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Femtosecond laser excited up-conversion luminescence from tungsten (molybdenum) ions doped silicate glasses

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Blue emission at 468 nm has been observed in tungsten ions doped Na_2O-CaO-SiO_2 glasses excited by 800nm femtosecond laser. The similar emission at 500nm was also observed in molybdenum ions doped silicate glasses. The intensity of emission depends on the power of femtosecond laser, which indicates that the upconversion emission is a two-photon-excited process. This emission is mainly due to the charge transfer between the *2p* orbital of O^{2-} ions and the nd^0 energy level of W^{6+} (Mo^{6+}) ions in WO_4^{2-} (MoO_4^{2-}) tetrahedron.

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1. Introduction

Up to the present, numerous lanthanide-based or transition metal ion-doped luminescent materials have been widely studied due to their applications in display, laser, storage, etc [1-4]. Tungsten ion, as one of the most famous transition metal activator, has been studied intensively in crystals, such as $CaWO_4$, $ZnWO_4$ and so on [5,6]. However, the research on luminescence from tungsten activated glasses is rare. Recently, Meng et al. studied the emissions from Ti^{4+} and Ta^{5+} doped silicate glasses excited by UV light and 800nm femtosecond laser [7,8]. The luminescent mechanism was discussed in the papers. Zeng et al. also reported the bluish green emission from Nb^{5+} doped glasses with the irradiation by 800nm femtosecond laser, and they ascribed this visible luminescence to the charge transfer from O^{2-} to Nb^{5+} ions [9]. In this paper, we study the visible upconversion emission of tungsten (molybdenum) ions doped Na_2O-CaO-SiO_2 glasses excited by 800 nm femtosecond laser. And the luminescent mechanism is also discussed in this work.

2. Experimental

Tungsten (molybdenum) ions doped silicate glasses was prepared by using high purity grade Na_2CO_3, $CaCO_3$, SiO_2, WO_3 and MoO_3 as the raw materials. The compositions (in mol %) of samples are designed as $20Na_2O$-$15CaO$-$65SiO_2$(NCS), $20Na_2O$-$15CaO$-$65SiO_2$-$0.5W_2O_5$(NCSW) and $20Na_2O$-$15CaO$-$65SiO_2$-$0.5Mo_2O_5$(NCSMo), respectively. 30 g batches were melted in a platinum crucible at temperature 1600 ºC for 2 hours. Subsequently, the melt was cast onto a graphite plate. The glasses were then cut and polished into 10×10×2 mm^3 plates for optical measurements.

A regeneratively amplified Ti:sapphire laser with 800 nm wavelength, 120 fs pulse duration, and 1 kHz repetition was used as the light source in our study. The laser beam was focused into the glass sample by an optical lens with focal length of 100 mm. The laser pulse energy could be adjusted by a neutral-density filter and be monitored by an energy meter. Upconversion luminescence spectra were recorded using Zolix SBP300 spectrofluorometer. Fluorescence emission spectra were recorded on a JASCO FP-6500 fluorescence spectrofluorometer by using a Xe lamp as the excitation source. The optical absorption spectra of the glasses were measured by JASCO V-570 spectrophotometer. All the measurements were performed at room temperature.

3. Results and discussion

Due to the excellent glass-forming ability, permanent stability and higher solubility for noble elements, Na_2O-CaO-SiO_2 silicate system is chosen as the host for metal ions doping. Fig. 1 shows the UV-Vis absorption spectra of blank NCS and NCSW glasses. Compared with NCS glass, the absorption edge of NCSW glass shifts slightly to low wavelength region, and the energy gap of NCSW is about 3.9 eV (320nm). This slight shift of

absorption edge due to the addition of WO_3 may be ascribed to the charge transfer from O^{2-} to W^{6+} ions.

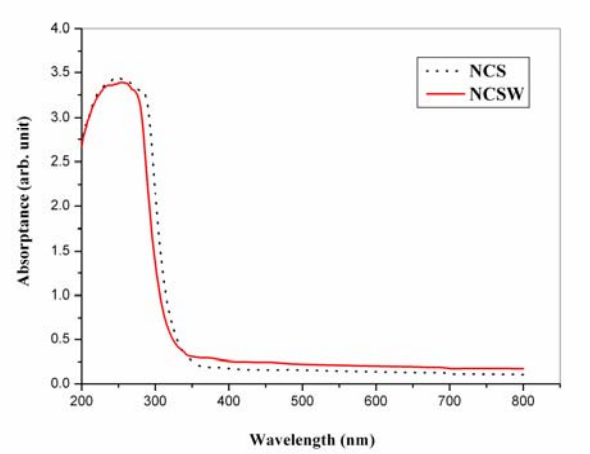

Fig. 1 Absorption spectra of $20Na_2O$-$15CaO$-$65SiO_2$-$0.5W_2O_5$ glasses.

The excitation and emission spectra of NCSW glass are illustrated in Fig. 2. A narrow excitation peak centered at 256nm is observed in the excitation spectrum. Under the excitation at 256nm, the NCSW glass yields a blue emission band centered at 468nm with full width at half maximum (FWHM) of about 125nm. The Stokes shift is as large as 2.20eV (17700cm^{-1}), and no overlap is observed in the excitation and emission spectra of NCSW glass. The digital photo of the NCSW glass under the excitation of 256nm monochromatic light from a xenon lamp is also displayed in the insert of Fig. 2, which exhibits the intense blue emission. When the NCSW glass is irradiated by 800nm femtosecond laser, a blue upconversion emission is observed obviously by naked eyes. The emission band centered at about 468 nm with the FWHM of about 150nm is shown in Fig. 2. The broadening of FWHM comparing with that of 256nm excitation may be due to the supercontinuum phenomenon of femtosecond laser when it irradiates on the transparent materials [11]. When the transparent material is irradiated by femtosecond laser, a supercontinuum phenomenon will occur, which shows spectral broadening of the incident femtosecond laser. Efimov et al. have reported that the spectral broadening of silicate glasses irradiated by 850nm femtosecond laser can spread from the IR to 220 nm [10]. As the laser intensity increases, the UV component of the supercontinuum increases. The tungsten activated luminant can show luminance band at different energy with the variety of excitation light energy, which will result in the broadening of FWHM with the excitation of 800nm femtosecond laser. Comparing the emission spectra under the excitation of 800nm and 256nm, their emission spectral profiles are almost the same except for the slight broadening, which indicates that the emissions in both excitation cases may come from an identical origin.

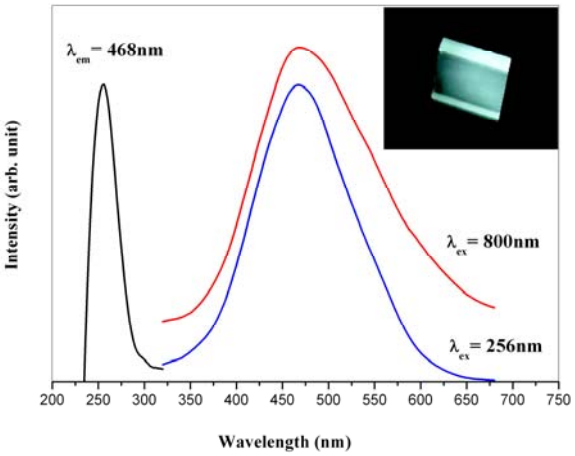

Fig. 2 Normalized excitation (λ_{em}=468nm) and emission spectra of $20Na_2O$-$15CaO$-$65SiO_2$-$0.5W_2O_5$ glasses under the excitation of 256 nm monochromatic light and 800nm femosecond laser, respectively.

Upconversion emission is usually associated with a multiphoton excitation process. And the multiphoton excitation process is determined by the following relation: $I \propto P^n$, where I is the integrated intensity of emission, P is pump power of the excitation laser, and n is the corresponding number of photons involved in the multiphoton absorption process. Fig. 3 displays the log-log relationship between the emission intensity and the pump power of the femtosecond laser for NCSW glass. The slope takes an initial value of 1.85, and decreases gradually with the enhancement of the pump power, which may be due to the breakdown of glass network or emergence of color centers induced by ultrashort pulsed laser with high power density. The results indicate that the visible upconversion emission under 800 nm femtosecond laser irradiation is a two-photon-excitation process.

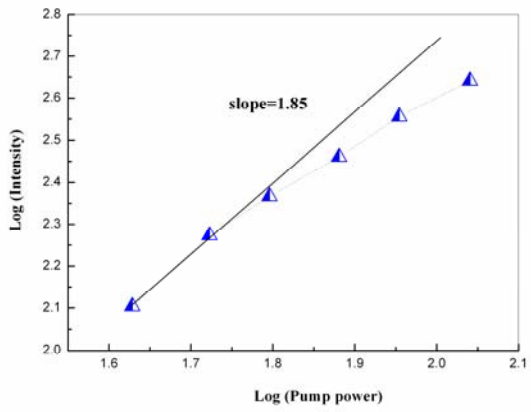

Fig. 3 Log-log relationship between the emission intensity and the pump power of the femtosecond laser for $20Na_2O$-$15CaO$-$65SiO_2$-$0.5W_2O_5$ glasses.

Although the emissions of W contained crystals and glasses have been studied by many researchers, the study on emission mechanism is rare. Usually, tungsten ions are existent as the term of tungstate tetrahedron (WO_4^{2-}) [2, 5]. $CaWO_4$ crystal, as one of efficient luminants, has been studied intensively [2,5,6]. A blue intrinsic luminescence of $CaWO_4$ crystal has been reported by many groups, which shifts to the lower energy region with the excitation of lower energy photons. When $CaWO_4$ crystal is excited at about 260nm, the emission spectral profile is almost the same as that in our study [5], which testifies that tungsten ions in NCSW glass are present as WO_4^{2-}. Michael et al have formulated a model for tungstate luminescent center based on the WO_4^{2-} ion in a crystal field of S_4 symmetry [12]. They recognized that the absorption transitions were ascribed to the charge transfer transitions from an oxygen *2p* electron into one of the empty tungsten *5d* orbitals. The electronic states responsible for the emission transition should be designated to the T_d symmetry group of the WO_4^{2-} ion. In the T_d symmetry of the WO_4^{2-} ion, four levels ($^1T_1$, $^1T_2$, $^3T_1$ and $^3T_2$) were existent. And the only allowed electric dipole transition was between the $^1A_1$ ground state and the $^1T_2$ excited state. Rack et al also founded the metal-to-ligand transition mechanism to interpret the blue luminescence from $Ta_2Zn_3O_8$ [13]. They ascribed the blue luminescence into Ta $5d^0$-O $2p^6$ transition in Ta-O_6 octahedral symmetry. The metal-to-ligand transition mechanism was also extended to explain the luminescence from MoO_6, WO_6 and TiO_6 octahedron. Meng et al studied the visible luminescence of Ti^{4+} and Ta^{5+} doped silicate glasses with the excitation of UV light or fetmosecond laser, and they also ascribed the luminescence to the charge transfer from O^{2-} to Ti^{4+} (Ta^{5+})ions [7, 8].

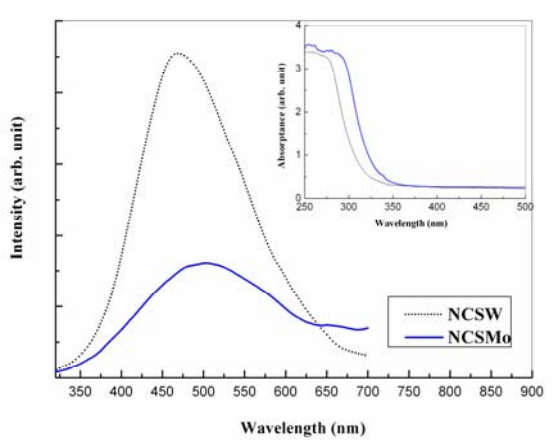

Fig. 4 Emission spectra of $20Na_2O$-$15CaO$-$65SiO_2$-$0.5M_2O_5$(M=W, Mo) glasses under the excitation of 800nm femosecond laser. The insert shows the absorption spectra of $20Na_2O$-$15CaO$-$65SiO_2$-$0.5M_2O_5$(M=W, Mo) glasses.

Combining results of the absorption, luminescence and luminescence mechanism discussed above, we attempt to ascribe the upconversion emission to the charge transfer between O^{2-} and W^{6+} ions. In NCSW glass, tungsten ions are mainly present as WO_4^{2-} tetrahedron. The electronic configuration of W^{6+} is [Xe]$5d^0$, and the *d*-*d* transition is forbidden in NCSW glass. The blue emission at 468nm from NCSW glass must be due to the charge transfer between O^{2-} and W^{6+} ions in WO_4^{2-} tetrahedron. An electron in the *2p* orbital (non-bonding) of oxide ions is excited into the W^{6+} $5d^0$ energy level by absorbing high energy 256 nm photons or two 800nm photons. The excited electron thermally relaxes to the lowest vibrational state of W^{6+} $5d^0$ energy level, and then relaxes to the *2p* orbital of oxide ions with the blue emission of 468 nm photon.

The luminescence of NCSMo glass under 800nm femtosecond laser irradiation is also studied in Fig.4. Comparing with the luminescence of NCSW glass, the emission peak shifts to 500 nm and the emission intensity is only about 30% of that from NCSW glass. Mo^{6+} ions are usually present as MoO_4^{2-} tetrahedron, and the luminescence mechanism of NCSMo glass may be similar to that of NCSW glass due to the same configuration of luminescent centers. In comparison with the absorption see the insert in Fig.4) and emission of NCSW glass, an obvious red shift has been observed. This red shift of NCSMo glass will result in the lower quenching temperature (T_q) comparing with that of NCSW glass [2]. Therefore, the luminescence intensity of NCSMo glass at room temperature will be lower than that of NCSW glass, and NCSW glass shows more efficient luminescence at room temperature.

4. Conclusions

In summary, visible emissions have been observed in tungsten and molybdenum doped Na_2O-CaO-SiO_2 glasses excited by 800nm femtosecond laser. Log-log relationship indicates that these emissions are two-photon-excited process. It is deduced that the nd^0 energy level of W^{6+} (Mo^{6+}) ions plays an important role in these upconversion emissions, and the visible emissions are mainly due to the charge transfer from the *2p* orbital of O^{2-} ions to the nd^0 energy level of W^{6+} (Mo^{6+}) ions in WO_4^{2-} (MoO_4^{2-}) tetrahedron. These tungsten and molybdenum doped silicate glasses with excellent stability and intense visible emissions are expected to be applied in the fields of three-dimensional displays, high density optical storage, etc.

Acknowledgements

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