Oxyfluoroborate 유리재료에서의 적외선-청색 상방 형광발생

Infrared-to-blue Upconversion in Tm-doped Oxyfluoroborate Glasses

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In recent years, there has been an increasing interest in Tm^{3+} doped crystals and glasses due to their potential applications as near infrared lasers and infrared to visible upconversion lasers for use in different fields such as medical surgery, eye safe laser radar, data storage, barcode reading and so on. Thulium ions have stable excited levels suitable for emitting blue upconversion fluorescence. Thulium doped fluoride and fluorophosphate glasses are widely investigated for upconversion with excitation at around 650 nm. As per our knowledge so far no upconversion studies have been reported in either oxide or oxyfluoride glasses. We observed strong blue upconversion emission at 452 nm in thulium doped oxyfluoroborate glass ($59H_3BO_3$ +20ZnO +20LiF +1Tm_2O_3) when excited in the range 750-800 nm using tunable cw Ti:Sapphire laser at room temperature.

The glass samples were prepared by melt quenching technique by melting the powders of batch composition in a platinum crucible at 950 ℃ for 30 min. in an electric furnace. The melt was then rapidly quenched on brass plates. The glass samples so obtained were polished before measuring their optical properties.

Figure 1(a) shows the upconversion spectra recorded in the 300-600 nm region under 788 nm excitation. The spectra consists of three bands at 365, 452 and 474 nm corresponding to $^1D_2$-$^3H_6$, $^1D_2$-$^3F_4$ and $^1G_4$-$^3H_6$ transitions respectively of which the band at 452 nm is the strongest. The spectra is similar to the upconversion spectra observed for flourophosphate glass with 657 nm excitation[1]. The wavelength dependence of upconversion efficiency varies with the ground state absorption profile. This means that incident light is absorbed only in transitions from the ground state and the energy transfer occurs between adjacent excited ions. The upconversion efficiency of the 452 nm emission has cubic dependence on power, indicating a three photon process. The present upconversion emission was observed at intensities higher than 1.6×10^4 W/cm^2. When the $^1D_2$ level is directly excited with 359 nm, the emission spectra consists of only one band at 452 nm. This indicates that nonradiative decay due to multiphonon relaxation to the next lower level $^1G_4$ is negligible as the energy gap (~6300 cm^{-1}) is large. FTIR measurements shows that maximum phonon energy of the present glass is 1072 cm^{-1} which is comparable to the phonon energy (1060 cm^{-1}) of fluorophosphate glasses.

Figure 1(b) shows the energy level diagram and excited state dynamics of upconversion. The first photon pumps an electron to the $^3H_6$ level. Then radiative and nonradiative transitions from the $^3H_6$ populates the $^3F_4$ level, where the second photon pumps the atoms to the $^1G_4$ level. The third photon then excites the atoms from the $^1G_4$ to $^1I_6$ levels. The radiative decay from the $^1I_6$ to $^1D_2$ levels is evident from the $^1D_2$-$^3F_4$ transition observed in Tm:YAG[(2)] when the $^1I_6$ level is directly excited at 290 nm. We propose two cross relaxation mechanisms also which can populate the $^1D_2$ level namely processes A and B. The emission peaks at 452 nm and 365 nm in the upconversion spectrum are due to the $^1D_2$-$^3F_4$ and $^1D_2$-$^3H_6$ transitions. Though the second and third stage pumping processes appears to be not in resonant with the energy gaps between the respective levels, this may be possible due to broadening of the energy levels in glasses.

In conclusion, the observed strong blue upconversion at 452 nm in oxyfluoroborate glass was found to be three photon processes. The phonon energy of the host is comparable to fluorophosphate glasses. Hence zinc-based oxyfluoroborate glasses can be also considered as hosts for 452 nm blue upconversion lasers.

References

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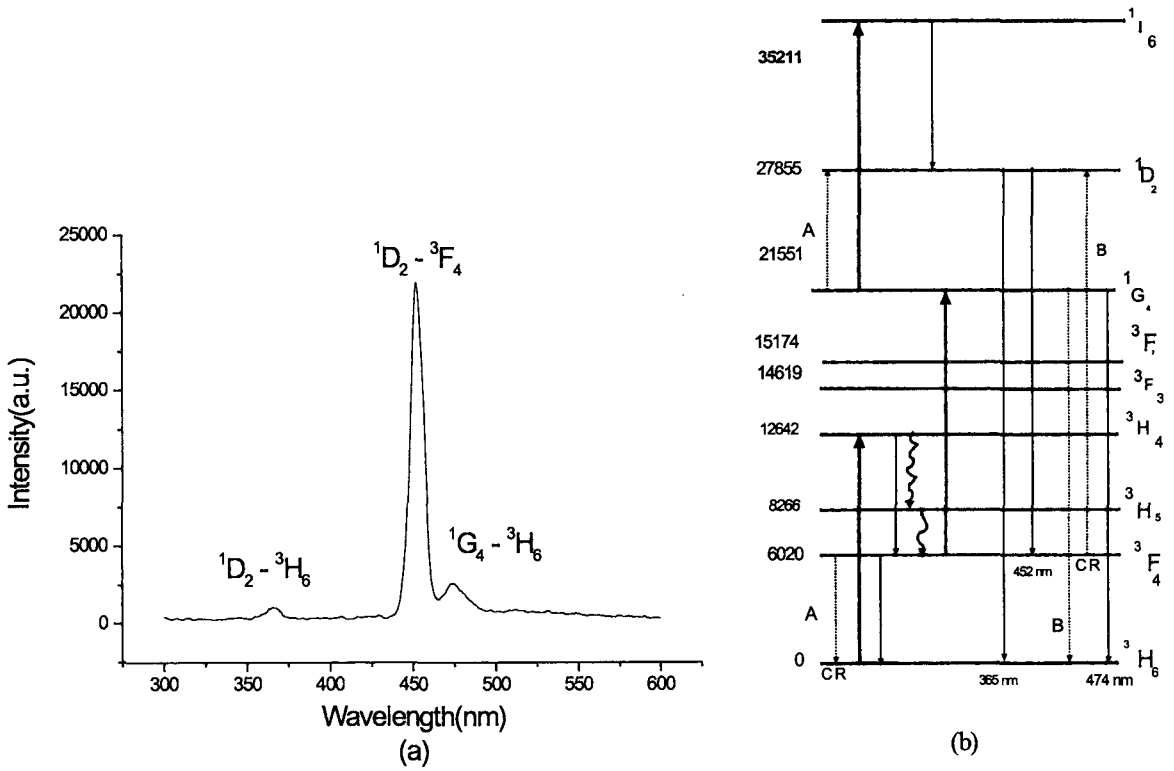

Fig.1 (a) Upconversion spectrum of oxy fluoroborate glass at 788nm excitation. (b) Partial energy level diagram of Tm^{3+} showing upconversion process. A and B represent cross-relaxations(CR).