Effects of additional Ce\(^{3+}\) doping on the luminescence of Li\(_2\)SrSiO\(_4\):Eu\(^{2+}\) yellow phosphor

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Additional Ce\(^{3+}\) doping improves the luminescence of Li\(_2\)SrSiO\(_4\):Eu\(^{2+}\), a yellow phosphor for ultraviolet or blue light-emitting diodes. By examining the photoluminescence of Li\(_2\)SrSiO\(_4\):Eu\(^{2+}\), Li\(_2\)SrSiO\(_4\):Ce\(^{3+}\), and Li\(_2\)SrSiO\(_4\):Ce\(^{3+}\), Eu\(^{2+}\), it was confirmed that the energy transfer from Ce\(^{3+}\) to Eu\(^{2+}\) ions contributes little to the enhanced luminescence of Li\(_2\)SrSiO\(_4\):Ce\(^{3+}\), Eu\(^{2+}\). Alternatively, we suggested that Ce\(^{3+}\) ions could stabilize the Li vacancies, inhibit the oxidation of Eu\(^{2+}\) to Eu\(^{3+}\), and consequently increase emission intensity, based on the characterizations with decay time and synchrotron light source x-ray absorption measurements. The proposed argument was validated with first principle calculations of the defect formation energies. © 2010 American Institute of Physics. [doi:10.1063/1.3308486]

Phosphors for light-emitting diode (LED) generally contain Eu\(^{2+}\) or Ce\(^{3+}\) ions as activators because they absorb ultraviolet or blue (380–460 nm) light from LEDs and efficiently emit visible light in common oxide, sulfide, or nitride hosts. Eu\(^{2+}\) and Ce\(^{3+}\) exhibit similar optical properties originating from the 4\(^f\)\(^{n}\)→4\(^f\)\(^{n-15}\) electronic transition, although there is a slight energy difference.\(^1\) Therefore, hosts with Eu\(^{2+}\) as an activator also can be used for Ce\(^{3+}\)-doped phosphors. Some researchers have tried simultaneous doping of Eu\(^{2+}\) and Ce\(^{3+}\) to a single host, as well. In most cases, the luminescence efficiency of Eu\(^{2+}\) emission is enhanced by additional Ce\(^{3+}\) doping, e.g., BaMgSiO\(_4\):Ce\(^{3+}\), Eu\(^{2+}\), BaGa\(_2\)S\(_4\):Ce\(^{3+}\), Eu\(^{2+}\), SrSi\(_2\)O\(_2\)N\(_2\):Ce\(^{3+}\), Eu\(^{2+}\), (Ba, Sr)\(_2\)ZnS\(_3\):Ce\(^{3+}\), Eu\(^{2+}\), and CaS:Ce\(^{3+}\), Eu\(^{2+}\).\(^2\)–\(^6\) A frequently cited reason for the enhancement is that the transferred energy from Ce\(^{3+}\) contributes to the luminescence of Eu\(^{2+}\) based on the overlap between the excitation band of Eu\(^{2+}\) and the emission of Ce\(^{3+}\) in the same host. However, in the strict sense, the effect of added Ce\(^{3+}\) on Eu\(^{2+}\) emissions should not be fully attributed to energy transfer without considering the other parameters that can be altered via multi-ions doping, such as defect level, electronic state, and crystalinity.\(^6\) As far as we know, this has not yet been seriously investigated. Therefore, it will be of use to elucidate the various effects of Ce\(^{3+}\) on Eu\(^{2+}\) emissions.

Among many phosphors, Li\(_2\)SrSiO\(_4\):Eu\(^{2+}\) was selected as the material to be examined because the emission of Li\(_2\)SrSiO\(_4\):Eu\(^{2+}\) is clearly increased by co-doping Ce ions. Although Zhang et al.\(^8\) studied Li\(_2\)SrSiO\(_4\):Ce\(^{3+}\), Eu\(^{2+}\), they investigated only the energy transfer phenomenon. In this study, after the energy transfer is assessed as the reason for luminescence enhancement, the possible another reason will be suggested and also be evaluated based on the experimental and theoretical results.

The Li\(_2\)SrSiO\(_4\):Eu\(^{2+}\) or Li\(_2\)SrSiO\(_4\):Ce\(^{3+}\), Eu\(^{2+}\) phosphors were prepared by solid-state reaction. Stoichiometric amounts of Li\(_2\)CO\(_3\) (Aldrich, 99.997%), SrCO\(_3\) (Aldrich, 99.995%), SiO\(_2\) (Kojundo, 99.99%), Eu\(_2\)O\(_3\) (Aldrich, 99.999%), and Ce\(_2\)O\(_3\) (Acros, 99.9%) were ground in an agate mortar for 30 min to mix them homogeneously. The mixtures were fired at 950 °C for 10 h under a reducing atmosphere (N\(_2)/H\(_2\)=95:5). Photoluminescence (PL) and photoluminescence excitation (PLE) were measured by spectrophotometers (Hitachi, F-7000) using a xenon lamp. Decay curves were acquired using a time-correlated single photon counting spectrometer with a nanosecond flash lamp (Edinburgh, FL920). All luminescent properties were measured at room temperature. Crystal structure and phase were analyzed using x-ray diffraction (XRD, Phillips X’pert Pro, Target Cu K\(_\alpha\), 40 kV, 40 mA). The Eu and Ce L\(_3\) x-ray absorption near-edge structure (XANES) spectra were recorded with a wiggler beamline BL17C at the National Synchrotron Radiation Research Center (NSRRC) in transmission mode for powdered samples. The chemical compositions of phosphors were measured by inductive-coupled plasma atomic-emission spectroscopy (ICP-AES, Shimadzu, ICP-S8100). The first-principle calculations based on density functional theory were performed using the Vienna \textit{ab initio} simulation package to estimate the formation energies of defects in Li\(_2\)SrSiO\(_4\) (Ref. 9) (See the section S1 in Ref. 10). Emission and excitation spectra of Li\(_2\)SrSiO\(_4\):\(x\)Ce\(^{3+}\)\(\times\)0.5%Eu\(^{2+}\) (\(x=0\%), 0.2\%, 0.4\%, 0.6\%, and 0.8\%) are shown in Fig. 1. As the doping concentrations of Ce ions increase from 0.2\%, 0.4\%, 0.6\%, and 0.8\%, the emission from Eu\(^{2+}\) ions are enhanced to through 129\%, 142\%, 162\%, and 180\% of Li\(_2\)SrSiO\(_4\):0.5%Eu\(^{2+}\) emission intensity, respectively. The shapes of Eu\(^{2+}\) emission spectra (around 586 nm) with Ce ions are identical to that without Ce, and the excitation spectra also show nearly identical shapes except for protrusions around 360 nm, which might be from Ce\(^{3+}\) absorption.

The emission and the excitation spectra of Li\(_2\)SrSiO\(_4\):Eu\(^{2+}\) and Li\(_2\)SrSiO\(_4\):Ce\(^{3+}\) are plotted in Fig. 2.
Due to the full overlap between the emission of Li$_2$SrSiO$_4$:Ce$^{3+}$ and the excitation of Li$_2$SrSiO$_4$:Eu$^{2+}$, energy transfer from Ce$^{3+}$ to Eu$^{2+}$ might be the probable process in Li$_2$SrSiO$_4$:Ce$^{3+}$, Eu$^{2+}$. If the luminescent enhancement is attributed to the energy transfer, it should be observed only when Li$_2$SrSiO$_4$:Ce$^{3+}$, Eu$^{2+}$ is excited at the wavelength where the excitation bands of Li$_2$SrSiO$_4$:Eu$^{2+}$ and Li$_2$SrSiO$_4$:Ce$^{3+}$ coexist. However, the intensity enhancement occurred between 400 and 550 nm where Ce$^{3+}$ cannot be sensitized, as well as between 250 and 400 nm where Ce$^{3+}$ strongly absorbs input light, as shown in Fig. 1 (See the section S2 in Ref. 10). This phenomenon cannot be explained only by the energy transfer.

To understand the probable origin of the enhanced luminescence, parameters contributing to PL intensities were examined based on the following equation:

$$I_{PL} \propto N^Q Q = \sigma \phi N Q = \sigma \phi N \tau_{rad}/\tau_{rad}. \quad (1)$$

The luminescent intensity ($I_{PL}$) is directly proportional to the product of the number of excited centers ($N$) and the quantum efficiency ($Q$). $\phi$, $\sigma$, and $N$ are the photon influx, the excitation cross section of each activator, and the total number of activators, respectively. $Q$ is determined by the ratio of total decay time ($\tau_{tot}$), which is experimentally measurable, and radiative decay time ($\tau_{rad}$) ($Q = \tau_{rad}/\tau_{rad}$). In Eq. (1), $\phi$ and $\sigma$ are fixed for the same phosphors with different activator concentrations in the same measurement conditions. Therefore, the intensity would be only determined by $Q$ or $N$. To check the dependence of $Q$ on the concentration of Ce doping, $\tau_{tot}$ of Eu$^{2+}$ emissions from Li$_2$SrSiO$_4$:Ce$^{3+}$, 0.5%Eu$^{2+}$ ($x=0.0\%$, 0.2%, 0.4%, 0.6%, and 0.8%) were measured. As shown in Fig. 3, luminescent decay curves show similar slopes and the trends independent of Ce concentrations. The fitted $\tau_{tot}$ are plotted in the inset of Fig. 3. Because $\tau_{rad}$ of an activator is fixed in the determined crystal structures, the constant $\tau_{tot}$ would mean the constant $Q$ of Eu$^{2+}$ emissions with respect to the Ce concentrations. Therefore, the PL enhancement might result from the increased $N$.

In spite of the fixed amount of Eu as 0.5% of Sr, $N$ can be changed by the fraction of Eu$^{2+}$ ions. The valence states of Eu in the tested samples are analyzed with XANES in the photon energy both below and above the Eu $L_3$ edge. The normalized Eu $L_3$-edge XANES spectra of Li$_2$SrSiO$_4$:Ce$^{3+}$, 0.5%Eu$^{2+}$ and Li$_2$SrSiO$_4$:Ce$^{3+}$, Eu$^{2+}$, Eu$^{3+}$, and BaMgAl$_{10}$O$_{17}$:Eu$^{2+}$, Eu$^{3+}$ are plotted in Fig. 4(a). The latter two samples are measured as references for Eu$^{3+}$ and Eu$^{2+}$ ions, respectively. The XANES spectra of the tested samples show two peaks (white lines) around 6975 and 6984 eV, which originate from the $2p_{1/2}$ and $2p_{3/2}$ transitions of Eu$^{2+}$ and Eu$^{3+}$, respectively. This means that the two valence states $2+$ and $3+$ of Eu ions coexist in all the tested samples. As Ce doping concentration increases, the relative intensities of absorption by Eu$^{2+}$ ions at 6975 eV and by Eu$^{3+}$ at 6983 eV systematically increase and decrease. For quantification, XANES spectra were deconvoluted into two Lorentzian (white lines) and one arc tangent (edge jump) functions (See the section S3 in Ref. 10). The area ratio of two Lorentzian functions can be regarded as the ratio of the amount of Eu$^{2+}$ and Eu$^{3+}$ ions because the sum of the two peak areas are nearly constant. Figure 4(b) clearly shows the increase in Eu$^{2+}$ fraction and the emission intensities of the phosphor with the increased Ce concentration. Their similar trend for the Ce concentrations proves that the luminescent enhancement mainly results from the increased number of Eu$^{2+}$ ions.

The above observation gives the following two questions: why does the valence state of Eu remain $3+$ despite the synthesis in a reducing atmosphere? Why do codoped Ce ions inhibit the oxidation of Eu$^{2+}$ or enhance the reduction of Eu$^{3+}$? To answer these, the effect of the Li vacancies ($V_{Li}^-$) should be considered, because the vacancies of alkali metals are easily formed during high temperature processes due to their high vapor pressure, and the defect conditions in crys-

![Fig. 1](image1.png)

FIG. 1. (Color online) PL (excited at 400 nm) and PLE (emitted at 586 nm) spectra of Li$_2$SrSiO$_4$:Ce$^{3+}$, 0.5%Eu$^{2+}$ ($x=0.0\%$, 0.2%, 0.4%, 0.6%, and 0.8%) (from bottom to top).

![Fig. 2](image2.png)

FIG. 2. (Color online) PL and PLE spectra of Li$_2$SrSiO$_4$:0.5%Eu$^{2+}$ (thin curves) and Li$_2$SrSiO$_4$:0.6%Ce$^{3+}$ (thick curves).

![Fig. 3](image3.png)

FIG. 3. (Color online) Decay curves of Eu$^{2+}$ emission (586 nm) excited at 450 nm in Li$_2$SrSiO$_4$:Ce$^{3+}$, 0.5%Eu$^{2+}$ ($x=0.0\%$, 0.2%, 0.4%, 0.6%, and 0.8%). Inset shows the fitted decay times of the samples.
and BaMgAl10O17:Eu2+

estimated with the first-principle calculations

of O vacancies, as observed by XANES of Eu ions

Ce can be identified as

vacancies by forming Eu3+ substitutions in Sr2+ sites instead

Eu ions are doped in the phosphor, they will stabilize Li

Li2SrSiO4 :

pair

cies, it will have O deficiencies as well and make a Schottky

Figure 4 shows the formation energies of several defect pairs in

Li2SrSiO4.

<table>
<thead>
<tr>
<th>Defect</th>
<th>Formation energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V Li+ + 1/2 V O</td>
<td>5.00</td>
</tr>
<tr>
<td>V Li+ + 1/2 V O + EuSr</td>
<td>5.53</td>
</tr>
<tr>
<td>V Li+ + EuSr</td>
<td>3.83</td>
</tr>
<tr>
<td>V Li+ + EuSr + CeSr</td>
<td>5.81</td>
</tr>
<tr>
<td>V Li+ + CeSr + EuSr</td>
<td>2.45</td>
</tr>
</tbody>
</table>

In summary, emission in Li2SrSiO4:Eu2+ is enhanced by increasing the amount of codoped Ce3+ ions. The energy transfer from Ce3+ to Eu2+ might not be related to the luminescence improvement. Through the decay time measurement and the valence state confirmation of Eu and Ce ions using XANES spectra, it was found that the enhancement might be attributed to the increased number of Eu2+ ions in the phosphor. For this, our explanation was that added Ce3+ ions prohibit the intrinsic Li vacancy from oxidizing Eu2+ to Eu3+ by compensating for the negative charge of the Li vacancy instead of Eu3+. This hypothesis was verified by comparing the formation energies of defect pairs, which were calculated via the first-principle calculations.

In summary, emission in Li2SrSiO4:Eu2+ is enhanced by increasing the amount of codoped Ce3+ ions. The energy transfer from Ce3+ to Eu2+ might not be related to the luminescence improvement. Through the decay time measurement and the valence state confirmation of Eu and Ce ions using XANES spectra, it was found that the enhancement might be attributed to the increased number of Eu2+ ions in the phosphor. For this, our explanation was that added Ce3+ ions prohibit the intrinsic Li vacancy from oxidizing Eu2+ to Eu3+ by compensating for the negative charge of the Li vacancy instead of Eu3+. This hypothesis was verified by comparing the formation energies of defect pairs, which were calculated via the first-principle calculations.

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10. See supplementary material at http://dx.doi.org/10.1063/1.3308486 for more information (Section S1, S2, S3, S4, and S5).