Journal of Alloys and Compounds 509 (2011) 5591–5595

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Investigation of structural properties and its effect on optical properties: Yb^{3+}/Tb^{3+} codoped in aluminum silicate glass

R.K. Verma, D.K. Rai, S.B. Rai*

Laser and Spectroscopy Laboratory, Department of Physics, Banaras Hindu University, Varanasi, UP 221005, India

ARTICLE INFO

Article history:
Received 23 October 2010
Received in revised form 18 January 2011
Accepted 30 January 2011
Available online 22 February 2011

PACS:
42.70.Hj
42.70.Ce

Keywords:
Glass ceramic
Optical properties
Upconversion
Energy transfer

ABSTRACT

Yb^{3+} doped and Yb^{3+}/Tb^{3+} codoped aluminum silicate glass with good transparency has been synthesized using the sol–gel process. X-ray diffraction (XRD), scanning electron microscopy (SEM), differential thermal analysis (DTA) and thermo gravimetric analysis (TGA) techniques have been used to distinguish between glassy and glass ceramic structures while FTIR spectrum is measured to see if the vibrational frequencies of prominent modes change and thus provide identifying feature. A study of the upconversion luminescence from Tb^{3+} indicates that cooperative energy transfer from Yb^{3+} to Tb^{3+} ions is not operative in the glass host but adds to the luminescence in the glass ceramic and the ceramic forms of the host. The exciting radiation is 976 nm from a diode laser. Dependence of the luminescent intensity as a function of the input radiation power indicates involvement of two incident photons. Emission of Yb^{3+} has also been investigated and it is observed that the cooperative emission (at 488 nm) is dependent on the concentration and temperature of the host. Luminescent emission spectrum of terbium ion on excitation by 355 nm radiation is also recorded and compared with the upconverted luminescence excited by 976 nm radiation.

1. Introduction

Rare earth doped glasses have attracted considerable interest of optical scientists due to their varied applications in optical devices [1,2]. On excitation by suitable incident radiation these ions emit through 4f–4f transitions made allowed by configuration mixing. The glass can also be converted easily through heat treatment into a ceramic form which brings in additional desirable characteristics [3,4]. Such a ceramic can exist in two forms one of which is largely transparent and is only partially crystalline while the other form is non transparent and is almost completely crystalline. These two types of glass-ceramic have different areas of application e.g. telecommunications, temperature sensors, high power solid state lasers, etc. for the transparent variety [5–7] and display devices, CFL, etc. for the nontransparent one in a powder form [8,9].

Yb^{3+} is one of the most studied lanthanide ion [10–12] especially as it has a simple electron level scheme. The two lowest states are $^2F_{7/2}$ (ground state) and $^2F_{5/2}$ about 10,000 cm^{-1} above. Energy levels with higher energy are of little interest in the present context. The excited $^2F_{5/2}$ state can decay mainly through radiative emission or excitation energy transfer to another suitable atom or ion. A surprising feature of Yb^{3+} ions emission is that though no absorption is usually seen at 488 nm in its absorption spectrum an emission at this wavelength has been seen. This has been explained as due to a cooperative emission [13]. Though, the process responsible for this emission is not very well understood it has been invoked in many upconversion studies [14–16]. Such codoped glasses have been shown to be of use in optical switching through optical bistability, planar laser, etc. [17,18]. In Yb^{3+}/Tb^{3+} codoped glass, it is known that Yb^{3+} transfers energy to Tb^{3+} ions and Tb^{3+} ions give emission through $^5D_3/^5D_4 \rightarrow {}^7F_J$ transitions. On excitation with 355 nm source it again gives emission after excitation by 976 nm radiation through $^5D_3/^5D_4 \rightarrow {}^7F_J$ transitions. Many workers have reported very weak or no transitions from the $^5D_3$ level [19,20].

In the present work we have synthesized Yb^{3+} doped and Yb^{3+}/Tb^{3+} codoped aluminum silicate glass using the sol–gel technique. The glass has then been converted into a transparent glass-ceramic and then a nontransparent ceramic. Structure of these glass-ceramic and ceramic has been studied. It is observed that Yb^{3+} ion does not give the cooperative emission in the silicate glass but does so in the glass ceramics. The intensity of the emission increases when the glass ceramic is converted into a ceramic form. Variation of its intensity with the input power shows that emission from Yb^{3+} is an up-converted luminescence. The Yb^{3+}/Tb^{3+} codoped glass gives a bluish green emission on 976 nm excitation due to energy transfer from Yb^{3+} ions to the Tb^{3+} ions. This emission has been compared with the down conversion emission when the glass is excited by 355 nm radiation.

* Corresponding author. Tel.: +91 542 230 7308; fax: +91 542 236 9889.
E-mail address: sbrai49@yahoo.co.in (S.B. Rai).

0925-8388/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2011.01.219

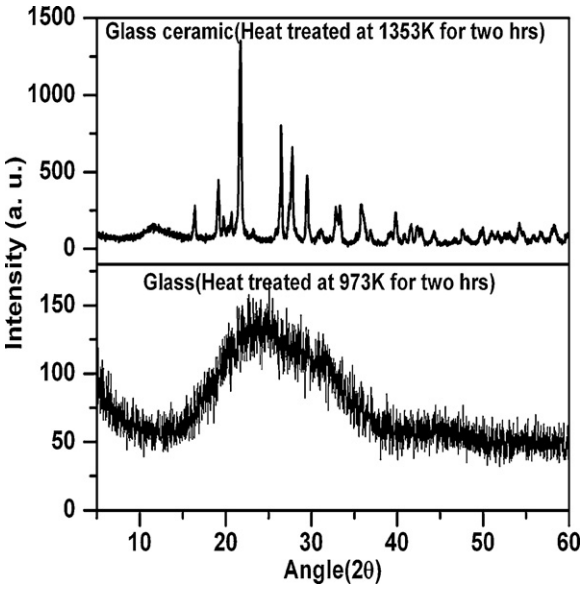

Fig. 1. Powder X-ray diffraction pattern of aluminum-silicate glass heat treated at 973 K and 1353 K.

2. Experimental

Yb^{3+} doped and Yb^{3+}/Tb^{3+} co-doped aluminum silicate glass samples were prepared by the well known sol–gel technique [21,22]. The starting materials are tetraethyl ortho silicate (TEOS), ethanol, distilled water in the ratio 1:2:4, 10% $Al(NO_3)_2$ and compound containing Yb and Tb. It is evinced that in the final products the concentration of Yb^{3+} ranges from 0.1 to 3 mol% and of Tb^{3+} from 0.1 to 1.5 mol%. The best results are seen when concentration was 2.5 mol% of Yb^{3+} and 1 mol% of Tb^{3+}. The above mixture was magnetically stirred continuously so as to obtain a clear homogeneous solution. The solution was then transferred to a Petri dish and was kept as such for three days at room temperature, changing it into a gel. The resulting gel was dried at 313 K for 4 weeks. The sample is then kept for two hours at 973 K, to remove all traces of the volatile residues and for densification of the gel.

The optical absorption spectrum of Yb^{3+} in a silica glass heat treated at different temperatures has been recorded using a Perkin Elmer Lambda-35 spectrophotometer. The fluorescence spectra were recorded using 355 nm radiation from an Nd:YAG laser. A iHR320, Horiba Jobin Yvon, spectrometer was used to disperse and detect the fluorescence signal. The radiative life time of $^4F_{5/2} \rightarrow {}^4F_{7/2}$ and $^5D_4 \rightarrow {}^7F_6$ transitions of Yb^{3+} and Tb^{3+} were measured using chopped continuous 976 nm radiation from a diode laser. Powder XRD was recorded for aluminum silicate glass heated at 2 different temperatures (973 K and 1353 K) for two hours. Surface morphology was characterized by ZEISS scanning electron microscopy (SEM), Model: SEM-Supra 40 operated at 5 kV.

3. Result and discussion

3.1. Structural analysis

Fig. 1 shows the XRD pattern of aluminum silicate glass heat treated at 973 K. No feature of crystallinity is observed in the case of glass. However, for the glass ceramic the sample heated at temperature above 1300 K for two hours shows some crystallinity with a broad peak, whereas the sample heated above 1353 K for two hours shows sharp peaks which befits a crystalline structure. This result suggests that as the ceramising process proceeds the sample becomes more and more crystalline. The crystallite size estimated using Scherer formula

$$t = \frac{0.9 \times \lambda}{\beta \cos\theta}$$

where t is the crystallite size for the (h k l) planes, λ is the wavelength of the incident X-ray [CuKα (0.154056)], β is the full width at half maximum (FWHM) and θ is the diffraction angle for (h k l) plane] is 2 μm for the fully crystalline phase. For the partially crystalline phase this is only 203 nm.

Fig. 2 shows SEM images of the dense glass ceramic. The ceramic particles are densely packed with some micro pores. Even at higher magnification, the surface looks flat and no obvious microspheres are observed as shown in Fig. 2(b).

3.2. Thermal analysis

The DTA and TGA curves for the as-synthesized glass are represented in Fig. 3. The glass transition and crystallization temperature could be easily marked from this. Most of the weight losses are seen

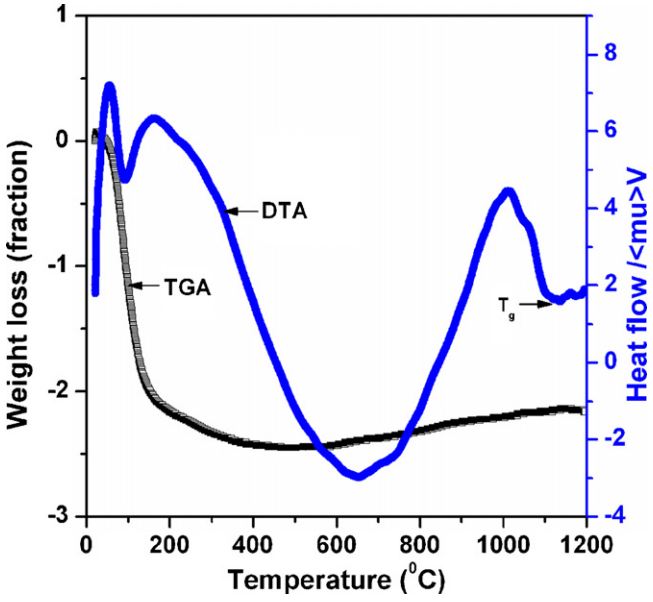

Fig. 3. DTA and TGA of as-synthesized aluminum silica glass.

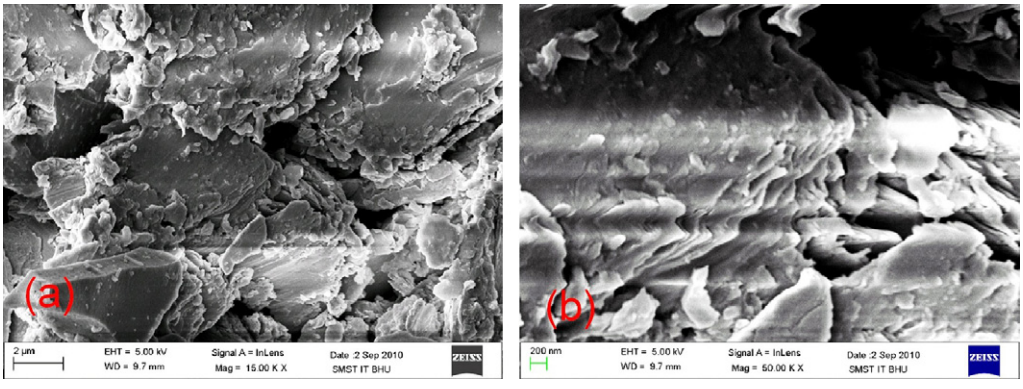

Fig. 2. SEM image of ceramic material and shows that particles are converted in micro-region.

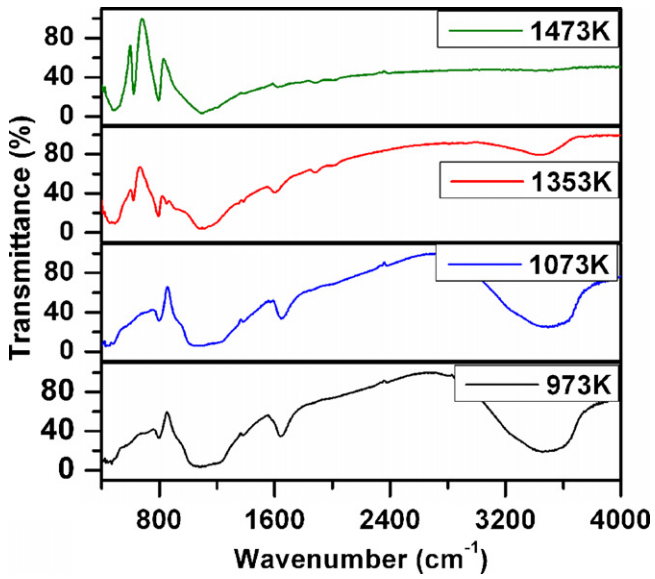

Fig. 4. FTIR spectra of glasses heat treated at 973 K, 1073 K, 1353 K, and 1473 K.

to appear between 773 K and 1073 K. This weight loss is attributed to removal of water compounds, nitrates and similar compounds which also serve as fluorescence quenching centers. A phase transition occurs at 1353 K indicating the stability of the silica glass upto reasonably high temperatures without damage.

3.3. FTIR analysis

Fig. 4 shows the Fourier transform infrared (FTIR) spectrum of the silica glass heat treated at different temperatures (i.e. 973 K, 1073 K, 1353 K and 1473 K). The sample heat treated at 973 K shows intense broad peaks at 3518 cm^{-1} and 1123 cm^{-1}. Two sharp peaks are also seen at 1680 cm^{-1} and 800 cm^{-1}. The peak at 3518 cm^{-1} is due to OH and at 1680 cm^{-1} is due to H–O–H bond. There is no significant change in the spectrum of the glass upto 1073 K. The H_2O and OH exist with great abundance in silica glass which act as quenching centers and this may be the reason for the non-observation of cooperative emission from Yb^{3+} in the glass. However, when the sample is heat treated at high temperatures these quenching centers decrease in number and the cooperative upconversion is observed. When the glass is heat treated at a still higher temperature (1473 K) the material becomes a ceramic. The quenching centers vanish and the efficiency of the emission is increased considerably. A broad continuum is also seen in the frequency region ~1100 cm^{-1} while another broad structure is seen with peaks at 800 cm^{-1} and 514 cm^{-1} in all the samples (irrespective of heat treatment). All these peaks are probably due to Si–O–Si vibration. The bending vibration of the Si–O–Si is expected around 790 cm^{-1} while the asymmetric stretching vibration of Si–O–Si is expected in the range 1000–1300 cm^{-1}. The peak at 514 cm^{-1} is probably due to the Si–O vibration.

3.4. Up-conversion spectrum with 976 nm excitation

The absorption of Yb^{3+} ion doped in the silica glass and in the glass ceramics is shown in Fig. 5(a). Absorption in the glass ceramics is many times stronger than in the glass. Stark splitting is also seen in the ceramic host. Further the FWHM of the absorption peak of Yb^{3+} ion in the ceramic is seen to be smaller than the FWHM in the glass. The emission from Yb^{3+} doped silica glass, the glass heat treated at 973 K, 1353 K and 1473 K are shown in the spectrum. The as-synthesized glass and the one heat treated at 973 K do not show any upconversion emission, while the two other samples heat

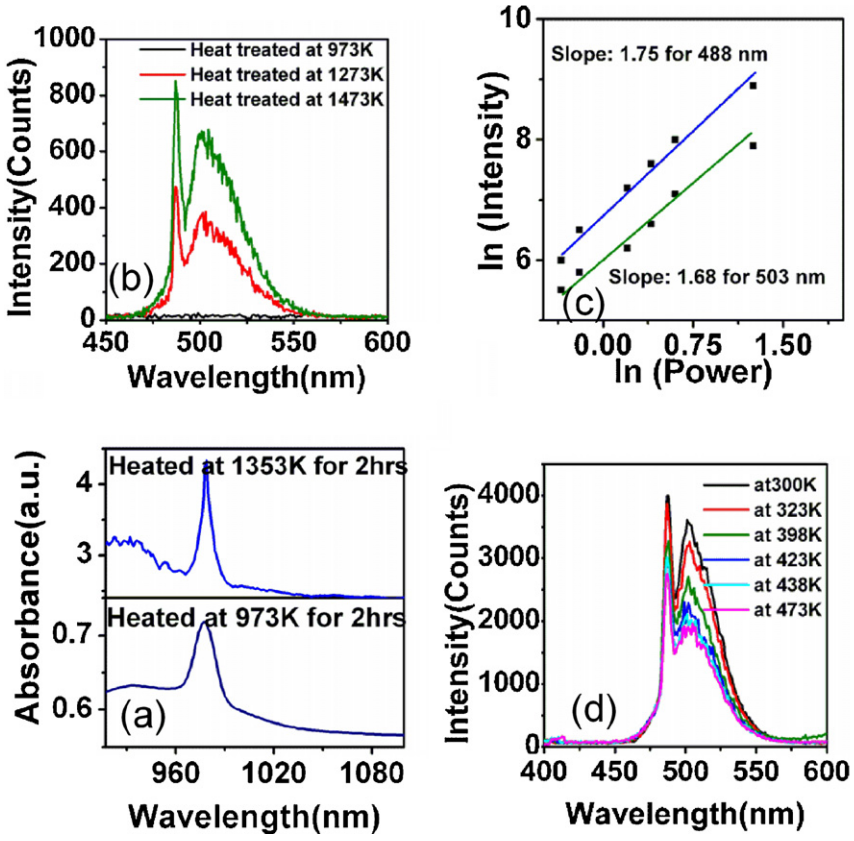

Fig. 5. (a) Absorption spectrum of Yb^{3+} in glass and glass ceramic, (b) emission spectrum of Yb^{3+} in glass, glass ceramic and ceramic, (c) power dependence of cooperative upconversion and (d) effect of heat treatment of cooperative upconversion.

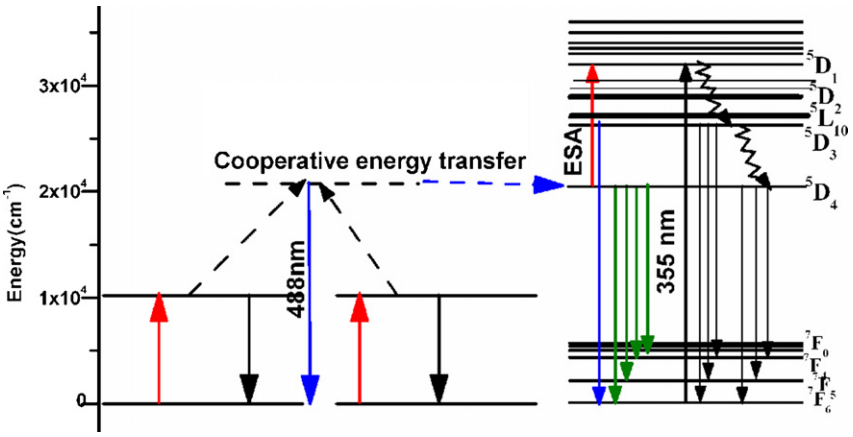

Fig. 6. Simplified energy level diagram of Yb^{3+} and Tb^{3+} and possible mechanism of frequency cooperative upconversion and energy transfer from Yb^{3+} to Tb^{3+}.

treated at 1353 K and at 1473 K show two peaks – one sharp at 488 nm and another broad one with peak at 503 nm. The intensity of the 488 nm emission also depends upon the concentration of Yb^{3+} doping [23].

The dependence of the up-conversion emission intensity on input power is shown in Fig. 5(c). The slope of the linear curve between ln(*I*) versus ln(*P*) is seen to be 1.77 and 1.68, for the 488 nm and the 503 nm emissions respectively. The departure from an integral value (expected = 2) in both cases shows that other processes especially non-radiative decay of the excited state are also involved. The observation that for the sample heat treated at higher temperature is smaller points to the increased contribution of non-radiative relaxation shown in Fig. 5(d).

3.5. Emission of Tb^{3+} ions through energy transfer from excited Yb^{3+} ions using 976 nm diode laser radiation

The upconversion emission from Tb^{3+} ions on 976 nm excitation in a Yb^{3+}/Tb^{3+} codoped silica glass, glass ceramic and ceramic have also been investigated. Since Tb^{3+} ions do not absorb the incident 976 nm radiation, its excitation is dependent on energy transfer from the excited Yb^{3+} ions. As is evident from the energy level schemes for Yb^{3+} and Tb^{3+} (Fig. 6) no transfer of excitation energy from an Yb^{3+} in $^2F_{5/2}$ level is possible and one is constrained to consider the energy transfer simultaneously from a pair of Yb^{3+} ions – both excited to the $^2F_{5/2}$ level. This excitation populates $^5D_4$ level of the Tb^{3+} ion and results in a strong green emission. A Tb^{3+} ion in this state can absorb radiation at 976 (or equivalent energy) either from a Yb^{3+} ion in $^2F_{5/2}$ state or from the input radiation. This raises the Tb^{3+} ion to a still higher energy level which can decay non-radiatively to the $^5D_3$ and $^5D_4$ emitting states as shown in Fig. 6.

$$Yb^{3+}(\text{Exc.})+Yb^{3+}(\text{Exc.})+Tb^{3+}(\text{G.S.})\rightarrow 2Yb^{3+}(\text{G.S.})+Tb^{3+}(^5D_4)$$
$$Tb^{3+}(^5D_4)+h\nu\rightarrow Tb^{3+}(\text{higher level})\rightarrow \text{Relaxation},\quad Tb^{3+}(^5D_3, {}^5D_4)$$
$$Tb^{3+}(^5D_4)\rightarrow Tb^{3+}(\text{G.S.})+h\nu'$$
$$Tb^{3+}(^5D_3)\rightarrow Tb^{3+}(\text{G.S.})+h\nu''$$

The observed emission spectrum of Yb^{3+}/Tb^{3+} codoped sample excited by 976 nm is shown in Fig. 7. The Tb^{3+} emission includes peaks at 489 nm, 544 nm (green strongest), 587 nm and 621 nm involving the electronic transitions $^5D_4\rightarrow{}^7F_6$, $^5D_4\rightarrow{}^7F_5$, $^5D_4\rightarrow{}^7F_4$ and $^5D_4\rightarrow{}^7F_3$. The other peaks seen at 379 nm, 413 nm, 437 nm and 457 nm correspond to electronic transitions $^5D_3\rightarrow{}^7F_6$, $^5D_3\rightarrow{}^7F_5$, $^5D_3\rightarrow{}^7F_4$ and $^5D_3\rightarrow{}^7F_3$. These latter peaks have rarely been observed in emission from terbium doped in silica or other high phonon frequency host materials. The Tb^{3+} ions in the $^5D_4$ level may further absorb a 976 nm photon or receive excitation

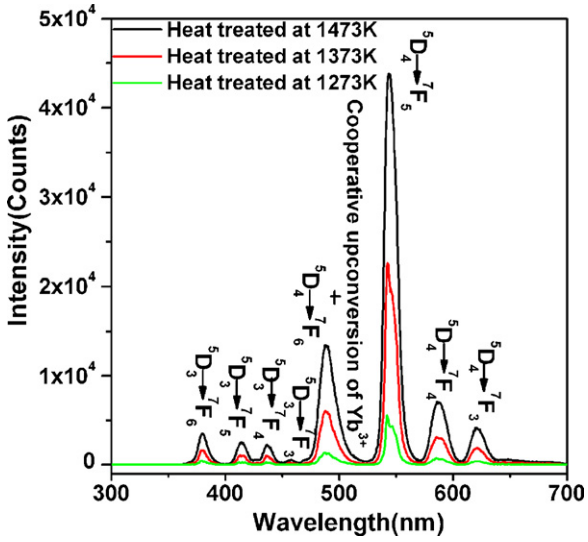

Fig. 7. Emission of Tb^{3+} ions through energy transfer of Yb^{3+} by 976 nm excitation source.

transfer from an excited $Yb^{3+}(^2F_{5/2})$ ion, raising the Tb^{3+} ions to the $^5D_1$ level which decays non-radiatively to $^5D_3$ and $^5D_4$ levels adding to the above mentioned transitions.

3.6. Emission from Tb^{3+} in a silica glass ceramic excited by UV radiation at 355 nm

The emission spectra of Tb^{3+} ions in glass, glass ceramic and ceramic host when excited by 355 nm radiation from an Nd:YAG laser are shown in Fig. 8. One finds that in this case while the emission intensity from the glass ceramic is larger than for glass, the intensity from the fully ceramic sample is smaller. This is probably due to increased scattering at the boundaries of the larger crystallites existing in the fully ceramised sample. The Tb^{3+} ion under excitation by the 355 nm radiation emits blue light attributed to $^5D_3\rightarrow{}^7F_J$ transitions at 379 nm, 413 nm, 437 nm and 457 nm and green light attributed to $^5D_4\rightarrow{}^7F_J$ transitions. The strongest peak appears at 543 nm and has a full width at half maximum (FWHM) of 88 nm. The $^5D_1$ state excited by the incident radiation $^5D_1$ populates the $^5D_3$, $^5D_4$ levels non-radiatively so the spectrum is similar to one observed on 976 nm excitation. Some of the emission peaks show Stark splitting (see Fig. 8). Since the energy difference between the $^5D_3$ and $^5D_4$ levels is approximately the same as the energy separation between the $^7F_0$ and $^7F_6$ levels, the excited ions

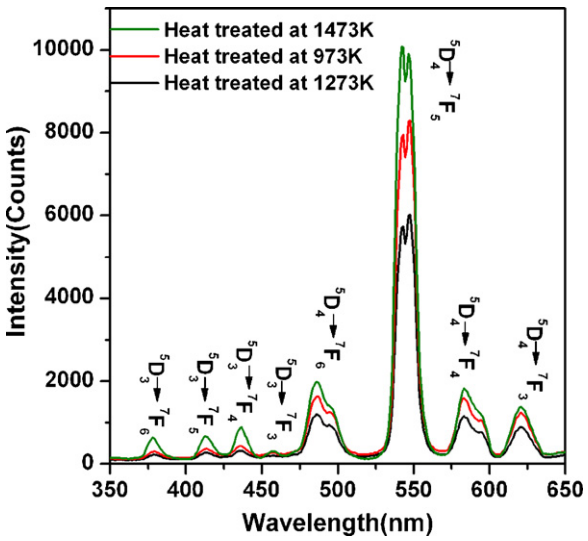

Fig. 8. Stokes emission of Tb^{3+} ions by 355 nm excitation source.

in $^5D_3$ level can relax to $^5D_4$ level while inducing an excitation of another Tb^{3+} ion from the $^7F_6$ to the $^7F_0$ level through the process of cross-relaxation. This process of cross relaxation increases the population of Tb^{3+} ions in the $^5D_4$ state relative to that in $^5D_3$ state reducing the intensity of the emission bands from the $^5D_3$ level. The Tb^{3+} ions in the higher levels of the ground state multiplet ^7F_J can reabsorb green radiation and promoted to $^5D_3$ level.

Excitation by the UV radiation is more efficient than the upconversion process as it involves a single incident photon. The upconversion process requires many steps including an energy transfer from a pair of excited donor ions which in itself is a less efficient process. The upconversion process however, creates visible emission from a lower energy photon while the UV excitation starts with a high energy photon and lowers its energy. There is also some difference between the two emissions in the intensity behavior for the three types of samples viz glassy, glass-ceramic and (fully) ceramic.

4. Conclusions

The cooperative energy transfer has been shown to be of importance for upconversion in Yb^{3+}/Tb^{3+} codoped host excited by 976 nm radiation. The evidence from Yb^{3+} doped host seems to indicate that in addition to the simultaneous pair relaxation of Yb^{3+} ions and the transfer of energy to Tb^{3+} ions, the observed absorption of Yb^{3+} at 488 nm also plays a significant role in excitation of Tb^{3+} ions. Emission from $^5D_3$ level, hitherto not observed in many cases has also been observed and may also involve an excited state absorption (ESA) process following the energy transfer from Yb^{3+}. Excitation by 355 nm also gives a similar spectrum in the codoped samples except that there is Stark splitting seen in some peaks. Minor deviations in intensity behavior are also noted.

Acknowledgements

The authors are grateful to AvH Germany for a gift of the Nd:YAG laser. One author to us (R.K. Verma) would like to thank UGC for meritorious scholarship. Grants from D.S.T., Government of India, New Delhi is also acknowledged.

References

[1] H. Suche, R. Wessel, S. Westenhoer, W. Sohler, W. Bosso, C. Carmannini, R. Corsini, Opt. Lett. 20 (1995) 596.
[2] F. Chen, X.L. Wang, K.M. Wang, Opt. Mater. 29 (2007) 1523.
[3] F. Lahoz, Opt. Lett. 33 (2008) 2982.
[4] D. Chen, Y. Yu, P. Huang, F. Weng, H. Lin, Y. Wang, Appl. Phys. Lett. 94 (2009) 041909.
[5] J. Xia, D. Chen, J. Qiu, C. Zhu, Opt. Lett. 30 (2005) 47.
[6] W. Strek, P.J. Deren, K. Maruszewski, E. Pawlik, W. Wojcik, G.E. Malashkevich, V.I. Gaishun, J. Alloys Compd. 275 (1998) 420.
[7] R.K. Verma, K. Kumar, S.B. Rai, Spectrochim. Acta A 74 (2009) 776.
[8] Y. Zheng, A. Clare, Phys. Chem. Glasses 46 (2005) 467.
[9] Z. Shan, D. Chen, Y. Yu, P. Huang, H. Lin, Y. Wang, J. Mater. Sci. (2010), doi:10.1007/s10853-010-4266-1.
[10] A.V. Kir'yanov, Y.O. Barmenkov, I.L. Martinez, Opt. Express 14 (2006) 3981.
[11] I.R. Martin, A.C. Yanes, M.E. Torres, V.D. Rodriguez, J. Appl. Phys. 89 (2001) 2520.
[12] Y. Qiao, L. Wen, B. Wu, J. Ren, D. Chen, J. Qiu, Mater. Phys. Chem. 107 (2008) 488.
[13] G.S. Maciel, A. Biswas, R. Kapoor, P.N. Prasad, Appl. Phys. Lett. 76 (2000) 1978.
[14] R.T. Wegh, A. Meijerink, Chem. Phys. Lett. 246 (1995) 495.
[15] X. Chen, Z. Song, Solid State Commun. 136 (2005) 313.
[16] N.K. Giri, D.K. Rai, S.B. Rai, Appl. Phys. B 89 (2007) 345.
[17] D.M. Baney, G. Rankin, K.W. Chang, Appl. Phys. Lett. 69 (1996) 1662.
[18] F. Auzel, Chem. Rev. 104 (2004) 139.
[19] D. Chen, Y. Yu, Y. Wang, P. Huang, F. Weng, J. Phys. Chem. C 113 (2009) 6406.
[20] B.C. Joshi, D.K. Upretil, C.C. Dhondiyal, B. Khulbey, Indian J. Pure Appl. Phys. 46 (2008) 702.
[21] Q. Guodong, W. Minquan, W. Mang, F. Xianping, H. Zhanglian, J. Lumin. 75 (1997) 63.
[22] A. Opalinska, M.N. Wolcyrz, W. Lojkowski, J. Misiewicz, J. Sci. Technol. 32 (2004) 195.
[23] F. Auzel, P. Goldner, Opt. Mater. 16 (2001) 93.