# 3.9 μm emission and energy transfer in ultra-low OH-, Ho3+ /Nd3+ co-doped fluoroindate glasses

**Abstract:** Ho3+/Nd3+ co-doped fluoroindate glass samples were prepared by melt-quenching. The absorption and emission spectra, and the differential thermal analysis (DTA) curve were measured and used to evaluate the spectroscopic parameters and thermal properties. An intense ~3.9 μm emission, ascribed to the transition Ho3+:5I5 →5I6,was observed under the excitation of a 808 nm laser diode and was ascribed to the efficient energy transfer process from Nd3+: 4F3/2 to Ho3+: 5I5, showing the Nd3+ role as a sensitizer. The optimal concentration ratio of Ho3+ and Nd3+ for ~3.9 μm emission was estimated to be 1:1. The spectroscopic performance suggests that the Ho3+/Nd3+ co-doped fluoroindate glass is a potential gain material for ~3.9 μm laser applications.

**Keywords**: fluoroindate glass, 3.9 μm emission, Ho3+/Nd3+ co-doped

# 1. Introduction

Lasers operating in the mid-infrared wavelength region (λ=3-5 μm) have been a research hotspot due to their wide applications in national defense, medical treatment, pollution detection, industrial processes and scientific research [1-8]. In comparison with other types of lasers, fiber lasers have the comprehensive advantages of diffraction-limited beam quality, superior thermal management and compactness, and have become a mainstream technology in the near-infrared wavelength region. At present, the output power of Tm3+ doped silica fiber lasers (λ~2 μm) have reached kilowatt levels when pumped by laser diodes, and benefited from the excellent mechanical and thermal performance of silica fibers [9]. Because of the large energy phonon (~1100 cm-1) and limited infrared transmission range (λ<2.5 μm) of silica, it is impossible to obtain lasers in silica fibers operating at λ~3-5 μm. Fluoride fibers have the advantages of low phonon energy and wide transmission widow, which can be used for mid-infrared lasers [10-15]. Among them, ZBLAN fibers showed superior performance and achieved laser output covering the range λ~2.7-3.9 μm [16-26]. In 2018, Aydin et al. demonstrated erbium-doped fluoride fiber laser at λ~2824 nm with an average output power of 41.6 W, which is the highest average output power achieved in a mid-infrared fiber laser [17]. In 2017, Mace et al. reported the first monolithic erbium-doped fluorozirconate fiber laser, which obtained a λ~3.55 μm laser with an output power of 5.6 W [27]. In 2019, luo et al. confirmed that the gain switch fiber laser had a maximum average power of 1.04 W at λ~3.46 μm [28]. In 1997, Schneider et al. presented room-temperature fluorescence at 3.9 μm in Ho3+ doped ZBLAN fibers with a output power of 11 mW in liquid nitrogen [29]. However, the λ~3.9 μm emission efficiency is strongly dependent on the host material phonon energy because of the small energy gap ΔE between the level of Ho3+: 5I5 and 5I6 according to the multi-phonon relaxation process which could be described by , where is the maximum phonon energy of the host material, , , C and α are the constants associated with the host material. Yet, λ~3.9 μm is close to the edge of the ZBLAN glass transparency window and the fibers loss increases accordingly. Fluoroindate glass is an alternative fluoride glass matrix with lower phonon energy than ZBLAN, and in 2018 it was used by Maes et al. to produce the longest wavelength room temperature fiber laser: a fluoroindate fiber doped with 10 mol % Ho3+ produced a λ~3.9 μm laser with ∼200 mW of output power when pumped by a λ~888 nm laser diode [30]. As the absorption coefficient of Ho3+: 5I5 is small, pumping at λ~888 nm is not efficient. The introduction of other rare earth ions is an efficient method to sensitize Ho3+ and enhance the pumping absorption efficiency. Recently, we introduced Nd3+ into the Ho3+ doped glass samples and observed an intense λ~3.9 μm emission, which has been attributed to the efficient sensitization effect of Nd3+ to Ho3+ under the excitation of λ~808 nm LD. Nd3+ can be excited to the (4F5∕2, 2H9∕2) level and then relax to the 4F3∕2 level, to transfer energy to the Ho3+: 5I5 level. Subsequently, the λ~3.9 μm emission was produced thanks to the radiative transition from the 5I5 level to the 5I6 level of Ho3+. The λ~3.9 μm emission is a self-terminated process, because the lifetime of the 5I6 level (~6.2 ms) is much longer than that of the 5I5 level (~135 μs) [30], thus population inversion cannot be directly achieved and depopulation of the 5I6 level is necessary to achieve lasing. The 5I6 level depopulated can be achieved through the energy transfer process of Ho3+: 5I6→Nd3+: 4I15/2.

In this work, we observed an intense emission at λ~3.9 μm and investigated the energy transfer mechanisms in Ho3+/Nd3+ co-doped fluoroindate glasses. The intense emission was attributed to the efficient energy transfer process from Nd3+ to Ho3+ and the deactivation effect relative to the process of Ho3+:5I6 to Nd3+: 4I15/2, showing that Ho3+/Nd3+ co-doped fluoroindate glasses are an excellent gain material for mid-IR μm laser applications.

# 2. Experiment

Glass samples with the molar compositions of 26InF3-14ZnF2-19BaF2-11GaF3-8SrF2-12PbF2-5LiF-(4-x)LaF3-xHoF3-1NdF3 (x=0.2, 0.5, 1,2, 3, 4, named as xHo-1Nd) and 26InF3-14ZnF2-19BaF2-11GaF3-8SrF2-12PbF2-5LiF-4LaF3-1HoF3 (named as 1Ho) were prepared from high purity (99.9%) raw materials by using the conventional melt-quenching method. The powders were put into a platinum crucible and then melted in a furnace at the temperature T~850 °C in a glove box, and then poured onto a preheated copper plate with annealing at T~240 °C for 3 h, after which they were slowly cooled to room temperature. The annealed samples were polished to the same thickness of 1.85 mm for subsequent optical measurements. The thermal characteristic was determined by differential thermal analysis (DTA) with a Seiko TG/DTA6200 analyzer at a heating rate of 10 K/min. The Perkin Elmer Lambda 750 UV-VIS-NIR spectrophotometer and Perkin Elmer FTIR infrared Fourier spectrometer were used to measurement the absorption spectrum in the range λ~200-1000 nm and the transmission spectrum in the range f λ~1-11 μm, respectively. Fluorescence spectra were recorded with a computer controlled Zolix Omni-λ300i Monochromators and Spectrographs with an InGaAs detector or a liquid nitrogen cooled InSb detector. The decay characteristics of the excitation levels were measured using a tunable optical parametric oscillator (OPO). OPO was tuned to λ~808 nm and λ~880 nm, in order to excited Nd3+: 4F5/2+2H9/2 and Ho3+: 5I5 levels, respectively. All measurements were performed at room temperature.

# 3．Results and Discussions

Fig. 1 shows the transmission spectrum in the range λ~1000-11000 nm and the images of the obtained glass samples with different Ho3+ doping compositions. Fig. 2 shows the absorption spectrum in the range λ~200-1000 nm. Nine strong absorption bands of Ho3+ can be observed at λ~354, 416, 449, 483, 536, 641, 889, 1152, and 1946 nm, which correspond to the transitions starting from the ground state to higher levels 3H6, 5G5, 5G6, 5F3, 5F4, 5F5, 5I5, 5I6 and 5I7, respectively. Due to the strong absorption of Nd3+ at λ~796nm, the λ~808 nm laser diode can be used to pump the Ho3+/Nd3+ co-doped fluoroindate glass. As shown in the Fig. 1, the glass transmittance at 3.9 μm is about 92%, while the transmission window ends at λ~11 μm.

In addition, it can be seen that there is no obvious absorption of OH- near λ~3 μm and the absorption coefficient of OH- can be calculated by Equation:

(1)

which is calculated from the transmission spectrum of a 2 cm thick polished fluoroindate glass block and is about 0.0032 cm-1, where *T0* is the maximum transmittance, *T* is the transmittance at λ~3 μm, and *l* is the thickness of the glass. It was much lower than the OH- absorption coefficient of PbF2 crystal (0.03 cm-1) [31], fluorozirconate (0.031 cm-1) [32], fluoroaluminate (0.12 cm-1) [10] and fluoroindate (0.06 cm-1) [33] glasses.

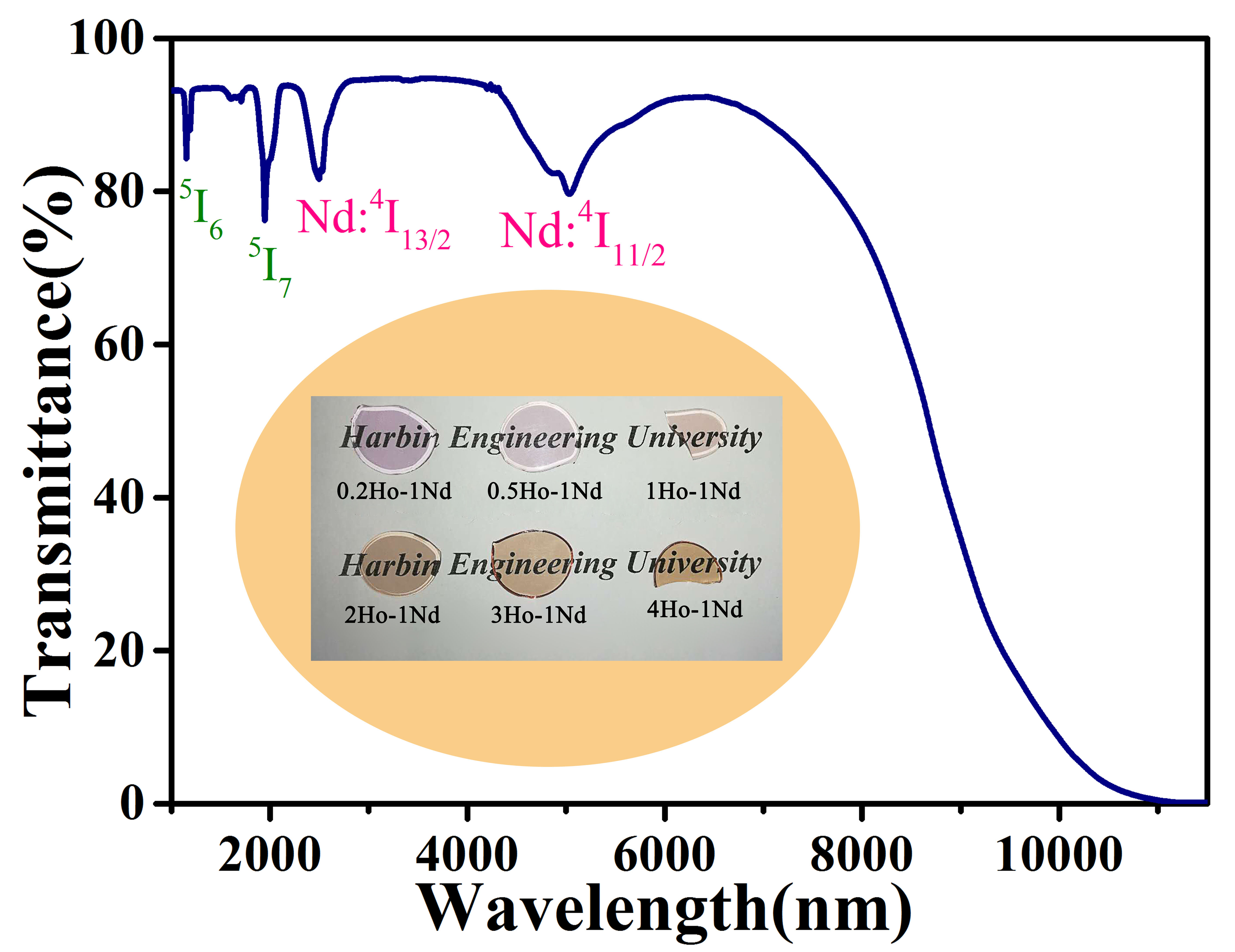


Fig. 1. IR transmission spectrum in the λ~1-11 µm range. Inset: image of the obtained glass samples with different Ho3+ doping compositions.

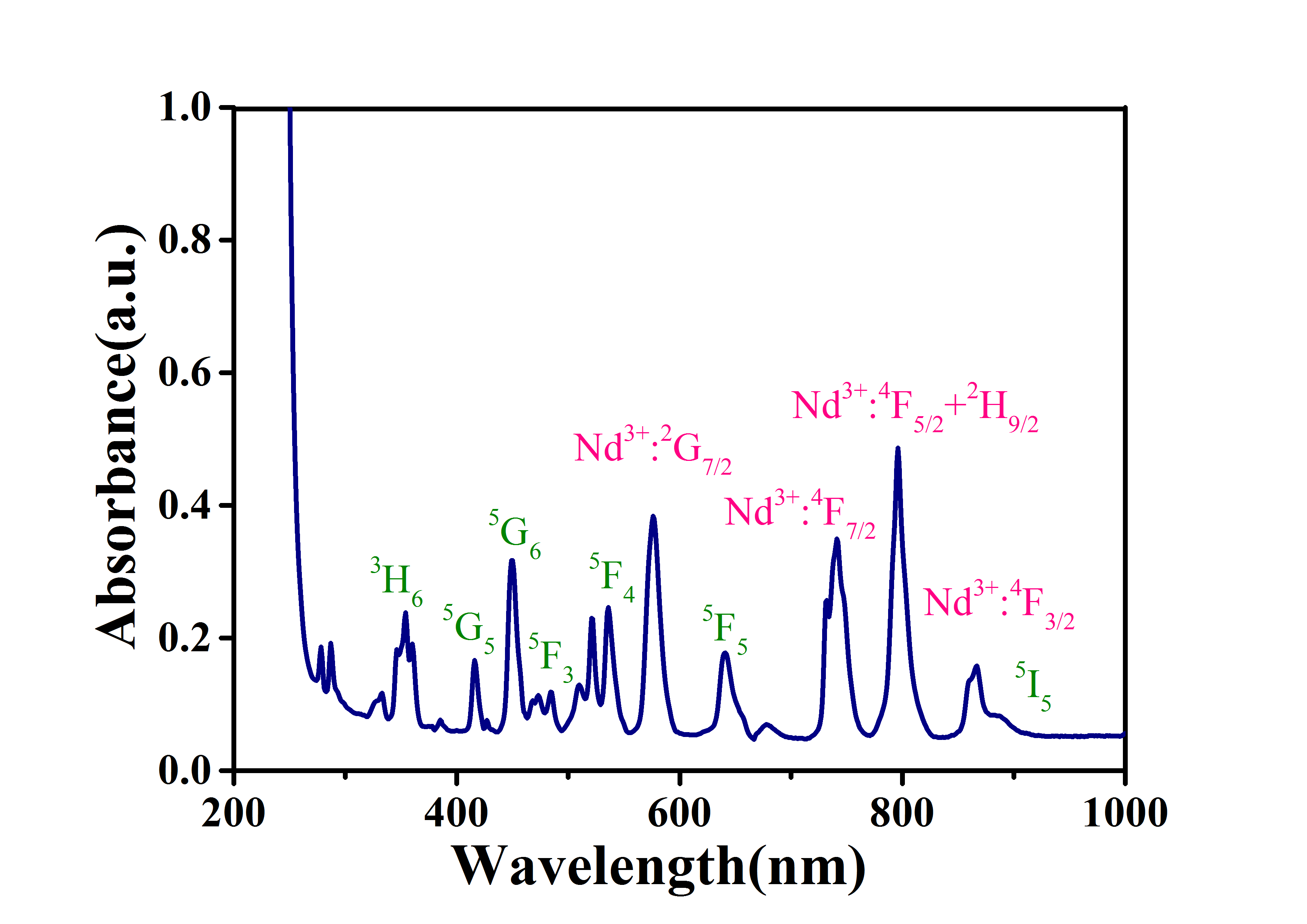


Fig. 2. Absorption spectrum of 1 mol % Ho3+/1 mol % Nd3+ co-doped fluoroindate glass in the range λ~200–1000 nm.

According to the simplified energy level diagram of Ho3+/Nd3+ co-doping shown in Fig. 3, it can be seen that under λ~808 nm laser excitation, Nd3+ transitioned from the ground state level 4I9/2 to the 4F5/2+2H9/2 level and then relaxed to the 4F3/2 level by non-radiative relaxation, then energy was transferred to the 5I5 level of Ho3+. Radiative transitions correspond to emission at λ~3.9 μm (5I5→5I6), λ~2.9 μm (5I6→5I7), 2 μm (5I7→5I8) and λ~1.2 μm (5I6→5I8), respectively. Since the lifetime of the upper level 5I5 is shorter than that of the lower level 5I6, the emission at λ~3.9 μm is self-terminating. Through the energy transfer from the 5I6 level of Ho3+ to the 4I15/2 level of Nd3+, the lifetime of the 5I6 level of Ho3+ could be shortened, thereby improving the λ~3.9 μm fluorescence efficiency. Besides, Nd3+ also have transitions at λ~1.9 μm (4F3/2→4I15/2), λ~1.6 μm (4I15/2→4I9/2), λ~1.33 μm (4F3/2→4I13/2), λ~1.06 μm (4F3/2→4I11/2) and λ~888 nm (4F3/2→4I9/2).

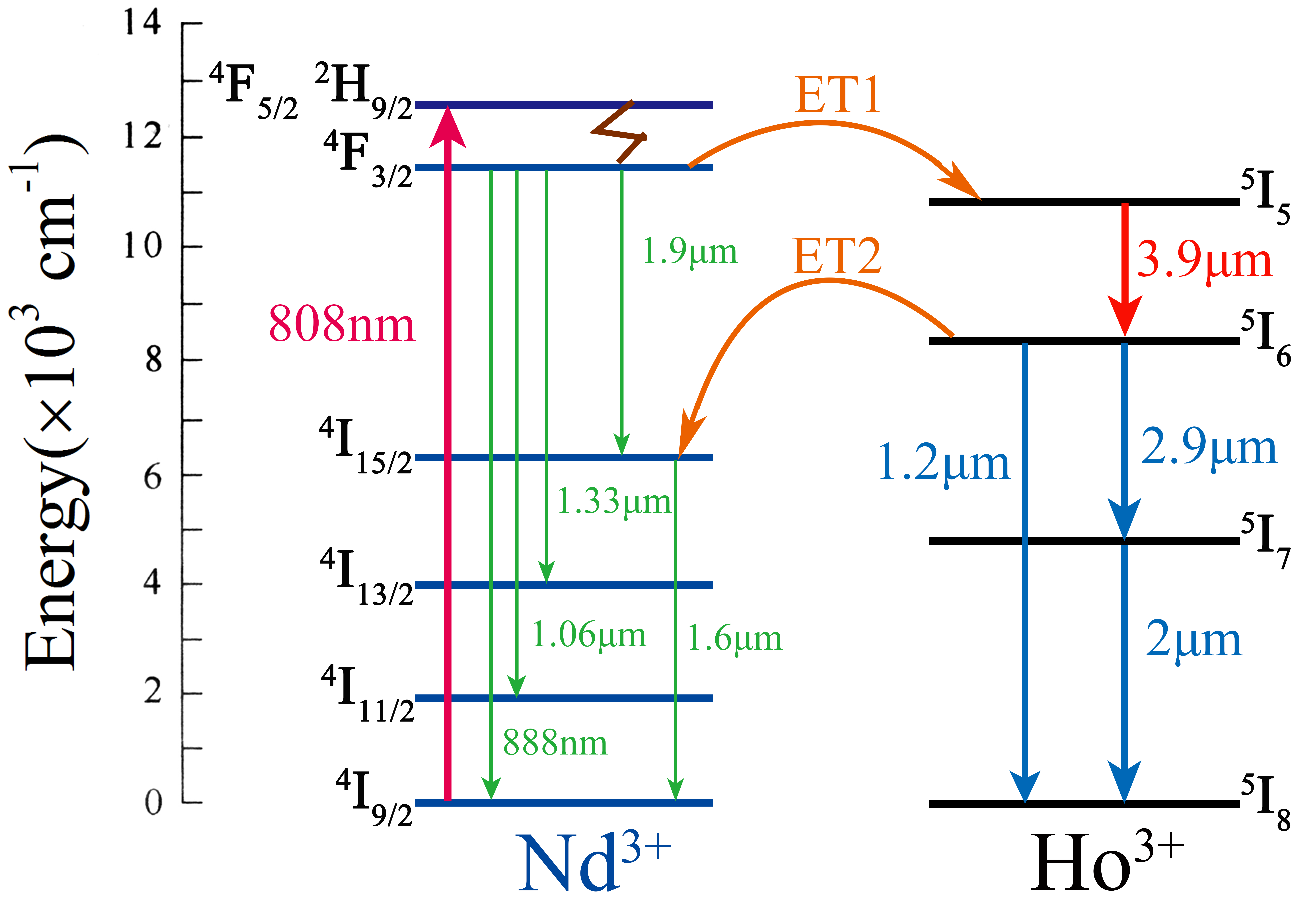


Fig. 3. Energy level diagram.

Fig. 4 shows the differential thermal analysis (DTA) curve of the fluoroindate glass samples: the transition and crystallization temperatures were Tg~259 ℃ and Tx~355 ℃, respectively. ΔT=Tx-Tg, which is an important parameter used to characterize the glass resistance to crystallization and ease of fiberization, was 96 ℃, showing that this glass has relatively good thermal stability and can be used as a material for drawing fibers.

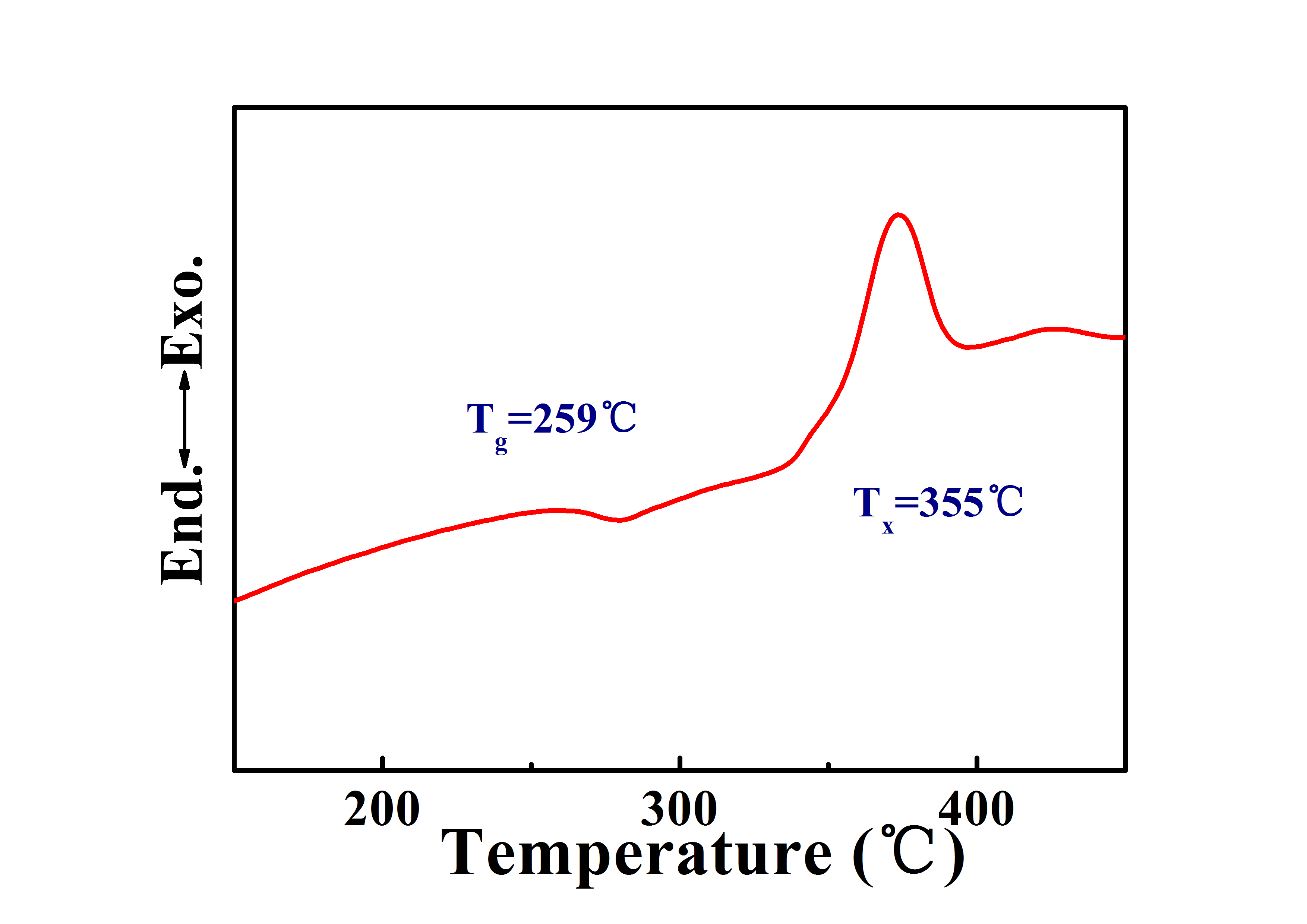


Fig. 4. DTA curve.

The emission spectra of the Ho3+/Nd3+ co-doped fluoroindate glasses around λ~3.9 μm, λ~2.9 μm, λ~2 μm and λ~1.2 μm, pumped by λ~808nm diode laser, are shown in Fig. 5 for various Ho3+ concentrations. When the Nd3+ concentration was fixed at 1 mol %, the luminescence intensity at λ~3.9 μm, λ~2.9 μm, λ~2 μm and λ~1.2 μm increased gradually with the Ho3+ concentration because of the efficient energy transfer from the Nd:4F3/2 to the Ho: 5I5 level. However, as the Ho3+ concentration continues to increase from 1 to 4 mol%, the luminescence intensity decreases due to concentration quenching.

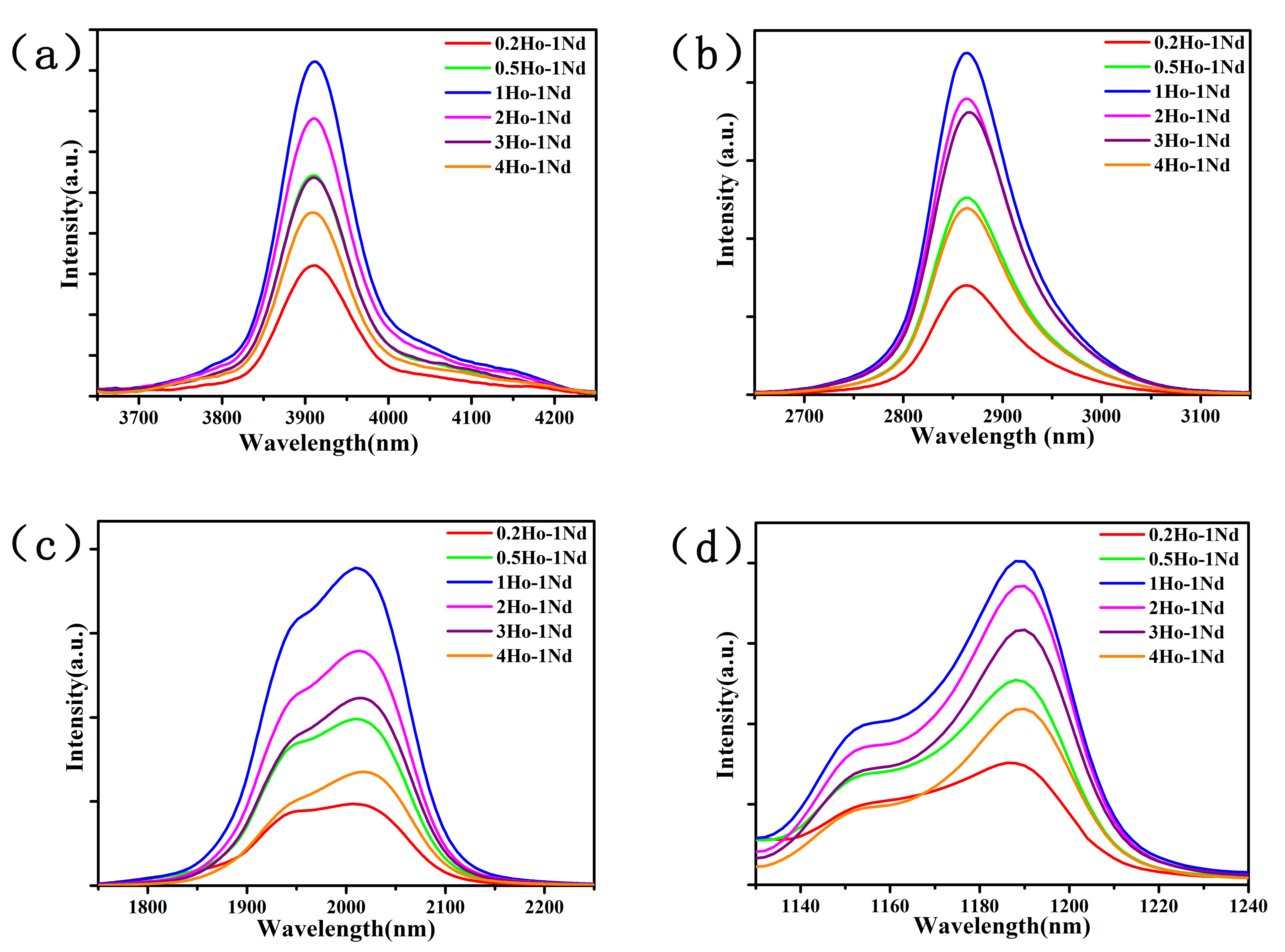


Fig. 5. Emission spectra of the Ho3+ /Nd3+ co-doped fluoroindate glasses at (a) λ~3.9 μm, (b) λ~2.9 μm, (c) λ~2 μm, (d) λ~1.2 μm for different Ho3+ concentrations under λ~808 nm laser diode excitation. The Nd3+ concentration is fixed at 1 mol%.

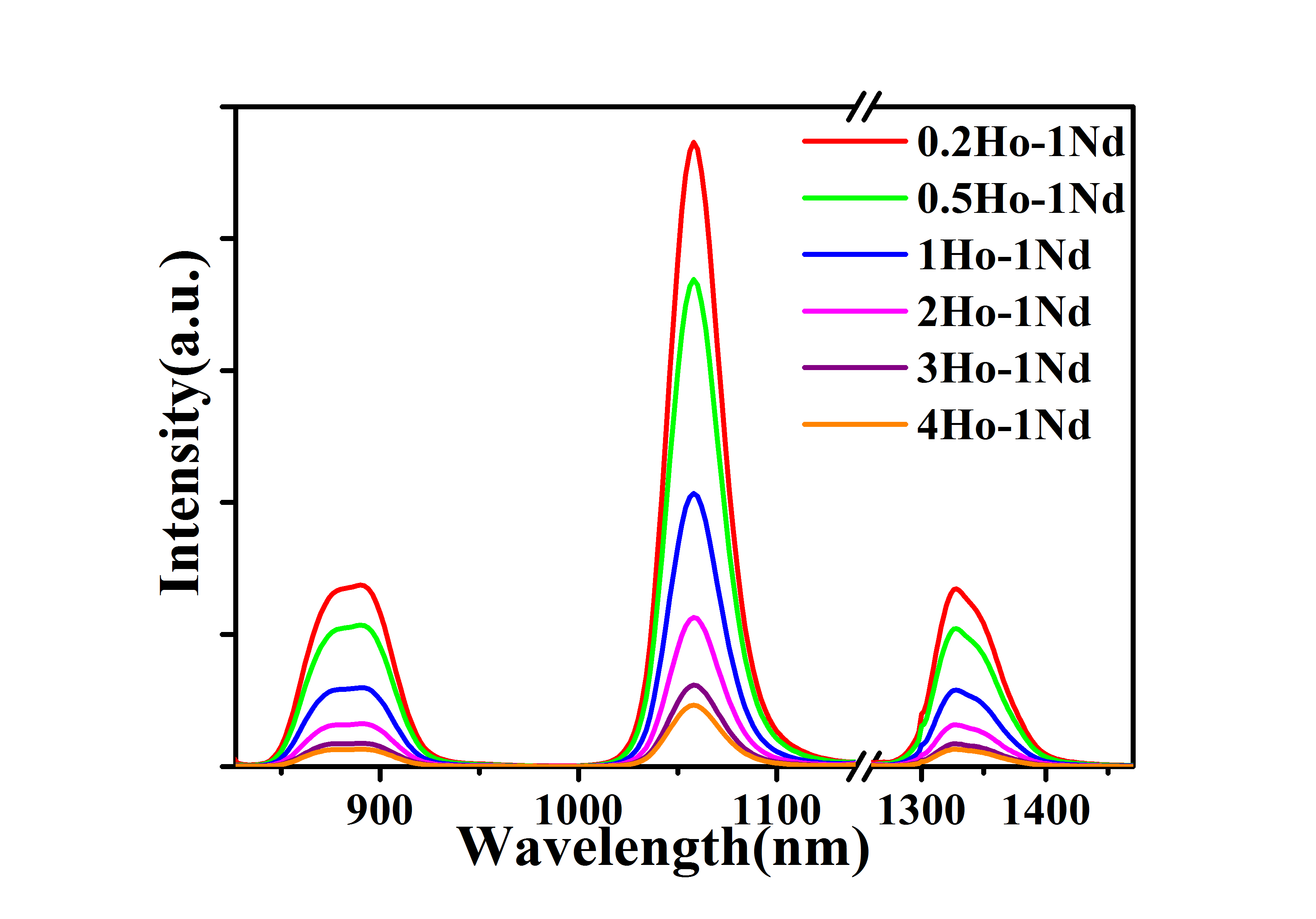


Fig. 6. Emission spectra of the Ho3+/Nd3+ co-doped fluoroindate glasses at λ~888 nm, λ~1.06 μm and λ~1.33 μm for different Ho3+ concentrations under λ~808nm laser diode excitation. The Nd3+ concentration is fixed at 1 mol %.

Fig. 6 shows the emission at λ~888 nm, λ~1.06 μm, λ~1.33 μm of Nd3+ under the pumping of an λ~808 nm laser. The peaks are associated to radiative transitions from the same 4F3/2 level, and are weakened monotonously as Ho3+ concentration increases from 0.2 to 4 mol%, confirming the efficient energy transfer from the Nd3+:4F3/2 to the Ho3+: 5I5 level.

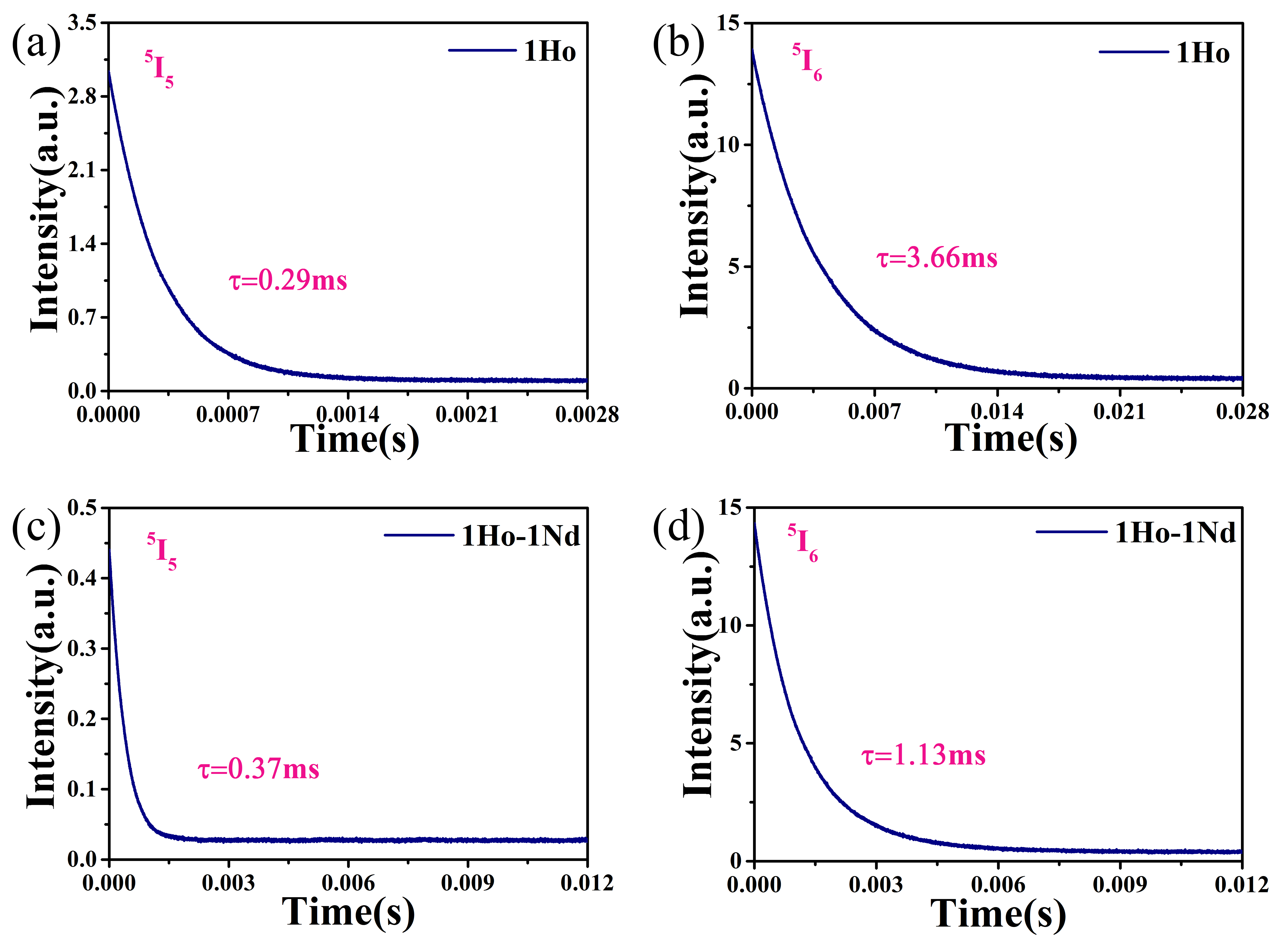


Fig. 7. Fluorescence decay curves of Ho3+: fluoroindate and Ho3+∕Nd3+: fluoroindate glasses for the 5I5 and 5I6 mainfold.

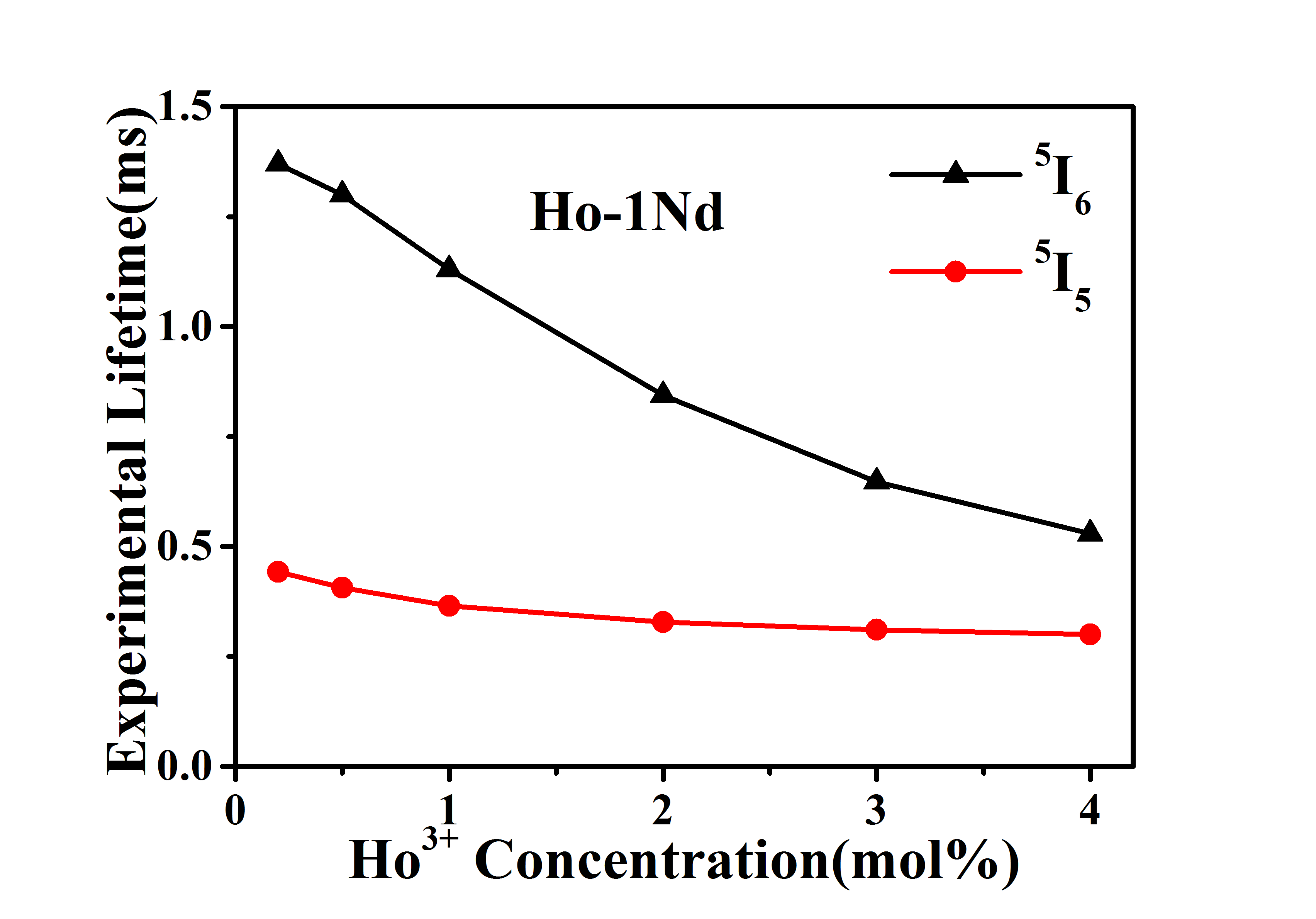


Fig. 8. Experimental lifetimes of 5I5 and 5I6 levels of Ho3+ in the Ho3+/Nd3+ doped fluoroindate glasses at different Ho3+ concentrations.

In order to compare the effect of doped Nd3+ on the energy level of Ho3+, we measured the fluorescence decay of Ho3+ doped and Ho3+/Nd3+ co-doped fluoroindate glasses, as shown in Fig. 7. Fig. 7 shows that Nd3+codoping increases the lifetime of the Ho3+ 5I5 energy level from 0.29 ms to 0.37 ms, which indicates an efficient energy transfer from Nd3+ to Ho3+ . At the same time, Nd3+ codoping reduces the lifetime of the Ho3+5I6 level from 3.66 ms to 1.13 ms, which confirms the occurrence of the ET2 process: Ho3+: 5I6→Nd3+: 4I15/2 in Fig. 3, thereby improving the luminous efficiency of 3.9 μm. Fig. 8 shows the effect of varying Ho3+ concentration on the lifetimes of the Ho3+: 5I5 and 5I6 levels. In the Ho3+/Nd3+ co-doped fluoroindate glasses, as the Ho3+ concentration increased, the lifetimes of the 5I5 and 5I6 levels gradually decreased.

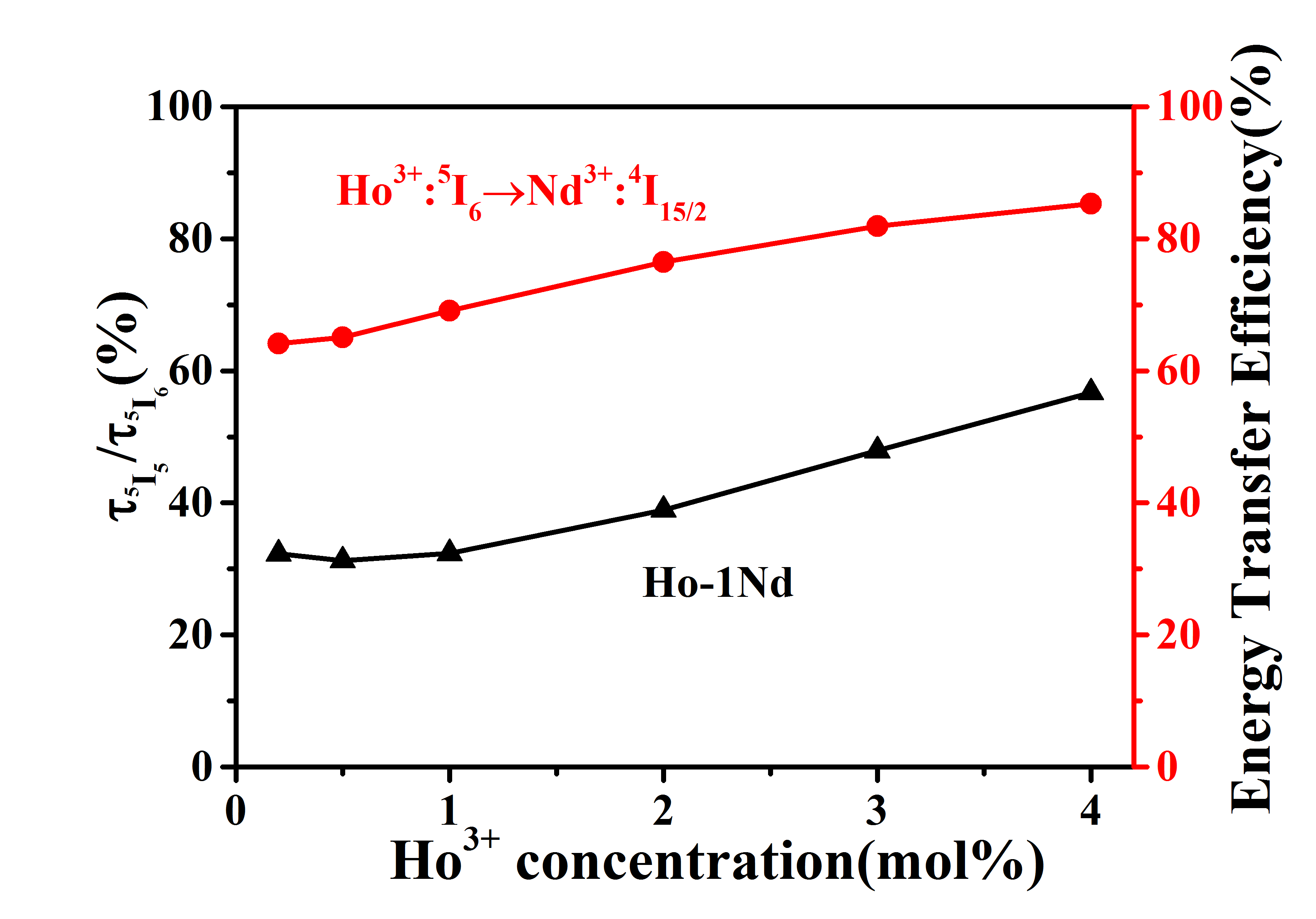


Fig. 9. Ratio of τ5I5 / τ5I6 and Ho3+: 5I6→Nd3+: 4I15/2 energy transfer efficiency in the Ho3+/Nd3+ co-doped fluoroindate glasses at different Ho3+ concentrations.

The energy transfer efficiency can be calculated by formula:

(2)

where *τ0* is the 5I6 energy level lifetime of Ho3+ in Ho3+ doped fluoroindate glass, and *τ* is the 5I6 energy level lifetime of Ho3+ in Ho3+/Nd3+ co-doped fluoroindate glass. As the concentration of Ho3+ increased, the energy transfer efficiency of Ho3+: 5I6→Nd3+: 4I15/2 increased from 64% to 85%, as shown in Fig. 9.

Fig. 9 shows the ratio of the 5I5 to the 5I6 energy level lifetimes of the Ho3+/Nd3+ co-doped fluoroindate glasses. The ratio of τ5I5 / τ5I6 in Ho3+ single doped fluoroindate glass was calculated from results presented in Fig. 7 as 0.079. The ratio Ho3+/Nd3+ in co-doped fluoroindate glasses increases from 32 % to 57 % as the Ho3+ concentration increases from 0.2mol% to 4mol%. Results indicate that both the Nd3+ introduction and Ho3+ concentration increase could result to a greater depletion of the laser lower level population, which would decrease the pump intensity necessary to get population inversion.

# 4. Conclusion

In summary, Ho3+/Nd3+ co-doped fluoroindate glass samples with different Ho3+ concentrations were prepared by the melt-quenching method. Nd3+ could act as sensitizers, effectively absorbing the energy of the λ~808 nm laser and transmitting it to Ho3+, thereby producing fluorescence at λ~3.9 μm, through the energy transfer Nd3+: 4F3/2 → Ho3+: 5I5. The λ~3.9 μm luminescence intensity was highest for Ho3+ and Nd3+ concentrations of 1 mol %, showing that the Ho3+/Nd3+ co-doped fluoroindate glass could be as a gain material for λ~3.9 μm laser applications.

# Funding

National Natural Science Foundation of China (NSFC) (61575050); National Key R&D Program (2016YFE0126500); The Fundamental Research Funds of the Central Universities (HEUCFG201841, 3072019CF2506); Key Program for Natural Science Foundation of Heilongjiang Province of China (ZD2016012); Open Fund of the State Key Laboratory on Integrated Optoelectronics (IOSKL2016KF03); 111 Project (B13015); Recruitment Program for Young Professionals (The Young Thousand Talents Plan).

# References

1. Majewski M.R., Woodward R.I. and Jackson S.D., *Dysprosium-doped ZBLAN fiber laser tunable from* 2.8 μm to 3.4 μm, pu*mped at 1.7* μm*.* Optics Letters, 2018.**43**(5):p.971-974.

2. Aydin Y. O., Fortin V., Maes F., et al. Diode-pumped mid-infrared fiber laser with 50% slope efficiency. Optica, 2017.**4**(2):p.235-238.

3. Bernier M., Faucher D, Caron N, et al., Highl*y stable and efficient erbium-doped 2.8* μm *all fiber laser.* Optics Express, 2009.**17**(19):p.16941-16946.

4. Chen R., Tian Y, Li B, et al., *Thermal and luminescent properties of 2 μm emission in thulium-sensitized holmium-doped silicate-germanate glass.* Photonics Research, 2016.**4**(6):p.214-221.

5. Bawden N, Matsukuma H, Henderson-Sapir O, et al., *Actively Q-switched dual-wavelength pumped Er3+ :ZBLAN fiber laser at 3.47 µm.* Optics Letters, 2018.**43**(11):p.2724-2727.

6. Qin Z, Hai T, Xie G, et al., *Black phosphorus Q-switched and mode-locked mid-infrared Er: ZBLAN fiber laser at 3.5 μm wavelength.* Optics Express, 2018.**26**(7):p.8224-8231.

7. Jackson S. D. C*ontinuous wave 2.9 μm dysprosium-doped fluoride fiber laser.* Applied Physics Letters, 2003.**83**(7):p.1316-1318.

8. Fortin V, Maes F, Bernier M, et al., *Watt-level erbium-doped all-fiber laser at 3.44 μm.* Optics Letters, 2016.**41**(3):p.559-562.

9. Lu Y., Feng G. F., Wang M., et al., *Tm3+-doped silica-glass fiber for similar to 2 μm fiber laser.* Applied Optics, 2019.**58**(7):p.1747-1751.

10. Wang S.B., et al., *Ho3+-doped AlF3-TeO2-based glass fibers for 2.1 μm laser applications.* Laser Physics Letters, 2017.**14**(5):p.4.

11. Jia S., et al., *2875 nm Lasing From Ho3+-Doped Fluoroindate Glass Fibers.* IEEE Photonics Technology Letters, 2018.**30**(4):p.323-326.

12. Huang F.F., L.L. Hu and D.P. Chen, *Observation of 2.8 μm emission from diode-pumped Dy3+-doped fluoroaluminate glasses modified by TeO2.* Ceramics International, 2014.**40**(8):p.12869-12873.

13. Lai X., et al., *High power passively Q-switched Er3+-doped ZBLAN fiber laser at 2.8 μm based on a semiconductor saturable absorber mirror.* Laser Physics Letters, 2018.**15**(8):p.5.

14. Falconi M.C., et al., *Design of an Efficient Pulsed Dy3+: ZBLAN Fiber Laser Operating in Gain Switching Regime.* Journal of Lightwave Technology, 2018.**36**(23):p.5327-5333.

15. Yang L.Y., et al., *Towards a Supercontinuum Generation in an All-Fiberized Holmium-Doped ZBLAN Fiber Amplifier.* Journal of Lightwave Technology, 2018.**36**(16):p.3193-3197.

16. Majewski M.R. and S.D. Jackson. *Recent progress in 3 micron class dysprosium-doped fluoride fiber lasers*. in *Conference on Fiber Lasers XIV - Technology and Systems*. 2017. San Francisco, CA.

17. Aydin Y.O., et al., *Towards power scaling of 2.8 μm fiber lasers.* Optics Letters, 2018.**43**(18):p.4542-4545.

18. Allain J.Y., M. Monarie, and H. Poignant, *Erbium-doped fluorozirconate single-mode fibre lasing at 2.71 μm.* Electronics Letters, 1989.**25**(1):p.28-29.

19. Fortin V., et al., *30 W fluoride glass all-fiber laser at 2.94 μm.* Optics Letters, 2015.**40**(12):p.2882-2885.

20. Shigeki T., et al., *12W Q-switched Er:ZBLAN fiber laser at 2.8 μm.* Optics letters, 2011.**36**(15):p.2812-2814.

21. Xiushan Z. and J. Ravi, *10-W-level diode-pumped compact 2.78 μm ZBLAN fiber laser.* Optics letters, 2007.**32**(1):p.26-28.

22. Crawford S., D. D. Hudson, and S. D. Jackson. *3.4 W Ho3+, Pr3+ Co-Doped Fluoride Fibre Laser*. 2014 Conference on Lasers and Electro-Optics (CLEO)-Laser Science to Photonic Applications. IEEE.

23. Zhu G., et al., *Fe2+:ZnSe and graphene Q-switched singly Ho3+-doped ZBLAN fiber lasers at 3 μm.* Optical Materials Express, 2013.**3**(9):p.1365-1377.

24. Jianfeng L., H. Tomonori, and S. D. Jackson, *Dual wavelength Q-switched cascade laser*. Optics Letters, 2012.**37**(12):p.2208-10.

25. Li J., T. Hu, and S. D. Jackson, *Q-switched induced gain switching of a two-transition cascade laser.* Optics Express, 2012.**20**(12):p.13123-8.

26. Jianfeng L., D. D. Hudson, and S. D. Jackson, *High-power diode-pumped fiber laser operating at 3 μm.* Optics Letters, 2011.**36**(18):p.3642-4.

27. Maes F., et al., *5.6 W monolithic fiber laser at 3.55 μm.* Optics Letters, 2017.**42**(11):p.2054-2057.

28. Luo H. Y., et al., *Watt-level gain-switched fiber laser at 3.46 μm.* Optics Express, 2019.**27**(2):p.1367-1375.

29. Schneider J., C. Carbonnier and U.B. Unrau, *Characterization of a Ho3+-doped fluoride fiber laser with a 3.9-μm emission wavelength.* Applied Optics, 1997.**36**(33):p.8595.

30. Maes F., et al., *Room-temperature fiber laser at 3.92  μm.* Optica, 2018.**5**(7):p.761-764.

31. Zhang P., et al., *Intense 2.8 μm emission of Ho3+ doped PbF2 single crystal.* Optics Letters, 2014.**39**(13):p.3942-5.

32. Huang F. F., et al., *Ho3+/Er3+ co-doped fluoride glass sensitized by Tm3+ pumped by a 1550 nm laser diode for efficient 2.0 μm laser applications.* Optics Letters, 2015.**40**(18):p.4297-4300.

33. Gomes L., et al., *The basic spectroscopic parameters of Ho3+ -doped fluoroindate glass for emission at 3.9 μm.* Optical Materials, 2016.**60**:p.618-626.