Structure Controlled Luminescence Properties in Cu and/or Sn Doped Borate Glasses

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ABSTRACT

The emission spectra of Cu and/or Sn doped sodium borate glasses were investigated for controlled glass structure. The results demonstrate that emission of metal ions was enhanced with increasing of B_2O_3 content. The broad emission band centered at 450 nm and 400 nm reflecting the reduction ability of the borate glass structure is attributed to the low valence state of metal ions Cu^+, Sn^{2+} respectively. The reduction ability of the glass structure was identified by the increasing Sn^{2+} proportion through XPS measurements. Moreover, the Cu–Sn co-doped sample exhibits remarkably enhanced Cu^+ ions emission which reveals the Sn^{2+} strong reduction effect on the Cu^{2+} ions. The effect of the structure variation on the mechanism of metal ions luminescence in borate glasses has been discussed.

KEYWORDS: Borate Glasses, Metal Ions, Luminescence, Structure Reduction.

1. INTRODUCTION

In the past decades investigations on novel optical glasses have been extensively reported due to their applications, in solid state lasers, fiber amplifiers, color displays, and solar cells.[1–6] Such applications rely on the luminescence properties of dopants, which, in most cases, are rare earth (RE) ions. In case of glass materials, due to the unique electron transition within 4f orbits, the narrow, pure emission of the RE ions usually reflect the excellent luminescence properties such as fluorescent stability and high quantum efficiency.[7,8] However, the higher prices of RE raw materials used for long lifetime luminescent materials restricts their application.[9] Other frequently reported dopants in glasses include ns^2 type emission centers ($n \geq 4$), like Sn^{2+}, Sb^{3+}, Pb^{2+}, Bi^{3+} and transition metal ions such as Mn, Ag and Cu ions. Both present broad excitation in UV bands and emit strong fluorescence in the visible (VIS) range.[10–15] Although the total quantum efficiency of the metal ions is relatively high comparing with RE ions, the emission is easily to be affected by the material compositions and chemical environments due to the outermost electron transition.[16,17] However, a concrete understanding involving the structure configuration and its relation with the formation of PL-emitter center is still missing. Given that the glass structure may be controlled around the metal ions, their luminescence is expected to be under control. So it is necessary to have a further research on understanding the influences of the local field on the metal ions emission centers.

In this work, Cu and/or Sn ions emission has been investigated by the variation of the microstructure in borate glasses according to a conventional melt-quenching method. As a favorable host, borate glass is employed here because of many good physical and chemical properties such as low melting point and simple preparation work. Even more notably, a controllable structure of $[BO_4]$ and $[BO_3]$ units in borate glasses was realized in our previous work,[18,19] which is beneficial for investigation of the interaction mechanism between the structural changes and metal ions emission, expecting to clarity of the origin of Cu and/or Sn metal luminescence.

2. EXPERIMENTAL DETAILS

2.1. Materials and Synthesis

1 mol% SnO_2 and/or 0.5 mol% CuO doped xB_2O_3-(92-x)Na_2O-8Al_2O_3 ($x = 60, 65, 70, 75, 80, 85$ mol%) glasses were prepared by a conventional melt-quenching method. The 60B1Sn and 60B0.5Cu used in this work represent the 60 mol% B_2O_3, 1 mol% SnO_2, 0.5 mol% CuO and so on. These glasses were prepared from high purity compounds (B_2O_3, Al_2O_3, Na_2CO_3, CuO and SnO_2, 99.99%). The initial batches were mixed well, and then melted in alumina crucibles at 1300 °C for about 40 min. The melts were poured on a stainless steel plate and cooled down to room

temperature. The prepared glass samples were annealed near their glass transition temperatures for 2 h. All the samples were cut and polished to good optical quality for the measurements.

2.2. Characterization

The photoluminescence spectra for glass samples were recorded on a HITACHIF-7000 fluorescence spectrophotometer using a static 150W Xe lamp as the excitation source. Optical absorption spectra were collected in the wavelength range of 200–2000 nm on a HITACHIU-4100 spectrophotometer. XPS studies were performed in a Phi 5000 Versa Probe II ESCA (electron spectroscopy for chemical analysis) System (Physical Electronics) with a monochromatic Al Kα X-ray source (1486.6 eV) operating at 15 kV, 25 W.

3. RESULTS AND DISCUSSION

Alkali borate glasses are classical glass systems which can exhibit rich structural chemistry owing to the coexistence group of $[BO_3]$ triangle and $[BO_4]$ tetrahedron in the matrix. They have been studied extensively over years to elucidate their structure, including the nature and relative population of the borate units building the glass network.[20] As reported in our previous work, the transition of $[BO_4]$ tetrahedron units to $[BO_3]$ triangle units was detected by changing the glass composition. The structure change leads to doped Eu^{3+} ions being reduced to Eu^{2+} ions, demonstrating the oxidation and reduction processes.[19] In this work, the Cu and/or Sn were doped in borate glasses expecting to clarity of the glass structure effect on their emission properties.

Herein, firstly, the emission spectra of Sn-doped samples were investigated in Figure 1. As can be seen, the samples exhibit a broad emission band ranging from 300 to 600 nm with a maximum centered at about 400 nm. Moreover, the enhanced broad emission is clearly observed with increasing of B_2O_3 content in borate glasses. As mentioned in our previous work,[18] the borate glass structure changed from $[BO_4]$ units to isolated $[BO_3]$ units leading to the increasing reduction ability of the matrix environment along with increase of glass former B_2O_3. It is expected that the glass structure induces changes of the Sn metal valence state, and the blue emission of Sn center will be enhanced in an environment with strong reduction property. Sn^{2+} emission is mostly discussed in references to the coexistence of Sn^{4+} ions.[10, 21, 22] Among these, 400–430 nm broad emission band is consistently attributed to the divalent Sn ions,[10, 22–24] because the transition probability of the Sn^{2+} ions is much higher than that of the Sn^{4+} ions being a parity-allowed transition. Moreover, data demonstrates the effect of glass composition on the Sn valence state, namely that the decreased alkali concentration leads to a destabilization of Sn^{4+} by increasing their peak potential and that increased Al^{3+} brings the asymmetry to the
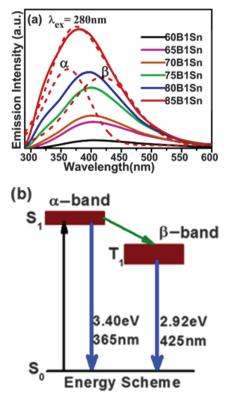

Fig. 1. (a) Emission spectra of Sn-doped samples dependence of B_2O_3 content under 280 nm light excitation, (b) Plausible energy Scheme for Sn^{2+} luminescence in borate glasses.

coordination of Sn^{2+}.[25] In the present work, however, the increased symmetry with B_2O_3 addition revealed the main structure reduction effect on the Sn emission properties. Therefore, the broad band luminescence in this work is probably due to the relaxation of twofold Sn^{2+}, which is reported to usually have two emission bands: α-band [singlet (S_1) -singlet (S_0), $\sim$4.1 eV] and β-band [triplet (T_1) -singlet (S_0), $\sim$3.1 eV].[26–28] The former is usually affected by the structure configuration while the latter is influenced by the amount of Sn^{2+} ions and easily quenched in the higher concentration condition.[24] In the Figure 1(a), using the 85 mol% B_2O_3 sample as example, the emission spectra is deconvoluted into two bands using Gaussian functions. The emission of α-band increased faster with the reduction environment induced by the structure controlled changes while the emission of β-band improved weakly when more Sn^{2+} ions were created. As it can be seen in the Figure 1(b), where possible energy levels for Sn^{2+} photoluminescence process in borate glasses are shown, the peak photon energies for S_1–S_0 excitation and T_1–S_0 relaxation are 3.40 eV and 2.92 eV, respectively. It is easily understood that the surrounding structure has changed the valence state of doped metal ions Sn the luminescence efficiency.

As mentioned above, the glass lattice may influence the chemical environment around Sn center leading to the variation of Sn valence state. To verify this, XPS

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measurements were performed in the Sn 3d region with 75 mol% B_2O_3 concentration. As shown in Figure 2, the Sn 3d energy level is composed of a doublet corresponding to Sn $^3d_{3/2}$ and Sn $^3d_{5/2}$, respectively. The double peak is believed to be associated with two valence states of both Sn^{2+} and Sn^{4+}, that are located at 487.06 and 495.47 eV for Sn^{2+} and at the 488.60 and 497.01 eV for Sn^{4+} ions. The peak separation i.e., the spin–orbit splitting between the two photoemission peaks (Sn $^3d_{3/2}$ and Sn $^3d_{5/2}$) is determined to be 8.41 eV, which is in agreement with the values in literature.[30] The inset shows the calculated the percentage of Sn^{2+} and Sn^{4+} in different B_2O_3 contained samples. It can be inferred that the content of Sn^{4+} ions gradually decreased while that of Sn^{2+} ions simultaneously increased, meaning that Sn^{4+} is reduced to Sn^{2+} ions with the addition of B_2O_3. It is therefore concluded that the reduction ability was induced by the structure effect, resulting in the change of metal ions valence state and, in turn, its luminescence properties.

To further understand the structure controlled metal ions emission, Cu doped borate glasses were used to identify the mechanism of interaction of metal ions with the glass structure. Figure 3(a) exhibits the luminescence properties of Cu-doped borate glasses with increasing of B_2O_3 contents. One can see that a strong blue emission band peaked at about 450 nm which is assigned to Cu^+ emission appears. Luminescence of Cu^+ comes from excited s state to ground d state ($d^9s \rightarrow d^{10}$) transition, which is strictly forbidden for free ions but partially allowed in solids by electronic coupling with lattice vibrations of odd parity.[29, 30] Cu^+ ions exhibit broad excitation in UV and wide emission in the 400–750 nm wavelength region, that are very sensitive to their environmental conditions, such as covalence, coordination number, and site symmetry.[31] Similarly, the emission intensity here presents on an increasing tendency, which demonstrated that the structure reduction produced the reaction process from Cu^{2+} ions to the Cu^+ emission. In general, divalent cupper ions dissolved in the glass matrix are responsible for the
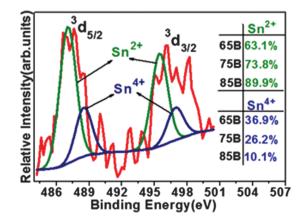

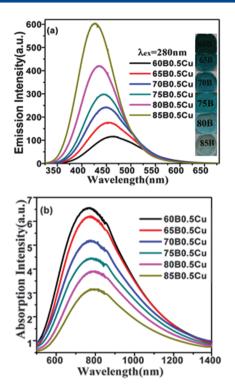**Fig. 2.** XPS spectra of Sn-doped borate glass with 75 mol% B_2O_3 concentration.

Fig. 3. Emission spectra of Cu-doped borate glasses dependence of B_2O_3 content with 280 nm excitation, (b) Absorption spectra of the Cu-doped samples with variation of B_2O_3 concentration.
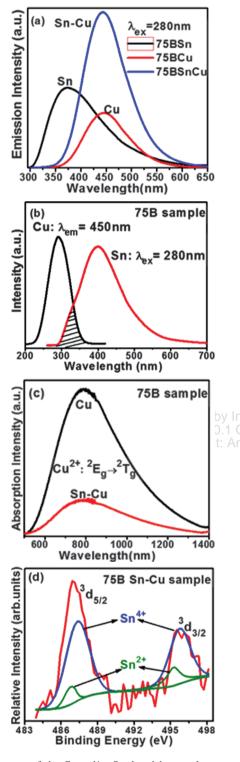
blue color of the material. This blue color gradually faded with the increase of B_2O_3 content as shown in Figure 1(a). The presence of the reduced Cu^{2+} ions can be confirmed in the absorption spectra in Figure 3(b). Previously reported work has ascribed the broad absorption band centered at around 790 nm to the electronic transition of $^2E_g \rightarrow ^2T_g$ of Cu^{2+} ions.[33-35] The lower absorption intensity in the figure proved that the reduction process of $Cu^{2+} \rightarrow Cu^+$, induced by the chemical environment around metal ions happened in the borate glass. In addition, the emission blue shifted further revealing the loosening tendency of the glass structure and the field effects around the Cu ions in the matrix.

According to the results above, the efficient blue emission of the reduced metal ions Sn^{2+} and Cu^+ was obtained by the structure adjustment in borate glasses, and the reduction capacity induced by the structure variation altered the valence state of metal ions and their fluoresce properties. Structure controlled metal ions photoluminescence can be also obtained in non-RE doped optical materials. In addition to the structure controlling, another way to improve metal ions luminescence is the classical energy transfer, which is further investigated in Cu–Sn co-doped borate glasses.

As depicted in Figure 4, emission, excitation, absorption and XPS spectra of Sn and/or Cu doped 75 mol% B_2O_3 glasses are compared. In Figure 4(a), Sn or Cu singly doped sample shows their characteristic emission respectively, while Cu–Sn co-doped samples only show

Fig. 4. Spectra of the Cu and/or Sn doped borate glasses containing 75 mol% B_2O_3. (a) Emission spectra under 280 nm light excitation (b) Sn emission and Cu excitation monitored at 450 nm (c) Absorption spectra (d) XPS spectra and the percentage of Sn valence state.

the broad emission of Cu^+ ions, peaked around 435 nm. Moreover, the luminescence of Cu–Sn co-doped sample is dramatically enhanced compared with Cu-doped sample. The energy transfer is first considered for the significant

enhancement of Cu^+ emission in co-doped sample. As demonstrated in Figure 4(b), partial overlapping between Sn emission and Cu excitation means the possibility of energy transfer from Sn^{2+} to Cu^+, such as the Cu^+ emission can be enhanced from the Sn^{2+}, while the amount of the Cu^{2+} and Cu^+ in the matrix remains constant before and after the Sn^{2+} is co-doped into the host. However, the decreased absorption intensity of Cu^{2+} ions in the co-doped sample is observed in comparison with Cu singly doped glass in Figure 4(c), meaning a lower probability of the energy transfer process from Sn^{2+} to Cu^+, which may be caused by some other potential factors. Many scholars payed their attention to Sn^{2+} ions as strong reducing agent to be the key factor for the reduction of the higher valence state of metals like Cu^{2+} to lower state Cu^+ and Cu^0, and even for their aggregation into Cu clusters and nanoparticles.[36] It is suggested that the majority of Sn^{2+} ions are consumed in the reduction of Cu^{2+} ions, thus Sn^{2+} luminescence is too weak to be observed and only the strong Cu^+ emission is observed due to the reaction of $Sn^{2+} + Cu^{2+} \rightarrow Sn^{4+} + Cu^+$ which occurs simultaneously. It can be seen in Figure 4(d), that the XPS spectra after Sn co-doped in glasses exhibits the relatively low percentage of Sn^{2+} and the higher proportion of Sn^{4+} ions, further showing the effect of Sn^{2+} reduction on Cu^{2+} and excluding the influence of a possible energy transfer. Consequently, it is believed that not only the structure reduction effect but also the Sn co-doping contributes to the enhanced Cu^+ emission. The blue emission efficiency was enhanced to a higher degree in the co-doped samples, indicating that the relative high fluorescence efficiency can be realized in metal ions doped optical materials by the structure adjustment.

For Cu–Sn coped glass samples, Figure 5 illustrates the emission and absorption spectra as a function of B_2O_3 concentration. Interestingly, it can be seen that co-doped samples only show the increased Cu^+ emission centered at about 450 nm while the Sn^{2+} emission cannot be observed. It revealed that strong reduction ability of Sn^{2+} promoted the process of forming large amount of Cu^+. As it can be inferred from the absorption spectra in Figure 5(b), the Cu, Sn co-doped borate glasses also exhibit the Cu^{2+} ions absorption presenting a remarkable decreasing trend that corresponds to the Cu^{2+} reduction process by Sn^{2+} ions.

In the network of the borate glasses, the $[BO_4]$ tetrahedron units are gradually replaced by $[BO_3]$ units leading to the change of local environment around the metal ions, inducing the reduction of Sn^{4+} to Sn^{2+} and Cu^{2+} to Cu^+. The reducing action of Sn^{2+} is further demonstrated by the reaction of Cu^{2+} in the co-doped glasses, obtaining a stronger blue light emission in RE-free actives glass materials. The mechanism of whether the structure induced Sn^{2+} formation and then Sn^{2+} ions lead to further enhancement of Cu^+ ions, or it was originated from other unknown factors should not be neglected. Therefore, further investigations and experiments are underway to clarity
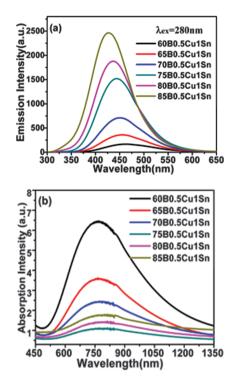
Fig. 5. (a) Emission spectra and (b) absorption spectra and of the Cu–Sn co-doped borate glasses with variation of B_2O_3 concentration.

the metal ions emission in glasses including the distribution, redox state, energy transfer process, and the correlation with coordination environment.

4. CONCLUSIONS

The UV-excited broad blue emission of Cu and/or Sn doped borate glasses is demonstrated at 400 and 435 nm respectively. This emission strongly depends on the chemical composition of the glass. With increasing B_2O_3 concentration, metal ions emission intensifies and it is considered that the variation of the glass structure induced the lower valence state emission of metal ions Cu and Sn. XPS measurements confirmed the local reduction environment created around metal ions in glasses. Moreover, most Sn^{2+} ions acted as reducing agent for the further reduction of Cu^{2+} ions, leading to the increase of the emission efficiency in metal ions activated materials. These results demonstrated that the metal ions luminescence can be controlled by the glass structure and contribute to efficient visible light emission in RE-free materials. According to the structural controlled broad emission bands, the authors emphasizes that Cu^+/Sn^{2+}-containing borate glasses will attract much attention from both scientific and industrial viewpoints.

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