The Crystal Structure and Photoluminescence Properties of a New Red Phosphor, Calcium Aluminum Silicon Nitride doped with Divalent Europium

K. Uheda[1)], N. Hirosaki[2)], H. Yamamoto[1)] H. Yamane[3)]
Y. Yamamoto[2)], W. Inami[4)], K. Tsuda [4)]
[1)] School of Bionics, Tokyo University of Technology
1404-1 Katakura, Hachioji, Tokyo 192-0982, Japan
uheda@bs.teu.ac.jp
[2)] Advanced Materials Laboratory
National Institute for Materials Science (NIMS)
[3)] Center for Interdisciplinary Research, Tohoku University
[4)] Institute of Multidisciplinary Research for Advanced Materials, Tohoku University

The white-LED composed of a blue LED combined with a yellow phosphor can be an excellent light source, e.g. for the LCD backlight. They have, however, a serious problem of poor color rendering when used as the backlight of full color LCDs, because they lack a red component. The problem is caused by a fact that there have been no red phosphors of oxides or oxysulfides, which show an efficient red emission under the blue light excitation of 450 nm. Accordingly, we have selected a nitride as a host lattice and developed a new, red phosphor by using Eu^{2+} as an activator. This paper introduces an efficient and stable red phosphor, $CaAlSiN_3:Eu^{2+}$.

The starting materials, Ca_3N_2, AlN, Si_3N_4 and EuN, were mixed in the molar ratio of $1-x:1:1:x$ ($0 \leq x \leq 1$), and then the mixed powder was pressed into a pellet in nitrogen atmosphere. $CaAlSiN_3:Eu^{2+}$ was obtained by firing the pellet at 1600 ºC for 2 h and subsequently at 1800 ºC for 2 h under nitrogen pressure of 1MPa.

The host lattice, $CaAlSiN_3$ (orthorhombic, $Cmc2_1$ (#36), a = 980.07(4), b = 564.97(2), c = 506. 27(2), Z = 4, R_p = 7.06, R_{wp} = 9.50) has an isotypic structure with $NaSi_2N_3$[I)] and $MgAlSiN_3$[II)]. Six MN_4 (M=Al, Si) tetrahedra form a ring by sharing the corner with each other. A Ca^{2+} ion is located at the center of the ring. The 6-memberd M-N rings form a sheet by linking together parallel to *a*-*b* plane (Fig. 1(a)). As shown in Fig. 1 (a) to (c), the sheets stack in the crystal by 2_1 rotating along *c*-axis alternately. Eu^{2+} ions doped in $CaAlSiN_3$ also occupy a part of the Ca site.

The emission spectrum of $CaAlSiN_3:Eu^{2+}$ is shown in Fig. 2. A broad band peaked around 650 nm is observed. This band can be assigned to the 5d-4f transition of Eu^{2+} ions. Meanwhile, the excitation spectrum is composed of a host absorption in the region below 250 nm and the 4f-5d absorption of Eu^{2+} from 330 to 480 nm. Consequently $CaAlSiN_3:Eu^{2+}$ shows intense red emission when irradiated by a blue (450 nm) or violet (405 nm) LED. The new red phosphor can be applied to the backlight of LCDs as well as to general lighting.

I) H. Jacobs; H. Mengis, *Eur. J. Solid State Inorg. Chem.*, 30 (1993) 45. II) R.K. Harris; M.J. Leach, *Chem. Mater.*, 4 (1992) 260

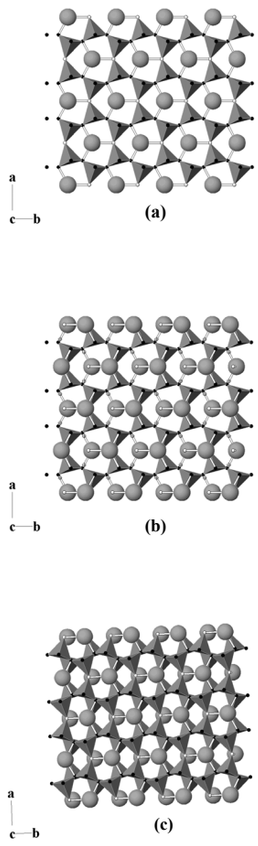

Fig. 1 The crystal structure of $CaAlSiN_3$.

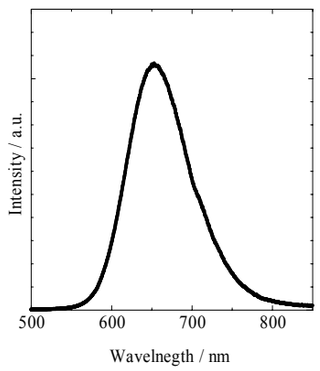

Fig. 2 The emission spectrum of Eu^{2+} ion in $CaAlSiN_3$ at room temperature

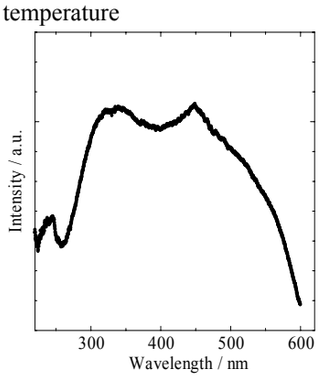

Fig. 3 The excitation spectrum of $CaAlSiN_3:Eu^{2+}$ at room temperature