doi:10.1246/cl.2010.604

A New Type of Red-emitting (La,Ca)OCl:Eu^{3+} Phosphors

Sun Woog Kim, Kazuya Jyoko, Toshiyuki Masui, and Nobuhito Imanaka*
Department of Applied Chemistry, Faculty of Engineering, Osaka University,
2-1 Yamadaoka, Suita, Osaka 565-0871

(Received March 18, 2010; CL-100265; E-mail: imanaka@chem.eng.osaka-u.ac.jp)

Red-emitting phosphors, $(La_{1-x}Ca_x)OCl{:}y\%Eu^{3+}$ ($0 \le x \le 0.17$, $1 \le y \le 5$), were synthesized in a single-phase form by a liquid-phase method and photoluminescence properties were characterized. The excitation peak intensity of the phosphor was increased with Ca^{2+} doping into the LaOCl lattice, corresponding to the successful enhancement of the emission intensity. The maximum emission intensity was obtained for $(La_{1-x}Ca_x)OCl{:}y\%Eu^{3+}$, where it was 63% of that of a commercial $Y_2O_3{:}Eu^{3+}$ phosphor.

Phosphors have been applied in displays and lamps and are significantly important materials in our daily life. In order to design a phosphor of high luminescence efficiency, it is significant to select the crystal structure of the host material, because the luminescent properties of phosphors remarkably depend on the interaction with the environment around the excited activators. Generally, the luminescent emission intensity increases with increasing the amount of activator. However, an excess amount of it in the host lattice usually causes concentration quenching, because the decrease in the mean activator–activator distance often induces nonradiative deactivation. Therefore, it is significant to select the crystal structure to avoid the concentration quenching, even if enough activator is doped in the host material.[1]

In our previous studies, we designed red- and green-emitting phosphors based on rare earth oxycarbonate,[2–9] rare earth oxysulfate,[10] and zirconium oxide phosphate.[11] These phosphors form layered structures, in which the energy transfer from an excited luminescence ion to another across the anion groups (CO_3^{2-}, SO_4^{2-}, and PO_4^{3-}) is inhibited by the long distance, and accordingly, phosphors based on such layer structures should be resistant to concentration quenching. In the series of these phosphors, a green-emitting phosphor, $(Gd_{0.95}Y_{0.05})_2O_2CO_3{:}11\%Tb^{3+}$, exhibited the highest relative emission intensity, which was 131% of that of a commercial $LaPO_4{:}Ce^{3+},Tb^{3+}$.[9]

In the case of red-emitting phosphors, on the other hand, the maximum emission intensity compared with that of the commercial $Y_2O_3{:}Eu^{3+}$ phosphor was attained up to only 49%, which was observed in $Gd_2O_2SO_4{:}10\%Eu^{3+}$.[10] In order to enhance the red-emission intensity in the present study, we have focused on tetragonal PbFCl-type rare earth oxychloride, ROCl (R = rare earths), as a host material of the phosphor, because PbFCl-type rare earth oxychloride has a layer structure similar to those of the phosphors previously studied in our laboratory. In the rare earth oxychloride structure, the $(RO)_n^{n+}$ layers (R = rare earths) are separated by chloride anions in the direction to the *c* axis,[12–16] and the rare earth ions are surrounded by four O^{2-} and four Cl^- ions with the C_{4v} symmetry.[14] In the series of the rare earth oxychlorides, LaOCl has the highest thermal stability,[17] which is advantageous for obtaining phosphor particles of high crystallinity.

In this study, in order to further enhance the emission intensity, some of the La^{3+} ions in the LaOCl host lattice are substituted with Ca^{2+} ions. Since the ionic radius of Ca^{2+} (0.112 nm for 8 coordination)[18] is smaller than that of La^{3+} (0.116 nm for 8 coordination),[18] partial substitution of the La^{3+} site with Ca^{2+} results in the shrinkage of the oxychloride lattice, which will enhance the charge-transfer efficiency from O^{2-} to Eu^{3+}. Furthermore, smaller electronegativity of Ca^{2+} (1.00)[19] than that of La^{3+} (1.10)[19] will also contribute to promote the O^{2-} to Eu^{3+} charge transfer by the decrease in the electron attractive force of the host lattice cations. In the present study, therefore, red-emitting (La,Ca)OCl:Eu^{3+} phosphors were synthesized and the luminescent properties were characterized.

A stoichiometric mixture of La_2O_3, $CaCO_3$, and Eu_2O_3 was dissolved in 3 mol dm^{-3} aqueous HCl solution, adjusting the amount of Eu^{3+} between 1 and 5% and the amount of Ca^{2+} between 0 and 17%. The solvent water was evaporated at 170 °C for 12 h, and then the resultant powder was calcined at 700 °C for 12 h in air.

The samples were characterized by X-ray powder diffraction (XRD; Rigaku Multiflex) to identify the crystal structure, and the sample composition was analyzed by X-ray fluorescence spectroscopy (XRF; Rigaku ZSX100e). The mean particle size of the phosphors was estimated by measuring the diameters of 100 particles on the SEM photographs. Photoluminescence (PL) excitation and emission spectra were recorded at room temperature with a spectrofluorophotometer (Shimadzu RF-5300PC), where the emission spectra were obtained for excitation at 300 nm, and the excitation spectra were recorded for the emission peak at 617 nm. The relative emission intensity of the $(La_{1-x}Ca_x)OCl{:}Eu^{3+}$ phosphor was estimated by comparing the integrated area of the emission peak at 617 nm for Eu^{3+} with that of a commercial $Y_2O_3{:}Eu^{3+}$ phosphor.

The sample composition analyzed by XRF was confirmed for each sample to be stoichiometric as summarized in Table 1. X-ray powder diffraction (XRD) patterns for the $(La_{1-x}Ca_x)OCl{:}2\%Eu^{3+}$ ($0 \le x \le 0.17$) phosphors are shown in Figure 1. All the XRD patterns were attributed to be a single phase of tetragonal PbFCl-type rare earth oxychloride structure with high crystallinity, and no impurity phase was observed in these

Table 1. Theoretical and analyzed composition of the samples

Theoretical composition	Analyzed composition
LaOCl:2%Eu^{3+}	$(La_{0.98}Eu_{0.02})O_{1.2}Cl_{0.61}$
$(La_{0.95}Ca_{0.05})OCl{:}2\%Eu^{3+}$	$(La_{0.93}Ca_{0.05}Eu_{0.02})O_{1.19}Cl_{0.58}$
$(La_{0.90}Ca_{0.10})OCl{:}2\%Eu^{3+}$	$(La_{0.88}Ca_{0.10}Eu_{0.02})O_{1.13}Cl_{0.65}$
$(La_{0.85}Ca_{0.15})OCl{:}2\%Eu^{3+}$	$(La_{0.83}Ca_{0.15}Eu_{0.02})O_{1.08}Cl_{0.70}$
$(La_{0.83}Ca_{0.17})OCl{:}2\%Eu^{3+}$	$(La_{0.81}Ca_{0.17}Eu_{0.02})O_{1.07}Cl_{0.70}$

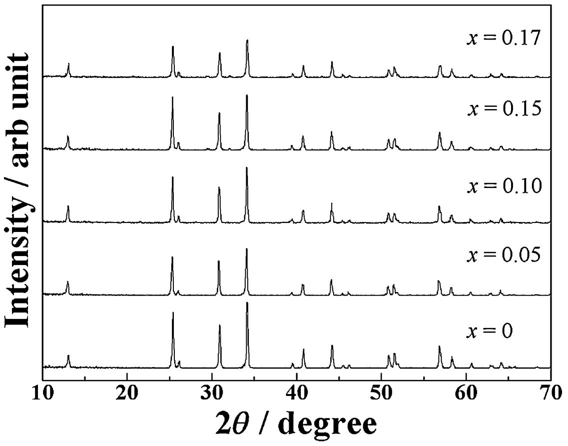

Figure 1. XRD patterns for the $(La_{1-x}Ca_x)OCl{:}2\%Eu^{3+}$ ($0 \leq x \leq 0.17$) phosphors.

Table 2. Lattice volume and particle size of the samples

Samples	Lattice volume ($\times 10^{-3}/nm^3$)	Particle size /μm
$LaOCl{:}2\%Eu^{3+}$	116.22	0.54
$(La_{0.95}Ca_{0.05})OCl{:}2\%Eu^{3+}$	116.05	2.53
$(La_{0.90}Ca_{0.10})OCl{:}2\%Eu^{3+}$	115.83	2.86
$(La_{0.85}Ca_{0.15})OCl{:}2\%Eu^{3+}$	115.58	3.64
$(La_{0.83}Ca_{0.17})OCl{:}2\%Eu^{3+}$	115.51	3.99

patterns. A peak shift to higher diffraction angle is observed with the increase in the amount of Ca^{2+} in the LaOCl lattice, because the La^{3+} site (0.116 nm)[18] in the host material is partially substituted with the smaller Ca^{2+} cation (0.112 nm)[18] to form solid solutions. The effect of the Ca^{2+} content on the lattice volume of the $(La_{1-x}Ca_x)OCl{:}2\%Eu^{3+}$ phosphors is summarized in Table 2. The lattice volume decreases monotonically with the increase in the Ca^{2+} content, which indicates that La^{3+} is partially substituted with Ca^{2+}. In addition, anion vacancies have to be produced within the lattice to maintain charge compensation, because Ca^{2+} has lower valence (divalent) than La^{3+} (trivalent).

Figure 2 illustrates the excitation spectra for the emission at 617 nm in the $(La_{1-x}Ca_x)OCl{:}2\%Eu^{3+}$ phosphor samples. The excitation spectra of all samples consist of strong broad bands from 230 to 350 nm, corresponding to charge-transfer state (CTS) between Eu^{3+} and O^{2-}. Some weak peaks between 350 and 500 nm correspond to the f–f transitions of Eu^{3+} ion between the ground state and the excited levels of $4f^6$ configuration. In addition, the peak position of the CT bands depends on the excitation energy for the electron transfer from O^{2-} to Eu^{3+} in $(La_{1-x}Ca_x)OCl{:}2\%Eu^{3+}$ phosphor. As mentioned above, the electronic attractive force between O^{2-} and La^{3+} is decreased by the Ca^{2+} doping into the LaOCl lattice, because of the lower electronegativity of Ca^{2+} (1.00)[19] than that of La^{3+} (1.10).[19] As a result, the excitation energy for the electron transfer from O^{2-} to Eu^{3+} becomes smaller than that before the Ca^{2+} substitution for La^{3+} in the oxychloride lattice. Therefore, the CT band of the $(La_{1-x}Ca_x)OCl{:}2\%Eu^{3+}$ phosphors shifts to the longer wavelength (lower energy) side with increasing the Ca^{2+} content.

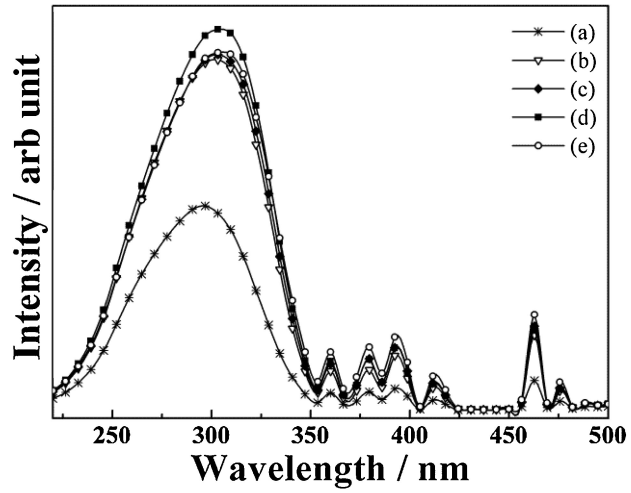

Figure 2. Excitation spectra of the $(La_{1-x}Ca_x)OCl{:}2\%Eu^{3+}$ phosphors; (a) $x = 0$, (b) 0.05, (c) 0.10, (d) 0.15, and (e) 0.17.

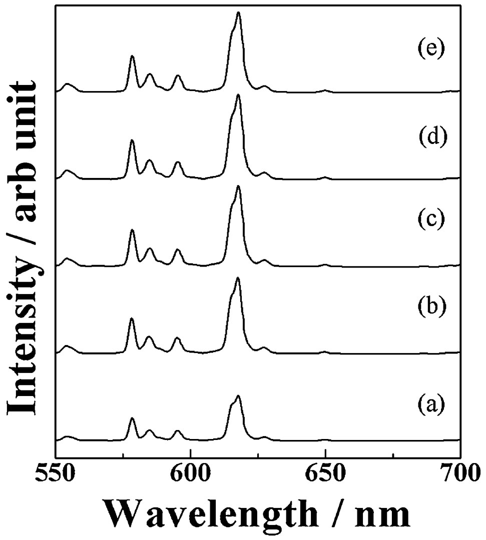

Figure 3. Emission spectra of the $(La_{1-x}Ca_x)OCl{:}2\%Eu^{3+}$ phosphors; (a) $x = 0$, (b) 0.05, (c) 0.10, (d) 0.15, and (e) 0.17.

Figure 3 depicts the emission spectra of the $(La_{1-x}Ca_x)OCl{:}2\%Eu^{3+}$ phosphors under excitation at 300 nm. All emission peaks correspond to the transition from the $^5D_0$ excited level to ^7F_J ($J = 0$, 1, 2, 3, and 4) ground levels of Eu^{3+}. Since the symmetric environment around the Eu^{3+} ions in the host oxychloride lattice is the same in the samples, the photoluminescent emission wavelengths of these phosphors are essentially equivalent, and there is no spectral shift due to the introduction of Ca^{2+} in host lattice.

However, a clear difference was observed in the emission peak intensities. Figure 4 shows the dependence of the emission intensity on the Eu^{3+} concentration in the $(La_{1-x}Ca_x)OCl{:}y\%Eu^{3+}$ ($0 \leq x \leq 0.17$, $1 \leq y \leq 5$) phosphors. The emission intensity was successfully enhanced by the Ca^{2+} doping into the LaOCl lattice. The increasing of the emission intensity can be attributed to the lattice shrinkage and decrease of

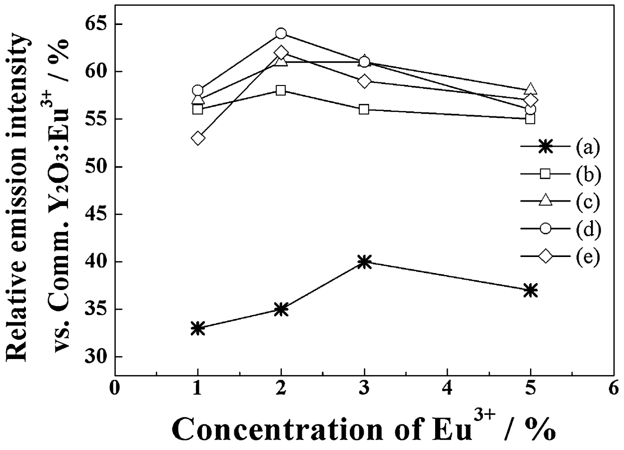

Figure 4. Dependence of the emission intensity on the Eu^{3+} concentration in the $(La_{1-x}Ca_x)OCl{:}y\%Eu^{3+}$ $(0 \le x \le 0.17, 1 \le y \le 5)$ phosphors; (a) $x = 0$, (b) 0.05, (c) 0.10, (d) 0.15, and (e) 0.17. The excitation wavelength is 300 nm for $(La_{1-x}Ca_x)OCl{:}y\%Eu^{3+}$ and 254 nm of $Y_2O_3{:}Eu^{3+}$.

electronegativity of the host cation, leading to the effective energy transfer from O^{2-} to Eu^{3+} as discussed above. In addition, it has also been suggested that oxide anion vacancies might act as a sensitizer for the energy transfer to the rare earth ion due to the strong mixing of CTS.[20–22] The f–f transition intensity is also largely influenced by the Ca^{2+} doping, because the mean particle size of the $LaOCl{:}Eu^{3+}$ phosphors was increased, as summarized in Table 2. The increase in the particle size contributes to the enhancement of the emission intensity.

The effect of Ca^{2+} doping is significant, but the excess amount of Ca^{2+} beyond the optimum concentration brings about an negative effect for the enhancement of the emission intensity. This is probably due to the imperfect atomic arrangement in the LaOCl host matrix, because the distortion in the host matrix leads to fluorescence quenching.[23] The ionic radius of Ca^{2+} (0.112 nm)[18] is smaller than that of La^{3+} (0.116 nm),[18] so that the excess Ca^{2+} doping should introduce extra strain into the LaOCl lattice. Therefore, emission quenching is induced beyond the optimum Ca^{2+} concentration.

The emission intensity also depends on the Eu^{3+} content. The luminescence emission intensity increases with the amount of Eu^{3+} until it reaches a maximum and then decreases due to the concentration quenching. The maximum emission intensity was obtained at a composition of $(La_{0.85}Ca_{0.15})OCl{:}2\%Eu^{3+}$, and the relative emission intensity was 63% that of the commercial $Y_2O_3{:}Eu^{3+}$ phosphor. The relative emission intensify is increased by 14% compared with that of the conventional layered structure $Gd_2O_2SO_4{:}10\%Eu^{3+}$ (49%) previously reported.[10]

In summary, red-emitting phosphors based on lanthanum–calcium oxychloride, $(La_{1-x}Ca_x)OCl{:}y\%Eu^{3+}$ $(0 \le x \le 0.17, 1 \le y \le 5)$, were synthesized by a liquid-phase method. The oxychloride phosphors with stable tetragonal PbFCl-type structure were obtained in a single phase. The photoluminescent intensity was effectively enhanced by the Ca^{2+} doping into the host $LaOCl{:}Eu^{3+}$ lattice. By the optimization of the composition, the maximum emission intensity was obtained for $(La_{0.85}Ca_{0.15})OCl{:}2\%Eu^{3+}$. The relative emission intensity was 63% compared with that of the commercial $Y_2O_3{:}Eu^{3+}$ phosphor. The optimum Eu^{3+} value in the present $(La_{1-x}Ca_x)OCl{:}y\%Eu^{3+}$ phosphors is 2–3%, which is not so different from that of the conventional $Y_2O_3{:}Eu^{3+}$ phosphor. However, the lattice volume of LaOCl (0.117 nm³) is about 1/10 of that of Y_2O_3 (1.19 nm³). This fact obviously gives evidence of the merit to form layered structure. In the present stage, unfortunately, more amount of Eu^{3+} than in the conventional phosphor could not be dissolved into the host LaOCl lattice without concentration quenching, but enhancement of the Eu^{3+} content can be expected by the expansion of the lattice volume of the host material. For example, partial substitution of Cl^- with larger Br^- would be one of the effective ways.

The present work was supported by a Grant-in-Aid for Scientific Research No. 21750207 from the Ministry of the Education, Culture, Sports, Science and Technology of Japan.

References

1 T. Honma, K. Toda, Z.-G. Ye, M. Sato, *J. Phys. Chem. Solids* **1998**, *59*, 1187.
2 S. Tamura, K. Koyabu, T. Masui, N. Imanaka, *Chem. Lett.* **2004**, *33*, 58.
3 T. Masui, Y. Mayama, K. Koyabu, N. Imanaka, *Chem. Lett.* **2005**, *34*, 1236.
4 T. Masui, K. Koyabu, S. Tamura, N. Imanaka, *J. Mater. Sci.* **2005**, *40*, 4121.
5 K. Koyabu, T. Masui, S. Tamura, N. Imanaka, *J. Alloys Compd.* **2006**, *408–412*, 867.
6 K. Koyabu, Y. Mayama, T. Masui, N. Imanaka, *J. Alloys Compd.* **2006**, *418*, 230.
7 Y. Mayama, K. Koyabu, T. Masui, S. Tamura, N. Imanaka, *J. Alloys Compd.* **2006**, *418*, 243.
8 Y. Mayama, T. Masui, K. Koyabu, N. Imanaka, *J. Alloys Compd.* **2008**, *451*, 132.
9 S. W. Kim, T. Masui, H. Matsushita, N. Imanaka, *J. Electrochem. Soc.* **2010**, *157*, J181.
10 S. W. Kim, T. Masui, N. Imanaka, *Electrochemistry* **2009**, *77*, 611.
11 S. W. Kim, T. Masui, H. Matsushita, N. Imanaka, *Chem. Lett.* **2009**, *38*, 1100.
12 J. Hölsä, P. Porcher, *J. Chem. Phys.* **1981**, *75*, 2108.
13 U. Rambabu, A. Mathur, S. Buddhudu, *Mater. Chem. Phys.* **1999**, *61*, 156.
14 J. Hölsä, M. Lahtinen, M. Lastusaari, J. Valkonen, J. Viljanen, *J. Solid State Chem.* **2002**, *165*, 48.
15 S.-S. Lee, H.-I. Park, C.-H. Joh, S.-H. Byeon, *J. Solid State Chem.* **2007**, *180*, 3529.
16 G. Li, C. Li, C. Zhang, Z. Cheng, Z. Quan, C. Peng, J. Lin, *J. Mater. Chem.* **2009**, *19*, 8936.
17 W. W. Wendlandt, *J. Inorg. Nucl. Chem.* **1957**, *5*, 118.
18 R. D. Shannon, *Acta Crystallogr., Sect. A* **1976**, *32*, 751.
19 A. L. Allred, *J. Inorg. Nucl. Chem.* **1961**, *17*, 215.
20 O. A. Lopez, J. McKittrick, L. E. Shea, *J. Lumin.* **1997**, *71*, 1.
21 J.-C. Park, H.-K. Moon, D.-K. Kim, S.-H. Byeon, B.-C. Kim, K.-S. Suh, *Appl. Phys. Lett.* **2000**, *77*, 2162.
22 B. Liu, M. Gu, X. Liu, C. Ni, D. Wang, L. Xiao, R. Zhang, *J. Alloys Compd.* **2007**, *440*, 341.
23 M. K. Chong, K. Pita, C. H. Kam, *Appl. Phys. A: Mater. Sci. Process.* **2004**, *79*, 433.