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Blue-Silica by Eu\(^{2+}\)-Activator Occupied in Interstitial Sites

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Dong-Kyun Seo\(^g\) and Jung-Chul Park\(^{a,b}\)

Blue-emitting SiO\(_2\)Eu\(^{2+}\) compound has been successfully synthesized and characterized. The PL intensity of SiO\(_2\)Eu\(^{2+}\) compound is about 24 times higher than that of the O-defective SiO\(_2\) compound (without activators) which emits blue light. The valence state of Eu ions as the nature of the highly enhanced blue emission in resulting material, is determined to be Eu\(^{2+}\) using reference materials (EuCl\(_3\) and EuCl\(_2\)) in XPS measurements. The Eu\(^{2+}\)-activator ions occupied in the interstitial sites of SiO\(_2\) matrix, are confirmed by FT-IR, XPS, and \(^{29}\)Si MAS-NMR spectroscopy. Even though the void spaces formed structurally in both α-quartz and α-cristobalite can accommodate Eu\(^{2+}\) ions (ionic radius = 1.25 Å at CN = 8), SiO\(_2\)Eu\(^{2+}\) compound fired at 1300°C under hydrogen atmosphere is destined to be deficient in O or Si atoms, indicating the formation of the wider void spaces in SiO\(_2\) crystal lattice. A sputtered depth profile of SiO\(_2\)-related compounds obtained by time-of-flight secondary ion mass spectrometry (TOF-SIMS) corroborates the O-defective SiO\(_2\) induced by hydrogen. In particular, the interatomic potentials depending on the interstitial positions of Eu atom in α-cristobalite and α-quartz are calculated based on Lennard-Jones potential and coulomb potential; for α-cristobalite the minimum potential value is -51.47 eV, for α-quartz 221.8 eV, which reveals that the Eu\(^{2+}\)-activator ions more preferably enter the interstitial positions of α-cristobalite than those of α-quartz. Thanks to the stable Eu\(^{2+}\)-activator ions enclosed by Si-O linkages, SiO\(_2\)Eu\(^{2+}\) compound emits blue light and its PL emission intensity is about 24 times higher than that of the O-defective SiO\(_2\) compound. This phosphor material could be a platform for modeling a new phosphor and application in the solid-state lighting field.

1 Introduction

Silicone (27.2 wt %) is the most abundant element in the earth’s crust after oxygen (45.5 %), and silicone never occurs free but invariably occurs combined with 4-coordinated oxygen in nature. The [SiO\(_4\)] unit may occur as an individual group or be linked into chains, ribbons, sheets, or three-dimensional frameworks.\(^1\) Silica, or silicon dioxide (SiO\(_2\)) naturally occurs in both crystalline and amorphous forms. The various forms of the crystalline silica are: α-quartz, β-quartz, α-tridymite, β-tridymite, α-cristobalite, β-cristobalite, keatite, coesite, stishovite, and moganite.\(^2\) The most abundant form of the silica is α-quartz which is the most thermodynamically stable form of the crystalline silica in ambient conditions. Quartz has been used for a long time (several thousand years) in jewelry as a gem stone, and is used extensively in electronics as well as optical components industries.\(^3\) It is very interesting that Zolensky et al. reported that blue quartz phenocrysts from the Llano rhyolite (llanite), Llano County, and Texas, derived their coloration from Rayleigh scattering by abundant submicrometer-sized ilmenite inclusions, without experimental evidences.\(^4\) According to their results, the concentrations of rare-earth element (REE) in the blue quartz were determined as 0.910 ppm (Ce), 0.108 ppm (Sm), 0.016 ppm (Eu), 0.299 ppm (Tb), 0.332 ppm (Yb), and 0.064 ppm (Lu). It is well-known that in phosphor materials various activators, such as Nd\(^{3+}\), Pr\(^{3+}\), Sm\(^{3+}\), Eu\(^{3+}\), Eu\(^{2+}\), Ce\(^{3+}\), Tb\(^{3+}\), Tb\(^{3+}\) etc., have been widely used for flat panel displays and optoelectronic devices.\(^5\)-\(^8\) Among them, the divalent europium ions (Eu\(^{2+}\)) have been considered as a very important and useful activator which exhibits broad emission bands between ultraviolet (UV) and red spectral range associated with 4f\(^6\)5d\(^1\) - 4f\(^7\) transition.\(^9\)-\(^11\)

Considering various activator ions, it is presumed that the origin of blue coloration in quartz from the Llano rhyolite (llanite), Llano County, and Texas, may be due to the Eu\(^{2+}\) or Ce\(^{3+}\) ions occupied into the crystal lattice of quartz. Zolensky et al., however, argued that the blue quartz is originated from
Rayleigh scattering by the ilmenite inclusions because the large difference in the ionic radii of Si\(^{4+}\) (0.40 Å) and Eu\(^{3+}\) (1.31 Å) precludes direct substitution.\(^6\) It is very interesting that the blue emission induced by the O-related defects (without activator ions) in SiO\(_2\)-related compounds, was reported by several groups.\(^{12-18}\) Uchino et al. proposed that the blue-emitting center in oxidized porous silicone and nano-SiO\(_2\) materials, is a metastable defect pair consisting of =Si(O) and \(=\text{Si}\); on the basis of the density functional theory calculation, which was in good agreement with the peak positions of the PLE from the blue-emitting materials.\(^{19}\) McCrate et al. also presented that the intrinsic oxygen vacancy defect (OVD) on planar fused silica was experimentally detected by titration with fluorescent probe molecules, such as perylene-3,3′-planar fused silica was experimentally detected by titration with fluorescent probe molecules, such as perylene-3,3′-planar fused silica was experimentally detected by titration with fluorescent probe molecules, such as perylene-3,3′-planar fused silica was experimentally detected by titration with fluorescent probe molecules, such as perylene-3,3′-planar fused silica was experimentally detected by titration with fluorescent probe molecules, such as perylene-3,3′-planar fused silica was experimentally detected by titration with fluorescent probe molecules, such as perylene-3,3′-planar fused silica was experimentally detected by titration with fluorescent probe molecules, such as perylene-3,3′-planar fused silica was experimentally detected by titration with fluorescent probe molecules, such as perylene-3,3′-planar fused silica was experimentally detected by titration with fluorescent probe molecules, such as perylene-3,3′-planar fused silica was experimentally detected by titration with fluorescent probe molecules, such as perylene-3,3′-planar fused silica was experimentally 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Fig. 1 Rietveld refinement of the powder XRD profiles for SiO$_2$:Eu$_{0.002}$ (a) and undoped SiO$_2$ (b). The diffraction pattern is composed of the peaks from α-cristobalite as a main phase and α-quartz as a minor phase. Measured data, fitted results, expected reflection positions, and the difference between measured and fitted results are expressed as red open circles, black solid lines, black vertical lines, and blue solid lines, respectively. The peak intensities over 40 degrees in 2θ have been magnified 10 times for clarity.

Table 1 Relative Proportion of Phases, Structural Parameters and Reliability Factors for SiO$_2$:Eu$_{0.002}$ and SiO$_2$

<table>
<thead>
<tr>
<th>Compound</th>
<th>SiO$<em>2$:Eu$</em>{0.002}$ (α-Cristobalite)</th>
<th>SiO$<em>2$:Eu$</em>{0.002}$ (α-Quartz)</th>
<th>SiO$_2$:No-Eu (α-Cristobalite)</th>
<th>SiO$_2$:No-Eu (α-Quartz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weight present (%)</td>
<td>89.2(4)</td>
<td>10.8(13)</td>
<td>90.1(5)</td>
<td>9.9(17)</td>
</tr>
<tr>
<td>$R_{wp}$ (%)</td>
<td>1.51</td>
<td>2.12</td>
<td>2.98</td>
<td>4.53</td>
</tr>
<tr>
<td>$R_{bragg}$ (%)</td>
<td>11.1</td>
<td>13.0</td>
<td>13.0</td>
<td>13.0</td>
</tr>
<tr>
<td>Site occupancies</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Cell volume (Å$^3$)</td>
<td>172.12(14)</td>
<td>112.07(3)</td>
<td>171.55(16)</td>
<td>112.16(3)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>SiO$<em>2$:Eu$</em>{0.002}$ (α-Cristobalite)</th>
<th>SiO$_2$:No-Eu (α-Cristobalite)</th>
<th>SiO$<em>2$:Eu$</em>{0.002}$ (α-Quartz)</th>
<th>SiO$_2$:No-Eu (α-Quartz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si, 4a</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>x</td>
<td>0.2967(2)</td>
<td>0.2966(2)</td>
<td>0.470(2)</td>
<td>0.469(2)</td>
</tr>
<tr>
<td>y</td>
<td>0.2967(2)</td>
<td>0.2966(2)</td>
<td>0.470(2)</td>
<td>0.469(2)</td>
</tr>
<tr>
<td>z</td>
<td>0</td>
<td>0</td>
<td>z</td>
<td>z</td>
</tr>
<tr>
<td>Site occupancies</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$B_{iso}$ (Å$^2$)</td>
<td>1.39(3)</td>
<td>1.18(3)</td>
<td>0.5(1)</td>
<td>0.4(1)</td>
</tr>
</tbody>
</table>

| O, 8b    |                                     |                                 |                               |                           |
| x        | 0.2412(4)                          | 0.2428(5)                       | 0.439(2)                     | 0.433(2)                  |
| y        | 0.0985(4)                          | 0.1012(5)                       | 0.279(2)                     | 0.276(2)                  |
| z        | 0.1756(3)                          | 0.1757(3)                       | 0.786(2)                     | 0.783(2)                  |
| Site occupancies | 1 | 1 | 1 | 1 |
| $B_{iso}$ (Å$^2$) | 1.78(6) | 1.34(6) | 2.3(3) | 1.7(4) |

Table 2: Structural parameters for SiO$_2$:Eu$_{0.002}$ and SiO$_2$.
Table 2 Unit Cell Parameters and Phase Content between α-Quartz and α-Cristobalite in Silicas Fired under 4% H₂-Ar Atmosphere

<table>
<thead>
<tr>
<th>Compound</th>
<th>α-Cristobalite (weight %)</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>α-Quartz (weight %)</th>
<th>a (Å)</th>
<th>c (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ (Aldrich chemical)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>100%</td>
<td>4.91202(13)</td>
<td>5.40345(17)</td>
</tr>
<tr>
<td>SiO₂ (1500°C)</td>
<td>100%</td>
<td>4.97114(19)</td>
<td>6.9254(3)</td>
<td>9.97%</td>
<td>4.9043(6)</td>
<td>5.3844(10)</td>
</tr>
<tr>
<td>SiO₂ (1300°C)</td>
<td>90.03%</td>
<td>4.9731(3)</td>
<td>6.9362(4)</td>
<td>10.80%</td>
<td>4.9035(6)</td>
<td>5.38214</td>
</tr>
<tr>
<td>SiO₂:Euₜₐₐₕ (1300°C)</td>
<td>89.20%</td>
<td>4.9767(2)</td>
<td>6.9491(4)</td>
<td>10.80%</td>
<td>4.9035(6)</td>
<td>5.38214</td>
</tr>
<tr>
<td>SiO₂:Euₜₐₐₕ (1300°C)</td>
<td>99.07%</td>
<td>4.9733(2)</td>
<td>6.9341(3)</td>
<td>0.93%</td>
<td>4.90(5)</td>
<td>5.38(9)</td>
</tr>
</tbody>
</table>

undoped SiO₂, the Eu-doped SiO₂ compound showed no substantial difference in the crystal structure except for the temperature factors. For instance, the isotropic temperature factors, Bₐ₀ of Si and O atoms are 1.18(3) Å² and 1.36(6) Å² for the α-cristobalite phase in undoped SiO₂, while those are 1.39(3) Å² and 1.78(6) Å² in doped SiO₂:Eu₀.₀₀₂. The large temperature factors for SiO₂:Eu₀.₀₀₂ imply that the Eu doping into SiO₂ leads to the increase of structural disorder. Table 2 shows the weight percentages (%) of α-quartz and α-cristobalite as a function of firing temperature and Eu content. It is evident that the weight % of α-cristobalite is increased with increasing firing temperature and Eu content.

3.2 Photoluminescence Spectra

Fig. 2 presents the PL spectra of SiO₂:Eu₀.₀₁ synthesized under 4 % H₂-Ar atmosphere as a function of firing temperature. The highest excitation and emission intensity are observed in the SiO₂:Eu₀.₀₁ compound synthesized at 1300°C that is an optimal firing temperature. The excitation spectra of SiO₂:Eu₀.₀₁ compounds monitored at 438 nm, consist of broad bands between 220 nm and 420 nm, which may be ascribed to the allowed 4f⁷–4f⁷5d transitions of Eu²⁺. The emission spectra monitored under the 323 nm excitation, show symmetric bands centered around 438 nm, which is associated with blue-emission. The excitation and emission spectra of SiO₂:Euₓ compounds synthesized at 1300°C as a function of Eu content are shown in Fig. 3. The PL maximum intensity is observed at x = 0.002, then decreased with increasing Eu concentration. The optimum concentration of Eu in the SiO₂:Eu compound is...
noteworthy that the PL pattern of SiO$_2$ is very similar to that of SiO$_2$:Eu$^{2+}$Cl (17 mole%). The intensity of SiO$_2$:Eu$^{2+}$Cl (17 mole%) is about 2.4 times higher than that of SiO$_2$:Eu$^{2+}$ (mole(NH$_4$Cl)/mole(SiO$_2$)), which is well consistent with PL results as previously shown in Fig. 3. The excitation behavior of SiO$_2$:Eu$^{2+}$ compound synthesized at 1300°C under 4% H$_2$-Ar atmosphere with the mole ratio = 4 (mole(NH$_4$Cl)/mole(SiO$_2$)) was compared with a commercial BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ (BAM:Eu$^{2+}$) phosphor (obtained from Nichia corp., Japan). The excitation and emission spectra of SiO$_2$:Eu$^{2+}$ and BAM:Eu$^{2+}$ are shown in Fig. 7. The excitation and emission spectra are very similar except the difference in the PL intensity. The relative emission intensity of SiO$_2$:Eu$^{2+}$ monitored at 323 nm is about 40% compared to a commercial BAM:Eu$^{2+}$. The Commission International de l’Eclairage (CIE) coordinates of SiO$_2$:Eu$^{2+}$ and BAM:Eu$^{2+}$ monitored under UV light at 300 nm, are $x = 0.145$, $y = 0.068$ and $x = 0.143$, $y = 0.065$, respectively as shown in the inset of Fig. 7. According to CIE coordinates, it directly indicates that the SiO$_2$:Eu$^{2+}$ compound emits deep blue.

### 3.3 Infrared Spectroscopy

1300°C under 4% H$_2$-Ar atmosphere, which is probably due to the Eu ions occupied into the SiO$_2$ matrix. For SiO$_2$:Eu$^{2+}$Cl (x = 0.002, 0.005, and 0.010) with and without NH$_4$Cl addition. For SiO$_2$:Eu$^{2+}$Cl (x = 0.002 and 0.05). When Eu$^{2+}$ ions are occupied into the SiO$_2$ matrix, the broad absorption bands are shown between 220 nm and 450 nm, whereas absorption bands are not shown in α-quartz and α-cristobalite in the region. It might indicate the broad absorption bands between 220 nm and 450 nm are associated with the 4f→5d transition of Eu$^{2+}$. Also, the absorption bands of SiO$_2$:Eu$^{2+}$ (0.002) are still stronger than that of SiO$_2$:Eu$^{2+}$ (0.010), which is probably due to the Eu ions occupied into the SiO$_2$ matrix.

**Fig. 5** Excitation and emission spectra of SiO$_2$:Eu$^{2+}$ with and without NH$_4$Cl (4 moles).

**Fig. 6** Diffuse reflectance spectra of SiO$_2$-related compounds.

0.002, which implies that SiO$_2$ crystal lattice is difficult to accommodate the large amount of Eu$^{3+}$-activator ions. It should be noted that NH$_4$Cl is widely used as a flux and lubricant chemical in solid-state reaction because of a relatively low melting point (340°C) and boiling point (520°C).

In this work, NH$_4$Cl plays an important role in SiO$_2$:Eu compounds as a flux and lubricant which forces Eu$^{2+}$ to enter the interstitial sites of SiO$_2$ matrix. As shown in Fig. 4, the PL intensity of SiO$_2$:Eu$^{2+}$Cl (4 moles) is increased. With the higher mole ratio between NH$_4$Cl and SiO$_2$ (mole(NH$_4$Cl)/mole(SiO$_2$)), the maximum PL intensity is observed at the mole ratio 4. It is very noteworthy that the PL pattern of SiO$_2$ (No-Eu, 4 mole NH$_4$Cl) is similar to that of SiO$_2$:Eu$^{2+}$Cl (4 mole NH$_4$Cl) is similar to that of SiO$_2$:Eu$^{2+}$Cl except the difference of the PL intensities, indicating the blue emissions induced by the O-related defects (without activator ions) in SiO$_2$-related compounds as mentioned in introduction. It is very remarkable that the PL intensity of SiO$_2$:Eu$^{2+}$Cl is about 24 times as high as that of SiO$_2$ (No-Eu, 4 mole NH$_4$Cl) fired at 1300°C under 4% H$_2$-Ar atmosphere, which is probably due to the Eu ions occupied into the SiO$_2$ matrix. For SiO$_2$:Eu$^{2+}$ Cl (x = 0.002, 0.005, and 0.010) with and without NH$_4$Cl addition. For SiO$_2$:Eu$^{2+}$Cl (x = 0.002 and 0.05). When Eu$^{2+}$ ions are occupied into the SiO$_2$ matrix, the broad absorption bands are shown between 220 nm and 450 nm, whereas absorption bands are not shown in α-quartz and α-cristobalite in the region. It might indicate the broad absorption bands between 220 nm and 450 nm are associated with the 4f→5d transition of Eu$^{2+}$. Also, the absorption bands of SiO$_2$:Eu$^{2+}$Cl (0.002) are still stronger than that of SiO$_2$:Eu$^{2+}$ (0.010), which is probably due to the Eu ions occupied into the SiO$_2$ matrix.

**Fig. 7** PL spectra of SiO$_2$:Eu$^{2+}$Cl and a commercial BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$ (BAM) phosphor (obtained from Nichia corp., Japan). The inset shows the CIE chromaticity for two phosphors depending on the excitation UV light.
Fig. 8 presents the IR spectra of SiO$_2$-related compounds. The absorption band at 1092 cm$^{-1}$ in the spectra of α-quartz is associated with Si−O asymmetrical stretching vibrations, those at 799 and 780 cm$^{-1}$ with Si−O symmetrical stretching vibrations, that at 696 cm$^{-1}$ with Si−O symmetrical bending vibrations, and those at 512 and 460 cm$^{-1}$ with Si−O asymmetrical bending vibrations. After firing α-quartz at 1500°C, the IR spectrum of α-quartz is completely transformed into that of α-cristobalite with a notable new band at 621 cm$^{-1}$ corresponding to Si−O asymmetrical bending vibrations. In SiO$_2$:Eu$^{2+}$ compounds fired at 1300°C under 4% H$_2$-Ar atmosphere, there is no considerable wavenumber shift in IR modes except that the lower absorbance and greater broadness of IR modes compared with those of α-cristobalite.

The IR modes in SiO$_2$ compound (without Eu) fired at 1300°C under 4% H$_2$-Ar atmosphere, reveals that the Eu ions occupied in SiO$_2$ matrix might have an effect on the SiO$_2$ internal modes. As a consequence of the interaction, (Eu$^{2+}$⋯[O-Si-O]$^{4-}$⋯Eu$^{2+}$), the local symmetry of SiO$_2$ matrix may be partially collapsed, which results in the modification of the [SiO$_4$] internal modes, i.e., the lower absorbance and greater broadness of IR modes because there is not enough Eu content to induce the chemical shift of the vibration modes of SiO$_2$:Eu compounds. It should be noted that the variation of the IR modes by Eu ion doped in SiO$_2$ matrix means that there is a pseudo-covalent bond character between Eu ion and O ion sharing with SiO$_4$ tetrahedral units. Thus, it might indicate that Eu ions are occupied in the SiO$_2$ interstitial sites formed structurally, particularly, in wider ones formed under 4% H$_2$-Ar atmosphere.

### 3.4 X-ray Photoelectron and Solid NMR Spectroscopy

In order to examine the valence state of Eu ions occupied into the SiO$_2$ matrix, XPS analysis was performed. All the XPS spectra were fitted after a Shirley background correction. Fig. 9 presents the wide-scan XPS spectra of EuCl$_2$ (Eu$^{2+}$) and EuCl$_3$ (Eu$^{3+}$) reference compounds. It should be pointed out that it is very difficult to obtain fully reduced Eu$^{2+}$ in metal oxide-phosphor compounds based on the standard reduction potential (Eu$^{3+}$/Eu$^{2+}$ = -0.36 V vs. standard hydrogen electrode (SHE)), which indicates that the reduction of Eu$^{3+}$ to Eu$^{2+}$ requires an annealing process at high temperature (≥1000°C) under a reducing atmosphere, such as H$_2$ or H$_2$-Ar mixture gas. Additionally, the thermodynamically unstable Eu$^{2+}$ ions are prone to be easily oxidized by foreign molecules, such as H$_2$O, O$_2$ etc., in particular, under X-ray irradiation in XPS measurements. As shown in the inset of Fig. 9, the fact that the new band around 128 eV is observed in EuCl$_2$ compound, supports the partial oxidation of Eu$^{2+}$ to Eu$^{3+}$. Fig. 10 presents
Eu 3d and Eu 4d XPS spectra of EuCl\textsubscript{2} and EuCl\textsubscript{3}. The Eu 4d binding energies of EuCl\textsubscript{3} (top at right) are assigned to the Eu\textsuperscript{2+} 4d\textsubscript{5/2} (137.3 eV) and Eu\textsuperscript{3+} 4d\textsubscript{5/2} (142.9 eV).\textsuperscript{28-30} The spin-orbital splitting value for Eu\textsuperscript{3+} ion is 5.6 eV, which is in good agreement with that as previously reported.\textsuperscript{28} The Eu 4d binding energies of EuCl\textsubscript{2} (bottom at right) are assigned to Eu\textsuperscript{2+} 4d\textsubscript{5/2} (128.4 eV), Eu\textsuperscript{2+} 4d\textsubscript{3/2} (134.2 eV), Eu\textsuperscript{3+} 4d\textsubscript{3/2} (136.7 eV), and Eu\textsuperscript{3+} 4d\textsubscript{5/2} (142.3 eV), which is well consistent with XPS results as previously reported.\textsuperscript{31-36} Notably, Jiang et al. synthesized EuCl\textsubscript{2} nanoprism and nanorods and presented Eu 4d XPS spectra, as follows.\textsuperscript{36} Eu\textsuperscript{2+} 4d\textsubscript{5/2} (128.2 eV), Eu\textsuperscript{2+} 4d\textsubscript{3/2} (~134 eV), Eu\textsuperscript{3+} 4d\textsubscript{5/2} (~136 eV), and Eu\textsuperscript{3+} 4d\textsubscript{3/2} (142.2 eV), which is in good agreement with our result. They mentioned, additionally, that Eu 4d XPS spectrum showed the clear presence of Eu\textsuperscript{2+} (128.2 eV) and Eu\textsuperscript{3+} (~134 eV) although the Eu\textsuperscript{3+} ions on the surface were oxidized to Eu\textsuperscript{3+} (~136 eV and 142.2 eV). As shown in Fig. 10 (bottom at right), the spin-orbital splitting values of Eu\textsuperscript{3+} and Eu\textsuperscript{2+} ion (for EuCl\textsubscript{2}) are 5.6 eV and 5.8 eV, respectively. Interestingly, the Eu\textsuperscript{2+} 4d\textsubscript{5/2} peak at 128.4 eV consists of two components with the spin-orbit splitting value of 5.8 eV, which may be attributed to the different sites of the Eu\textsuperscript{2+} 4d\textsubscript{5/2} induced by the partial oxidation of Eu\textsuperscript{3+}. From the XPS measurement for EuCl\textsubscript{2} and EuCl\textsubscript{3} reference compounds, it clearly shows that EuCl\textsubscript{2} (Eu\textsuperscript{2+}) compound is more sensitive than EuCl\textsubscript{3} (Eu\textsuperscript{3+}) in oxidation induced by X-ray irradiation. By the aid of the Eu 4d binding energy for EuCl\textsubscript{2} and EuCl\textsubscript{3} reference compounds, the XPS 3d binding energies of reference compounds could be precisely assigned as presented in Fig. 10. The Eu 3d binding energies of EuCl\textsubscript{3} reference compound (top at left) are assigned to the Eu\textsuperscript{3+} 3d\textsubscript{5/2} (1136.5 eV) and Eu\textsuperscript{3+} 3d\textsubscript{3/2} (1166.1 eV) with the small amount of Eu\textsuperscript{2+} state at lower binding energy. On the other hand, the peaks of the Eu\textsuperscript{3+} 3d binding energies for EuCl\textsubscript{2} reference compound (bottom at left) are strongly intensified compared with those of EuCl\textsubscript{3} compound, i.e., Eu\textsuperscript{3+} 3d\textsubscript{5/2} (1126.3 eV) and Eu\textsuperscript{3+} 3d\textsubscript{3/2} (1155.9 eV) in Si\textsubscript{2}O\textsubscript{5} related compounds.

Fig. 11 High-resolution Eu 3d XPS spectra and PL emission spectra of SiO\textsubscript{2}-Eu\textsuperscript{3+} and SiO\textsubscript{2}-Eu\textsuperscript{2+}.

Fig. 12 \textsuperscript{29}Si MAS-NMR spectra of SiO\textsubscript{2}-related compounds; (a) α-quartz, (b) α-cristobalite after firing α-quartz at 1500°C under H\textsubscript{2}, (c) SiO\textsubscript{2} fired at 1300°C under H\textsubscript{2}, (d) SiO\textsubscript{2}-Eu\textsuperscript{3+} \textsubscript{2868} fired at 1500°C under H\textsubscript{2}, (e) SiO\textsubscript{2}-Eu\textsuperscript{2+} \textsubscript{2868} fired at 1300°C under H\textsubscript{2}, and (f) SiO\textsubscript{2}-Eu\textsuperscript{2+} \textsubscript{2868} fired at 1300°C under H\textsubscript{2}. The spinning side-bands are marked by arrows.

Eu\textsuperscript{2+} 3d\textsubscript{5/2} (1156.2 eV). In particular, it is reasonable that the Eu\textsuperscript{2+} valence state in EuCl\textsubscript{2} compound is prone to be easily oxidized under X-ray irradiation as presented in Eu 3d as well as Eu 4d XPS spectra. It should be noted that the difference in 3d binding energies between Eu\textsuperscript{2+} and Eu\textsuperscript{3+} (9.7 eV) is somewhat larger than that in 4d binding energies (8.3 eV). It is reasonable considering that the 3d electrons are closer to the nucleus than the 4d electrons and thus their binding energies are more strongly affected (\(\Delta B.E \propto 1/r\)). In order to examine the valence state of Eu ions occupied into the interstitial sites of SiO\textsubscript{2}, XPS measurements were performed and its results were presented in Fig. 11. As the PL spectrum (top at right) of SiO\textsubscript{2}-Eu\textsuperscript{2+} \textsubscript{2868} compound synthesized under 5% H\textsubscript{2}-Ar mixture gas, shows the characteristic of Eu\textsuperscript{2+}, 4f\textsuperscript{6}d\textsuperscript{6}→4f\textsuperscript{6} transition with a broad band between 380 nm and 520 nm corresponds to the blue emission. The Eu 3d XPS binding energies of SiO\textsubscript{2}-Eu\textsuperscript{2+} \textsubscript{2868} consist of 4 components, Eu\textsuperscript{2+} 3d\textsubscript{5/2} (1126.1 eV), Eu\textsuperscript{2+} 3d\textsubscript{3/2} (1135.8 eV), Eu\textsuperscript{3+} 3d\textsubscript{5/2} (1155.9 eV), Eu\textsuperscript{3+} 3d\textsubscript{3/2} (1165.4 eV). Considering the PL emission spectrum, it is evident that the Eu\textsuperscript{2+} ions in SiO\textsubscript{2}-Eu\textsuperscript{2+} \textsubscript{2868} compound is easily oxidized under X-ray irradiation. After thermal treatment of SiO\textsubscript{2}-Eu\textsuperscript{2+} \textsubscript{2868} compound under O\textsubscript{2} atmosphere at 1300°C for 3h, the PL emission spectrum (bottom at right) was obtained. As its PL behavior shows the characteristic of Eu\textsuperscript{3+} with a line spectrum at 616 nm corresponding to the red emission, it is evident that the Eu\textsuperscript{3+} ions occupied into the SiO\textsubscript{2} matrix are nearly oxidized to Eu\textsuperscript{3+}. Thus, the Eu\textsuperscript{3+} 3d XPS spectrum (bottom at left) is predominantly obtained after thermal treatment of SiO\textsubscript{2}-Eu\textsuperscript{2+} \textsubscript{2868} compound under O\textsubscript{2} atmosphere at 1300°C for 3h. From XPS measurement, the valuable information was obtained; the valence state of Eu ions occupied into the SiO\textsubscript{2} matrix is predominantly Eu\textsuperscript{2+}, associated.
with the blue emission. However, XPS as a surface analysis technique, can’t tell the total presence of Eu$^{3+}$ in SiO$_2$:Eu$^{2+}_{0.05}$ compound even though there exists in small amount of Eu$^{3+}$. Thus, XPS results evidently imply that the Eu$^{2+}$ ions stabilized in SiO$_2$ matrix are easily oxidized under X-ray irradiation in XPS measurements. $^{29}$Si MAS-NMR spectra of SiO$_2$ compounds are given in Fig. 12. The chemical shifts for α-quartz (a) and α-cristobalite (b), after firing α-quartz fired at 1500°C under 4% H$_2$/Ar) are -107.7 ppm and -109.3 ppm, respectively, which is in good agreement with those as previously reported.$^{37}$-$^{39}$ α-quartz (a) and α-cristobalite (b) show essentially no “side-bands” and no “chemical shifts”, indicating that there are neither different Si sites nor metal cations as shown in Fig 12. α-quartz is transformed into the mixed phase (c) with 10 wt% of α-quartz and 90 wt% of α-cristobalite after firing at 1300°C under 4% H$_2$/Ar atmosphere, and the chemical shift of the mixed phase is -109.5 ppm which is similar to that of α-cristobalite. It is very notable that in SiO$_2$:Eu$^{2+}$ compounds, “the spinning side-bands are appeared” depending on the Eu content; two weak side bands in SiO$_2$:Eu$^{2+}_{0.05}$ fired at 1500°C under 4% H$_2$/Ar (d) and SiO$_2$:Eu$^{2+}_{0.05}$ fired at 1300°C under 4% H$_2$/Ar (e), and six intense ones in SiO$_2$:Eu$^{2+}_{0.05}$ fired at 1300°C under 4% H$_2$/Ar (f). It is well-known that the spinning side-bands are originated from the dipolar interactions between the nuclear spin and the unpaired electron spins of the paramagnetic ions.$^{40}$-$^{44}$ in this system between $^{29}$Si spin and the unpaired electron spins of the Eu$^{2+}$ ions. Thus, the fact that there are the spinning side-bands in MAS-NMR spectra of SiO$_2$:Eu$^{2+}$ compounds, supports that the Eu$^{2+}$ ions are occupied with a pseudo-covalent bond character in the interstitial sites of SiO$_2$ crystal lattice.

3.5 Hydrogen Assisted SiO$_2$-defects: Nano-SIMS Measurements.

It is well-known that the reducing atmosphere plays an important role in the controlling of oxygen vacancies as well as charge valences of metal ions in metal oxides. Certainly, this is the fact that the additional charges should be compensated in order to incorporate metal ions of lower valence into the interstitial sites as well as to replace Si$^{4+}$ with metal ions of lower valence in SiO$_2$ matrix. The types of the point defect in silicon dioxide can be classified into intrinsic and extrinsic point defect. Intrinsic point defects involve vacancies caused by the missing host atoms and self-interstitials by additional host atoms at an interstitial position. Extrinsic point defects relate to foreign atom different from the host crystal. Defects in a perfect silicon dioxide could include O (or Si) vacancies, their interstitials, Si-Si (or O-O) homobonds, and under-coordinated silicons or oxygens.$^{45}$ Many authors considered hydrogen to be an intrinsic defect because it has been commonly found in silicon dioxide.$^{46}$-$^{48}$ Mysovsky et al.$^{47}$ argued that the oxygen-deficient vacancy combined a hydrogen atom, $E'_2$ center consists of a hydrogen substituting for an oxygen atom in α-quartz as the following reaction:

\[ \equiv \text{Si-O-Si} + \text{H} \rightarrow \equiv \text{Si-H} + \text{Si} + \text{O} \text{ (interstitial)} \quad (1) \]

The neutral oxygen vacancy (ODC(Ⅰ)) could be converted to $\equiv$Si-O-H groups by thermal reaction with hydrogen molecules according to the following reaction:$^{51}$-$^{52}$

\[ \equiv \text{Si-Si} + \text{H}_2 \rightarrow 2(\equiv \text{Si-O-H}) \quad (2) \]

The formation mechanism of hydrogenic trapped-hole species in α-quartz was proposed by Nuttall et al.$^{46}$ which indicates that the hydrogen ions (4H$^+$) incorporated into α-quartz structure substitute for Si$^{4+}$ as the following reaction:

\[ 4(\equiv \text{Si-O}) - \text{Si(defect)} + 4\text{H}^+ \rightarrow 4(\equiv \text{Si-O-H}) \quad (3) \]

The variation of the O/Si signal ratios of SiO$_2$ compounds is clearly seen depending on the firing condition as presented in Fig. 13. A sputtered depth profile of SiO$_2$ compounds obtained by time-of-flight secondary ion mass spectrometry (TOF-SIMS) corroborates the O-defective SiO$_2$ induced by hydrogen as discussed above. The O/Si signal ratio of α-quartz as received (Aldrich chemical) is the highest value, whereas those of SiO$_2$:Eu$^{2+}_{0.05}$ and SiO$_2$:Eu$^{2+}_{0.05}$ fired at 1300°C under H$_2$ atmosphere are lower than that of commercially available α-quartz, indicating that the oxygen atoms are predominantly missing at high temperature under hydrogen atmosphere. Moreover, α-cristobalite obtained after firing α-quartz at 1500°C under H$_2$ atmosphere shows the constant and lowest O/Si ratio. Although our Nano-SIMS analysis does not allow quantification of H content in the samples, the observed O/Si signal ratios are consistent with this formation mechanism.

3.6 Interstitial and Vacancy Mechanism of Eu$^{2+}$ Doping in SiO$_2$ Matrix

The incorporation of Eu$^{2+}$ ions into SiO$_2$ matrix may be explained in three different ways. The first explanation is that Eu atoms can replace silicon atoms forming a substitutional solid solution in a SiO$_2$ crystal. However, the direct substitution of Si$^{4+}$ with Eu$^{2+}$ is difficult because of the difference in the
Fig. 14 The schematic representations of the crystal structures for α-cristobalite (top) and α-quartz (bottom). Si and O atoms are represented by blue and red spheres. Structural voids are represented by grey spheres with radius of 1.25 Å (Eu$^{3+}$ at C.N. = 8).

Fig. 15 XRD pattern of SiO$_2$:Eu$^{3+}$ fired at 1300°C in O$_2$ atmosphere. The inset shows the PL emission spectra.

ionic radii of Si$^{4+}$ (0.26 Å) and Eu$^{2+}$ (1.30 Å). Moreover, to best of our knowledge, there has been no report on the 4-coordinated Eu$^{2+}$ (or. Eu$^{3+}$) in metal oxides as well as organometallic complexes. As a second explanation, the Eu atoms can distribute in the boundary of SiO$_2$ grains to form microscopic regions of europium oxide. The europium oxide can react with SiO$_2$ grains to generate Eu-containing silica compounds such as Eu$_2$SiO$_4$ and Eu$_3$SiO$_4$. Several authors have reported the formation of Eu$_2$SiO$_4$ and Eu$_3$SiO$_4$ on Eu-doped silica films in the studies. Li et al. reported that Eu-doped SiO$_2$ films annealed in N$_2$ at temperature higher than 800 °C exhibited a broad emission band between 400 and 800 nm which was attributed to the formation of Eu$_2$SiO$_4$ giving rise to intense yellow luminescence. In Eu-doped SiO$_2$ films, the broad emission peak centered at 610 nm between 500 and 750 nm was observed due to the Eu$^{3+}$ ions stabilized in the Eu$_2$SiO$_4$ and Eu$_3$SiO$_4$ crystalline structures. In our Eu$^{3+}$-doped SiO$_2$ compounds, the broad emission bands centered at 440 nm between 380 and 540 nm are observed indicating blue-emission. Moreover, Rietveld analyses within the Eu-doping range from 0.002 to 0.05 show that there is no trace of impurities which agree with the phase diagram of the EuO-SiO$_2$ system. As a third explanation, we speculate that the Eu atoms can incorporate into the structural void spaces (interstitial sites). Both α-cristobalite and α-quartz have open structures as shown in Fig. 14. As the void spaces formed in α-cristobalite structure are somewhat larger than those in α-quartz structure, it is presumed that Eu$^{3+}$ ions preferably occupy the interstitial sites of α-cristobalite. Compared with the ionic radius between Eu$^{3+}$ (1.25 Å at C.N. = 8) and Eu$^{2+}$ (1.066 Å at C.N. = 8),$^{53}$ Eu$^{3+}$ ions are more favorable to the void spaces of SiO$_2$ matrix on condition that no other phases is formed in the EuO-SiO$_2$ solid-solution. However, in the Eu-doped SiO$_2$ compound fired at 1300°C in air, the impurity phase of Eu$_2$SiO$_4$ (at Eu-doping range of 0.01) is clearly observed in XRD pattern and this compound exhibited a faint reddish-emission attributed to the formation of Eu$^{3+}$ ions as shown in Fig. 15, which indicates that in air atmosphere, Eu$^{3+}$ ions cannot occupy the interstitial sites of SiO$_2$ matrix and but react with SiO$_2$ giving rise to the formation of Eu$_2$SiO$_4$ in air atmosphere within the Eu-doping ranges from 0.002 to 0.05. On the contrary, Eu$^{2+}$ ions can enter the interstitial sites at 1300°C under 4% H$_2$-Ar atmosphere. Thus, it is presumed that Eu$^{2+}$ ions can be stabilized in the interstitial sites of SiO$_2$ matrix through the oxygen vacancies and partial fragmentation of tetrahedron linkages caused by hydrogen assistance. It should be noted that Eu$_2$O$_3$ (without adding SiO$_2$) was fired at 1300°C under 4% H$_2$-Ar atmosphere and obtained a red-emitting Eu$_2$O$_3$ with a monoclinic structure. Based on the experimental results, Eu$^{2+}$ doping mechanism in SiO$_2$ matrix could be postulated, as follows: i ) the reduction of Eu$_2$O$_3$ (Eu$^{3+}$) to EuO (Eu$^{2+}$) at high temperature (≥1000°C) under hydrogen atmosphere, ii ) the entrance of Eu$^{2+}$ ions in the interstitial sites of SiO$_2$ matrix through the oxygen vacancies and partial fragmentation of tetrahedron linkages caused by hydrogen assistance, iii ) the block of subsequent oxidation of the Eu$^{2+}$ ions enclosed by Si-O linkages compared with the isolated Eu$^{2+}$ species.

3.7 Theoretical Comparison of Interstitial Positions of Eu Atom in α-Cristobalite and α-Quartz: Interatomic Potential

We theoretically calculate the interatomic potentials depending on the interstitial positions of Eu atom in α-cristobalite and α-quartz, and compare their energy values. As shown in Fig. 16, α-cristobalite and α-quartz have large interstitial void spaces. When an Eu atom is located in the void spaces, the interatomic chemical forces between atoms exert. Atoms have strong repulsion forces when their distance is shorter than sum of their atomic radii. Ions have electric repulsion or attraction, depending on their charges.
The former can be modeled by Lennard-Jones potential\textsuperscript{58} and the latter can be modeled by coulomb potential.\textsuperscript{58} The potential can be written as

\[ U(r) = \sum_i \varepsilon_i \left( \frac{r_i}{\bar{R}_i} \right)^{12} - 2 \left( \frac{r_i}{\bar{R}_i} \right)^6 + \sum_i \sum_j k_{ij} \varepsilon_{ij}^2 \frac{Z_{i}^+ Z_{j}^-}{|r_i - r_j|}, \quad (4) \]

where first sum is the Lennard-Jones potential of nearby ions and second sum is the coulomb potential. Index \( i \) is related to the surrounding atoms in the crystal ( \( \varepsilon_i \) : bond dissociation energy, \( \bar{R}_i \) : the location of \( i \)th atom, \( r_i \) : the minimum potential distance between \( \text{Eu}^{2+} \) and \( i \)th atom, \( Z_{i}^\pm \) : charge number of \( \text{Eu}^{2\pm} \), \( Z_i \) : charge number of \( i \)th atom). There are two kinds of atoms around \( \text{Eu}, \text{O} \) and \( \text{Si} \). For \( \text{O} \), we choose \( \varepsilon_i \) as \( \text{Eu}-\text{O} \) bond dissociation energy 473 KJ/mol = 4.903 eV.\textsuperscript{59} \( r_i \) is chosen as sum of ionic radius of \( \text{Eu}^{2+} \) (1.30 Å) and crystal radius \( \text{O}^- \) (1.34 Å), \( Z_i \) for \( \text{O} \) charge number is -1 from consideration of half ionic character. For \( \text{Si} \), it does not form a bond with \( \text{Eu}^{2+} \) ions. We choose \( r_i \) as sum of ionic radius of \( \text{Eu}^{2+} \) (1.30 Å) and crystal radius of \( \text{Si} \) (0.26 Å) and determine value \( \varepsilon_i \) as 4.892 eV which gives same repulsion force as \( \text{Eu} \) and \( \text{O} \) Lennard-Jones force when atomic distance is compressed to 80% of their sum of radii. \( Z_i \) for \( \text{Si} \) charge number is 4, \( \text{O} \) charge number -2 and \( Z_{\text{Eu}} \) is 2. The local minimum point of this potential in three dimension can be found numerically, by successively following the negative gradient of potential (force) which gives steepest descent. Starting from initial position, search next potential minimum in finite interval of force direction, and repeat the procedure until it converges. In α-cristobalite case, the minimum position is shown in Fig. 16. Crystal unit cell parameters are given by \( (a, b, c) = (4.912, 4.912, 5.404) \) Å, \( \alpha, \beta, \gamma \) = (90, 90, 120) (°degree) and \( \text{Eu} \) minimum position is (-0.0301, 0.0014, 0.6674) in unit cell coordinate. Nearby oxygen coordinates are (0.4136, 0.2676, 0.7857), (0.1460, -0.2676, 0.5476), (-0.4136, -0.1460, 0.8801), (-0.2676, 0.1460, 0.4524). Their distances from \( \text{Eu} \) are 2.005, 2.014, 2.008, 2.011 Å. Minimum potential value is calculated to be 221.8 eV. The results suggest that it is more difficult to put \( \text{Eu} \) atom into α-quartz than α-cristobalite. In α-cristobalite case, minimum potential is negative as well as the distances between atoms at minimum point are large. Only two oxygens around 2.5 and 2.7 Å and next nearest oxygen distances are larger than 4 Å. In α-quartz case potential value is positive, which implies instability. Also the nearby oxygen distances are almost identically 2 Å at minimum potential point, showing quite regular and closely packed structure. It is reasonable to infer that Interstitial positioning of \( \text{Eu} \) is more easily done in α-cristobalite case than α-quartz case.

4 Conclusions

Blue-emitting silica by \( \text{Eu}^{2+} \)-activator ion occupied in the interstitial sites of \( \text{SiO}_2 \) matrix, has been successfully synthesized and characterized. The PL excitation spectra of \( \text{SiO}_2: \text{Eu}^{2+}:0.01 \) compounds monitored at 438 nm, consist of broad bands between 220 nm and 420 nm, which may be ascribed to the allowed 4f\textsuperscript{3}– 4f\textsuperscript{5}d transitions of \( \text{Eu}^{2+} \), which is in good agreement with XPS results. The emission spectra monitored under the 323 nm excitation, show symmetric bands centered around 438 nm, which is associated with blue-emission. From FT-IR spectra of \( \text{SiO}_2 \) compounds with and without \( \text{Eu}^{2+} \)-activator ions, it clearly shows that the lower absorbance and greater broadness are observed in the IR modes of \( \text{SiO}_2: \text{Eu}^{2+} \) compounds compared with those of α-quartz and α-cristobalite without \( \text{Eu}^{2+} \)-activator ions, indicating that the \( \text{Eu}^{2+} \)-activator ions are well located in the interstitial sites of \( \text{SiO}_2 \) matrix with a pseudo-covalent bond character between \( \text{Eu} \) ion and \( \text{O} \) ion sharing with \( \text{SiO}_4 \) tetrahedral units.\textsuperscript{29} \( \text{Si} \) MAS-CNR...
NMR spectra corroborates the interpretation of IR results. The fact that there are the spinning side-bands in MAS-NMR spectra of SiO$_2$:Eu$^{2+}$ compounds, supports that the Eu$^{2+}$ ions are occupied with a pseudo-covalent bond character in the interstitial sites of SiO$_2$ crystal lattice. The interatomic potentials depending on the interstitial positions of Eu atom in α-cristobalite and α-quartz are calculated using Lennard-Jones potential and coulomb potential; for α-cristobalite the minimum potential value is $-51.47\, eV$, for α-quartz $221.8\, eV$, and for γ-quartz the potential is $390.3\, eV$, compared to those of α-cristobalite and α-quartz.

Thanks to the Eu$^{2+}$-activator ions more preferably enter the interstitial sites of α-cristobalite than those of α-quartz. The interatomic potentials depending on the interstitial positions of Eu atom in α-cristobalite and α-quartz are calculated using Lennard-Jones potentials depending on the interstitial positions of Eu atom in α-cristobalite and α-quartz.

Acknowledgements

This research was financially supported by the Ministry of Education (MOE) and National Research Foundation of Korea (NRF) through the Human Resource Training Project for Regional Innovation (2014H1C1A1066859). One of the authors, S. J. Kim, acknowledges support from the National Research Foundation (NRF) of Korea (Grant No. 2009-0094046). Dr. Seen Ae Chae at the KBSI is acknowledged for carrying out NMR experiments. We would like to thank NSFs Major Research Instrumentation (NSFARRA award #0960334) and Arizona State University for acquisition and installation of the Nano-SIMS 50L.

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