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Colorless transparent fluorescence material: Sintered porous glass containing rare-earth and transition-metal ions

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Transparent fluorescence oxide glass with high emission yields has been prepared. Porous glass was impregnated with rare-earth and transition-metal ions and consequently sintered at 1100 °C into a compact nonporous glass. Reduction sintering is indispensable for obtaining fluorescence glass with high emission yield. Sintering of glass impregnated with Eu ions in a reducing atmosphere enhances the emission intensity by about 15 times than that sintered in air. The Eu\textsuperscript{2+} and Ce\textsuperscript{3+} ions and Sn\textsuperscript{2+} and Cu\textsuperscript{+} ions incorporated in SiO\textsubscript{2} glass obtained by reduction sintering exhibit intense fluorescence in the near-ultraviolet and visible ranges, their emission yields are 97%, 70%, 100%, and 90%, respectively. © 2005 American Institute of Physics. [DOI: 10.1063/1.1946897]

Oxide glass is an attractive host matrix for the emission ions of rare-earth and transition-metal ions because it has excellent optical and mechanical properties, is very stable in chemistry, and can easily be formed into any shape. However, a major obstacle to using such glasses as host matrices is concentration quenching resulting from interaction among emission activator ions in the glass. Despite the extensive research on glasses doped with rare-earth ions and the wealth of glass-forming systems that have been investigated, the number of commercially available glasses doped with rare-earth ions are quite limited; specifically only Nd\textsuperscript{3+} -doped alkaline earth ions are distribution quenching from a large number of residual OH\textsuperscript{−} groups present in the porous glass. Impurity traces (<10 ppm) of heavy-metal and transition-metal ions in sodium-silicate glass exhibit fluorescence phenomenon, implicating that the concentration quenching of these ions in oxide glass may be very low. Concentration quenching is associated with the relative proximities of activator ions in the glass. Rare-earth and transition-metal ions are of low solubility in oxide glass and easily lead to segregation or phase separation at very low concentrations. Study of 29Si magic angle spinning nuclear magnetic resonance spin-lattice relaxation has shown the presence of clusters of Nd ions even at ppm concentrations in silicate glass. Addition of Al\textsubscript{2}O\textsubscript{3} to oxide glass can partially inhibit phase separation and has a beneficial effect on concentration quenching. However, satisfactory methods to suppress concentration quenching through glass synthesis are still lacking and may be impossible.

To avoid concentration quenching, at present, we propose a physical method to uniformly distribute the rare-earth and transition-metal ions in oxide glass by means of the microscopic voids in porous glass. Porous glass is very useful for impregnation with different ions for the purpose of making various functional materials, such as nonlinear optical materials of quantum-confined semiconductor nanocrystals. The emission properties of some rare-earth and transition-metal ions adsorbed onto porous Vycor glass [porous glass which mainly consists of silica (96%)], has been investigated by a number of researchers, including Anpo et al., Reisfeld et al., and Hazenkamp and Blasse. They obtained valuable information on the emission properties of some activator ions adsorbed onto porous Vycor glass; however, their resulting materials do not seem to be strong fluorescent glasses. We notice that in all these papers that, though the activator ions are distributed uniformly in glass, the porous Vycor glass was not sintered to a dense glass. The reason for the low fluorescent intensity of the rare-earth ions adsorbed onto porous Vycor glass may be impurity quenching from a large number of residual OH\textsuperscript{−} groups present in the porous glass. In addition, the microscopic pores of porous glass strongly scatter the UV light of excitation and also decrease the emission intensity. Sintering at a high temperature can eliminate the pores and most of the residual OH\textsuperscript{−} groups. The sintering process then, particularly, sintering in a reducing atmosphere, may be an important step in the process of preparing strong emission glass. This deduction is supported by the fact that 1% Al\textsubscript{2}O\textsubscript{3} · 99% SiO\textsubscript{2} (mol%) glass containing 1 wt % Eu\textsubscript{2}O\textsubscript{3}, prepared by sol-gel processing and heat treated under reducing conditions at 800 °C, exhibits strong emission characteristics at an emission yield of 90%.

In this letter, we propose a method of preparing high-SiO\textsubscript{2} glass containing rare-earth and transition-metal ions through a process of impregnation and sintering in a reducing atmosphere, and report a significant enhancement of emission due to the reduction sintering. The colorless transparent fluorescent glasses have potential for application in lasers, fiber lasers and amplifiers, solar concentrators, displays, fluorescent lamps, and transparent phosphors used in special places, such as high temperature and high humidity environments.
The porous glass in the present study was prepared using waste glass as described elsewhere. This method is similar to the treatment process used in manufacturing Vycor glass. Although the waste glass contains Na⁺, Ca²⁺, Al³⁺, and some colored ions, all cations except Si⁴⁺ can be leached out after the waste glass is remelted with B₂O₃ and leached by hot acid solution. The analytical composition of the porous glass obtained is 97.0% SiO₂·2.1% B₂O₃·0.8% Al₂O₃·0.05% Na₂O·0.05% CaO, which is close to that of Vycor glass or high-SiO₂ glass. The obtained porous glass is a transparent material with pore sizes of less than 40 Å and the pores nominally occupy about 40% of the volume of the glass. The impurity of the transition-metal ions in the glass is less than 10 ppm and the 50% transmission value of the glass sintered at 1100 °C in a reducing atmosphere is located near 225 nm for a thickness of 1 mm. The infrared (IR) absorption band due to OH⁻ stretching vibration (~2.7 μm) (Ref. 1) showed that the quantity of the residual OH⁻ groups in the glass sintered at 1100 °C is close to that of fused silica glass. The obtained porous glass was immersed into 0.01–0.1 M solution of europium and cerium nitrate or copper and tin chloride for 1 h and dried at room temperature. The porous glasses impregnated with these activator ions were then sintered at 1100 °C for 2 h in air or in a carbon crucible used for reducing conditions.

The glasses impregnated with europium ions and heat treated below 800 °C in air showed a very weak red emission band at about 610 nm (3D₀→7F₂) due to Eu³⁺ ions when excited by UV light at a wavelength of around 250 nm. When increasing heat treatment temperatures from 800 to 1100 °C in air, the red light gradually weakened and the blue light from an emission band at about 430 nm became strong. Namely, the Eu³⁺ ions were reduced to Eu²⁺ ions even though the porous glass had been sintered in air. Moreover, when the porous glass was sintered at 1100 °C in a reducing atmosphere, the blue light was further remarkably enhanced and the emission band at about 610 nm vanished completely. This result indicates that the nanosized pores in porous glass are a favorable environment for reducing Eu ions. Figure 1 shows excitation spectra and emission spectra of porous glasses impregnated with europium ions and sintered in air and a reducing atmosphere. The broad excitation and emission bands are attributed to the 4f⁶5d→4f⁷(5S₂) transition of the Eu²⁺ ions. The emission intensity of Eu²⁺ ions incorporated in the glass sintered in a reducing atmosphere is 15 times larger than that of the glass sintered in air. The Eu²⁺-ion-doped glass is colorless and transparent, and exhibits a remarkably strong blue fluorescence, which can be observed even in sunlight. To evaluate the emission properties, the emission yield of the Eu²⁺-ion-doped glass was measured by comparison with that of anhydrous quinine (C₂₃H₂₄N₄O₂) in 1.0N H₂SO₄ solution. The observed emission yield of the glass sintered in a reducing atmosphere is approximately 97%, which is higher than that of Eu²⁺-doped Al₂O₃·SiO₂ glass prepared by the sol-gel process. The method of manufacturing high-SiO₂ glass (Vycor glass) through glass phase separation has a long history and lends itself readily to mass production. Further, the glass can be easily formed into various shapes, such as plates, fibers, and tubes.

Figure 2 shows the excitation and emission spectra of porous glasses impregnated with Ce ions and sintered in air or a reducing atmosphere. The broad emission bands observed in both glasses are attributed to the 5d→4f transition of the Ce³⁺ ions. The emission intensity of Ce³⁺ ions incorporated in the glass is increased seven times by reduction sintering. The absorption and emission of Ce³⁺ ions in glass arises from transitions between 4f and 5d energy levels. Unlike 4f, 5d orbitals are exposed to significant interaction with the orbitals of surrounding atoms and ions which in turn influences the emission properties. As seen in Fig. 2, when the porous glass was co-impregnated with Al³⁺ and Ce³⁺ ions and sintered in a reducing atmosphere, the emission intensity was further enhanced two times. Moreover, the Al³⁺ and Ce³⁺ co-doped high-SiO₂ glass also exhibits an intense fluorescence on par with that exhibited by the Eu²⁺-doped high-SiO₂ glass. This result indicates that the nanosized pores in the porous glass can be modified through impregnation with a compound to form favorable local circumstances for the activator ions. However, as the peak from the Ce³⁺-doped high-SiO₂ glass is at about 405 nm and shifts to 385 nm with the addition of Al₂O₃, we only observed a weak blue fluorescence in comparison with the Eu²⁺-doped glass when these glasses were excited by a UV lamp at a wavelength 250 nm or 360 nm. The emission intensities of Eu²⁺ or Ce³⁺ ions incorporated in the glass are nearly independent of the solution concentration in the range of 0.01–0.1 M europium and cerium nitrate. The observed emission yield of Ce³⁺ ions incorporated in the glass is approximately 70%, as shown in Table I.
Further, some heavy-metal and transition-metal ions, such as Ag, Bi, Sn, In, Mn, Fe, Co, and Cu ions, were impregnated in the porous glasses. All of these glasses exhibited strong luminescence with UV irradiation after sintering in a reducing atmosphere. These glasses did not exhibit such strong luminescence when sintered in air. Figure 3 shows photographs of the glasses impregnated with Eu\(^{2+}\), Cu\(^{+}\), and Sn\(^{2+}\) ions and sintered in a reducing atmosphere before and after irradiation by a black light at a wavelength of 254 nm. It is seen that the luminescence from the glass with Cu\(^{+}\), and Sn\(^{2+}\) is comparable to that with Eu\(^{2+}\). Indeed, the emission bands of the glass with Cu and Sn are as intense as that with Eu, as shown in Table I. The intense emission at around 478 nm is assigned to the electronic transition 3d\(^{10}\)4s\(^{1}\) → 3d\(^{10}\) of the Cu\(^{+}\) ions.\(^{19}\) The glass containing Sn\(^{2+}\) shows the band at around 395 nm, which may be attributable to Sn-related defects in the SiO\(_2\) matrix.\(^{20}\) Fluorescent glass with metal ions as phosphors has merit in the diversity of positions of the emission band. The optical fluorescence of the metal ions is mostly related to the s and d levels, and the energy level of d orbitals is strongly correlated with the chemical environment around the ions. Accordingly, the emission intensities of metal ions incorporated in the glasses are strongly dependent on the preparation conditions, including concentration, co-doped compound, and sintering temperature. If these conditions are adequately controlled, any photoluminescence in the near-IR-UV and visible range (330–700 nm) is possible.

In conclusion, the porous glass is not only advantageous for uniform distribution of the rare-earth and transition-metal ions, but also favorable for redox reactions and modification of local circumstances for the activator ions in the microscopic voids. The process through which the porous glass is impregnated with activator ions and sintered in a special atmosphere provides a method for producing colorless transparent fluorescence materials. The very strong emissions from the Eu\(^{2+}\), Ce\(^{3+}\), Cu\(^{+}\), and Sn\(^{2+}\) ions incorporated in the high-SiO\(_2\) glasses may make them useful as colorless trans-
displays.

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### Table I. Emission properties of various ions in porous glass sintered in a reducing atmosphere.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Excitation wavelength (nm)</th>
<th>Emission peak (nm)</th>
<th>Emission yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu(^{2+})</td>
<td>280</td>
<td>435</td>
<td>97</td>
</tr>
<tr>
<td>Ce(^{3+})</td>
<td>320</td>
<td>385</td>
<td>70</td>
</tr>
<tr>
<td>Cu(^{+})</td>
<td>258</td>
<td>478</td>
<td>100</td>
</tr>
<tr>
<td>Sn(^{2+})</td>
<td>262</td>
<td>395</td>
<td>90</td>
</tr>
</tbody>
</table>

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FIG. 3. (Color) Photographs of glasses impregnated with Eu\(^{2+}\) ions (right), Cu\(^{+}\) ions (middle), and Sn\(^{2+}\) ions (left) and sintered in a reducing atmosphere: (a) Without UV irradiation and (b) under UV light (254 nm).