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Intense blue emission from tantalum-doped silicate glass

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The authors report on an intense blue emission centered at 420 nm under ultraviolet excitation from pentavalent tantalum ion-doped silicate glasses. The blue emission is distinctly different from emission due to defects in silica glass, which is also reflected in both absorption spectrum and remarkably enhanced emission. The authors suggest that localized Ta $5d^0$ energy level is responsible for the blue emission. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2335394]

Continuous efforts have been made to achieve effective blue emission, with an aim of realizing high power all solid-state blue lasers and full-color displays.[1] Semiconductor materials (e.g., GaNs and ZnO) have demonstrated their applications in an extended region due to particular advantages, such as wide direct band gap, commercial availability with large area, and high quality single crystals. Compared with bulk crystalline hosts, glass materials possess specific advantages, e.g., easy fabrication, low cost, high mechanical strength, and high chemical durability. Therefore, glasses play an indispensable role in a field of luminescent materials working in a wide range of wavelength, including ultraviolet, visible, and infrared regions. Usually, the emission in glass hosts is realized by incorporating rare earth (RE) ions or transition metal (TM) ions. The precondition is that REs and TMs possess electrons that incompletely fill *d* or *f* orbitals to induce electronic transitions, e.g., *f-f/d* transitions for REs and *d-d* transitions for TMs.

Among the group V elements in the Periodic Table, much attention has been paid to vanadium ions because of their promising applications in telecommunication systems.[2–4] Niobium complex NbO_4^{3-} has also been investigated as a possible blue phosphor.[5] In contrast, tantalum ions, usually existing as Ta^{5+}, have not received much attention, because its completely occupied outermost electronic shell is usually regarded as a disability in electronic transition. However, it is not always the case. Here we report on an intense blue emission from pentavalent tantalum ion-doped silicate glass. It is suggested that the localized Ta $5d^0$ energy level should be responsible for the blue emission.

The glass was prepared by using the conventional melt-quenching method from reagent SiO_2, $CaCO_3$, Na_2CO_3, and Ta_2O_5 as starting materials. $10CaO-20Na_2O-70SiO_2$ composition (in mol %) was chosen as a glass matrix and 1 mol % Ta_2O_5 was added by replacing SiO_2. In order to reduce the effect of hydroxyl ions on the luminescence, the initial powders were firstly calcined at 500 °C for 10 h in an electronic furnace and then ball milled in an agate container for 10 h. The final homogenous mixture was melted at 1550 °C for 1–4 h in a platinum crucible. The glass melt was poured onto a stainless steel plate and then pressed with another plate to obtain clear glass. The as-manufactured glass samples, which were colorless and bubble-free, were cut into a size of $5\times5\times1$ mm^3 and polished for optical measurements. For comparison of emission intensity, cerium-doped zinc borosilicate glass with a composition of $19SiO_2-20B_2O_3-60ZnO-1CeO_2$ (in mol %) was also prepared through the above procedures. Optical absorption spectrum was measured with a Jasco-V570 UV-vis-NIR spectrophotometer. Measurements of excitation and emission spectra were performed with a Hitachi 850 fluorescence spectrophotometer. Electron spin resonance (ESR) measurements were carried out by using a JES-TE100 ESR spectrometer operating at *X*-band microwave frequency to detect paramagnetic defects and impurities in the glasses.

Figure 1 shows the room temperature absorption spectra of $10CaO-20Na_2O-70SiO_2$ (SSC) and $10CaO-20Na_2O-69SiO_2-1Ta_2O_5$ (SSCT). Compared with SSC, SSCT obviously possesses a broader and flat absorption band. The UV absorption of SSC is located at 205 nm, while that of SSCT extends to 236 nm. It should be also noticed that the maximum absorption coefficient of SSC is about 27 cm^{-1}, while that of SSCT increases to 32 cm^{-1}. The charge transfer between O^{2-} and Ta^{5+} may be responsible for the absorption band of SSCT.

Figure 2 presents the excitation and emission spectra of SSC (a) and SSCT (b). The excitation spectrum of SSCT is characterized as a narrow band with full width at half maximum (FWHM) of 37 nm, while the emission a broad one with FWHM of 115 nm. A very weak emission band at 400 nm occurs for SSC when excited with 210 nm light, which may be imposed to impurity in raw materials (e.g., Fe^{3+}).[6] Relative to the maximum of the emission observed for SSC, the emission intensity of SSCT is ~100 times

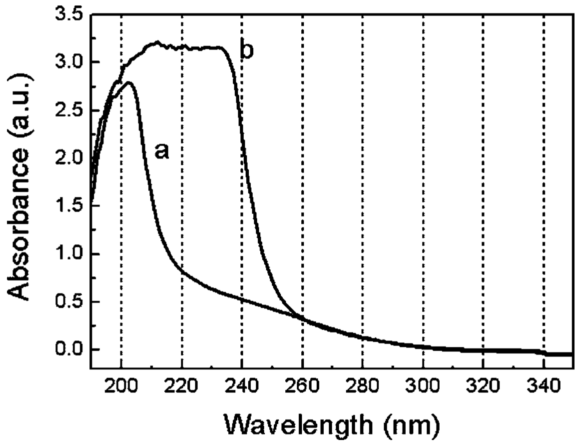

FIG. 1. Optical absorption spectra of SSC (a) and SSCT (b).

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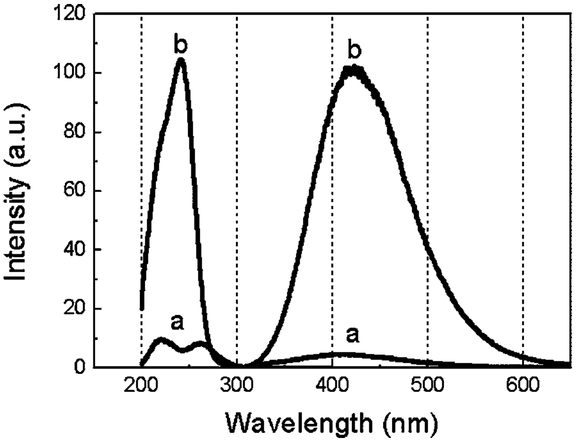

FIG. 2. Excitation (left) and emission (right) spectra of SSC (a) (monitored at 400 nm and excited at 210 nm), respectively and SSCT (b) (monitored at 420 nm and excited at 245 nm), respectively.

larger when excited at 254 nm, which is the working wavelength of commercial mercury UV lamps. When the samples were exposed to 254 nm UV lamp irradiation, the emission from SSC became invisible while tantalum ion-doped glass showed blue intense emission. The emission intensity for SSCT is approximately ten times higher than that for cerium-doped zinc borosilicate glass, the latter exhibiting strong blue emission under UV excitation.[7]

One possible origin of the blue emission from SSCT is defects induced by incorporation of tantalum ion. It is well known that there are various defects in silica glass, e.g., nonbridging oxygen hole center ($\equiv$Si–O$\uparrow$, $\uparrow$ means one unpaired electron.),[8] peroxy radicals ($\equiv$Si–O–O$\uparrow$),[9] E' ($\equiv$Si$\uparrow$),[10] and B_2 ($\equiv$Si–Si$\equiv$).[11] The ESR spectra of SSC and SSCT are shown in Fig. 3, in which three weak signals appear. The $g_1=4.2636$ signal should be ascribed to Fe^{3+} impurity[12] responsible for the 400 nm emission in SSC, while the other two may be associated with paramagnetic defects in silicate glasses[13–15] or impurities (e.g., Cu^{2+}, Fe^{3+}) (Ref. 16) in raw materials because similar signals are also observed in sodium carbonate used as the raw material in the present work. These paramagnetic defects present in silica glass have not been reported to emit photons at blue wavelength region, while the B_2 defect, a kind of diamagnetic one, can yield emission at 3.16 eV (392 nm) under UV irradiation. In that case, a strong emission band at 4.42 eV (280 nm) as well as a very weak emission at 2.74 eV (452 nm) is usually accompanied.[11] However, such emission bands were not observed for the present SSCT glass. In addition, the B_2 defect, reflected in the absorption spectrum, possesses an absorption band at 5.0 eV with absorption coefficient less than 1 cm^{-1}.[11] As described above, incorporation of tantalum ions resulted in a broader absorption band with absorption coefficient as large as 32 cm^{-1}, which indicates that the possible B_2 defect should have a negligible effect on the emission of SSCT.

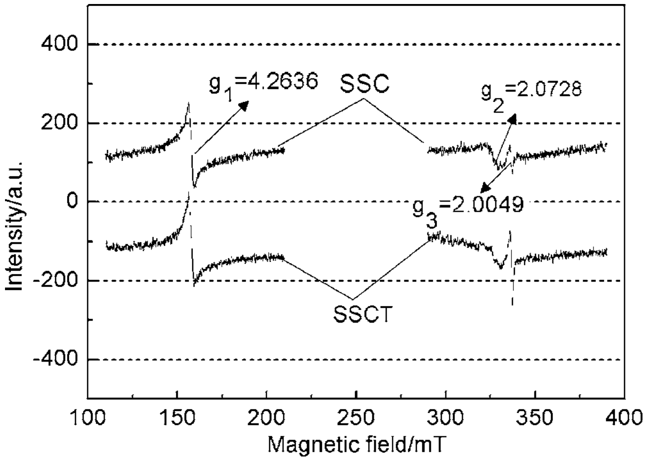

FIG. 3. Electron spin resonance spectra of SSC and SSCT.

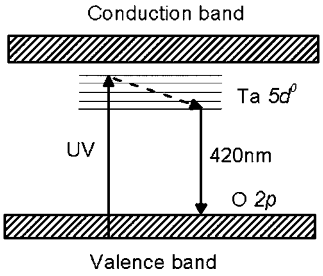

FIG. 4. Possible mechanism for emission from Ta^{5+} in SSCT.

Based on the above analyses, we intend to ascribe the remarkably enhanced blue emission to electronic transitions related to tantalum ions. Usually, the tantalum ions are present as a pentavalent state with the corresponding electronic configurations as $5d^0$. Therefore, the d-d transition does not take place. The 420 nm blue emission from tantalum ions is rarely known up to now. It was reported that $Ta_2Zn_3O_8$ thin film emitted photons at 385 nm when excited by 236 nm UV light and 420 nm blue emission could be observed by filtering.[17] In that case, the excitation spectrum was also characterized as a narrow band, while the emission spectrum exhibited a broad one. The spectral properties are similar to those of the present work. A metal-to-ligand radiative transition mechanism was proposed to interpret this unusual emission.[17] The excited state is the $5d^0$ state of the tantalum ions whereas the ground state is the $2p^6$ state associated with the oxide ions. Octahedrally coordinated $(TaO_6)^{7-}$ and other octahedrally coordinated transition metal ions (e.g., MoO_6, WO_6, and TiO_6) (Ref. 18) are known as rather efficiently luminescent centers via this metal-to-ligand transition. Furthermore, it is known that the NbO_4^{3-} complex is a kind of self-luminescent center, in which blue emission can be ascribed to the transition between Nb $4d$ and O $2p$ orbitals.[5] Given the similarities in spectral properties between $Ta_2Zn_3O_8$ and SSCT, we propose the following mechanism, as shown in Fig. 4. An electron in O $2p$ orbital is excited to Ta $5d^0$ by UV photon and then thermally relaxed to the lowest vibrational state of Ta $5d^0$ energy level. Finally, the excited electron relaxes to the valence band accompanied by emission of a blue wavelength photon.

In summary, we have realized an intense blue emission from tantalum ion-doped silicate glass. The localized energy level of tantalum ion is proposed to be responsible for the emission. The tantalum-doped glasses possess some specific advantages. Firstly, the glass investigated herein, a traditional soda lime silicate glass with excellent thermal stability, mechanical properties, and chemical durability, has been extensively utilized for commercial purposes in many fields. Secondly, valence control, which is necessary for other blue emitting activators, such as Eu^{2+}, Sn^{2+}, or Cu^{+}, is not required for tantalum-doped blue emitting glasses. In particular, it is of interest that the blue emission can also be realized by incorporating tantalum ions into nonsilicate glass hosts,[19] which indicates that tantalum ions will open up a new frontier in luminescent materials as a novel activator. Although complete understanding of the mechanism requires further investigation, the easy fabrication method and high emission intensity, together with the above-mentioned advantages for SSCT provide a promising material in display and blue laser fields.

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