003).
- [3] L. Bih, M. El Omari, J. M. Reau, M. Haddad, D. Boudlich, A. Yacoubi, A. Nadiri, *Solid State Ionics* **132**, 71 (2000).
- [4] K. Yukimitu, E. B. Araújo, J. C. S. Moraes, V. C. S. Reynoso, C. L. Carvalho, *J. Phys. D Appl. Phys.* **35**, 3229 (2002).
- [5] I. Ardelean, C. Andronache, C. Cîmpean, P. Pascuta, *Modern Phys. Lett. B*, **20**, 105 (2006).
- [6] Meng Wang, Lixia Yi, Youkuo Chen, Chunlei Yu, Guonian Wang, Lili Hu, Junjie Zhang, *Materials Chemistry and Physics*, **114**, 295 (2009).
- [7] T. Satyanarayana, I. V. Kityk, M. G. Brik, V. Ravi Kumar, N. Veeraiah, *J. Phys. B: Cond. Matter* **405**, 1872 (2010).
- [8] G. Ozen, A. Aydinli, S. Cenk, A. Sennaroglu, *J. Lumin.* **101**, 293 (2003).
- [9] Dong Jun Lee, Jong Heo, Se Ho Park, *J. Non-Crystalline Solids* **331**, 184 (2003).
- [10] Jiani Qi, Yinsheng Xu, Fei Huang, Liyan Chen, Ying Han, Bing Xue, Shaoqian Zhang, Tiefeng Xu Shixun Dai, *J. Am Ceramic. Soc.*, **97**, 471 (2014).
- [11] P. Babu, Hyo Jin Seo, Kyoung Hyuk Jang, R Balakrishnaiah, C.K. Jayasankar and A.S. Joshi, *J. Phys.: Condens. Matter* **17**, 4859 (2005).
- [12] A. Braud, P. Y. Tigreat, J. L. Doualan, R. Moncorge *Appl. Phys. B* **72**, 909 (2001).
- [13] G. Poirier, V. A. Jerez, C. B. de Araujo, Y. Messaddeq, S. J. L. Ribeiro, M.J. Poulain *Appl. Phys.* **93**, 1493 (2003).
- [14] T. Satyanarayana, M. A. Valente, G. Nagarjuna, N. Veeraiah, *J. Phys. Chem. of Solids* **74**, 229 (2013).
- [15] T. Satyanarayana, P. Krishna Kanth, G. Nagarjuna, B. Naga Mani, N. Srinivasa Rao, *Int. J. Sci. & Research*, **4**, 155 (2014).
- [16] S. V. G. V. A. Prasad, M. Srinivasa Reddy, V. Ravi Kumar, N. Veeraiah, *J. Lumin.* **127**, 637 (2007).
- [17] E. W. J. Oomen, *J. Lumin.*, **50**, 317 (1992).
- [18] J. R. Lincoln, W. S. Brocklesby, F. Cusso, J. E. Townsend, A. C. Tropper, A. Pearson, *J. Lumin.* **50**, 297 (1991).

*Corresponding author: satyamphysics@gmail.com