Narrow-Band Blue Emitting Phosphor $Ca_8Mg_7Si_9N_{22}:Eu^{2+}$ for pc-LEDs

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Electronic Supplementary Information (ESI):

Experimental section

Sample Preparation

$Ca_8Mg_7Si_9N_{22}:Eu^{2+}$ phosphors were prepared by a solid state reaction in a gas pressure sintering furnace (ZTQ-45-20, Shanghai chenhua electric furnace co. LTD) under 1 MPa N_2/H_2 (90:10) atmosphere. The starting materials include Ca_3N_2 (AR), amorphous Si_3N_4 (Alfa 95%), Mg powder (AR) and EuF_2 (Alfa 99.5%). The raw materials were mixed in an agate mortar and filled into tungsten crucibles under argon atmosphere in a glovebox (Beijing Mikrouna Mech.Tech.Co.Ltd, O_2 < 1 ppm, H_2O < 1 ppm). The tungsten crucibles were placed in the gas pressure sintering furnace and heated to 1550 °C with a rate of 400 °C/h, which maintained at that temperature for 6h and then followed by cooling down to 1000 °C at a rate 1 °C/min. After reaction, the furnace cooled to room temperature spontaneously with power switch off and the tungsten crucibles were opened in glovebox.

Characterization

X-ray diffraction (XRD) measurements were examined at ambient temperature on a Rigaku MiniFlex600 diffractometer (Japan) using a 0.4 deg min^{-1} scan speed, which were operated at 40 kV, 15 mA. The XRD patterns were recorded over the 2θ ranges from 10° to 120° in a step-mode with 0.01° step length. The Rietveld refinement on XRD data was performed by using the software TOPAS 5. Chemical component analyses were performed by a scanning electron microscopy (SEM, FEI Q25) with energy dispersive X-ray spectroscopy (EDX) (EDAX, Element System). The diffuse reflection spectrum was collected by a UV-3600 UV-vis-NIR spectrometer (Shimadzu, Japan) using the white powder $BaSO_4$ as a standard material. The PL and photoluminescence excited

(PLE) spectra were measured by powder samples at room temperature using a Hitachi F-4600 fluorescent spectrophotometer (Japan) with a 150 W Xe lamp as excitation source. High temperature PL spectra were investigated between 300K and 700K by using a charge coupled device (CCD) (Andor DU401A-BVF) with the excitation source of an *Opolette* ™ 355 LD laser, which has a spectral line-width of 4–7 cm^{-1} and a pulse duration of 7 ns. The controlling of temperature (300-700K) was realized using a temperature controller (OMRON E5CC-800) with a type-K thermocouple and a heating tube. The luminescence decay curve was measured by using a life time and steady state spectrometer (FLS1000, Edinburgh Instruments Ltd).

DFT Calculation

The DFT calculation of $Ca_8Mg_7Si_9N_{22}$ was performed with the Cambridge Serial Total Energy Package (CASTEP) code, in which plane wave basis set was chosen for the expansion of valance-electron wave functions at the local density approximation (LDA) level. There are two steps of calculations to obtain the electronic band structure of $Ca_8Mg_7Si_9N_{22}$. The first step was to optimize its crystal structure beginning with the crystallographic data refined from the XRD data by the Broyden-Fletcher-Goldfarb-Shannon (BFGS) method. In order to avoid calculation error, co-occupied $Si2_{0.125}/Mg1_{0.875}$ site were separated by reducing the space group symmetry to P1 (No.1). The second step was to calculate the band structure and density of states (DOS). For the calculations, energy cutoff of plane wave basis set was selected as 340 eV, and K -point sampling was chosen as 2 × 2 × 2 Monkhorst-Pack grid (separation ~0.04 $Å^{-1}$). Criterion for the self-consistent field (SCF) was eigenenergy convergence within 1.0×10^{-7} eV/atom. Pseudopotential of each atom was constructed from the CASTEP database.

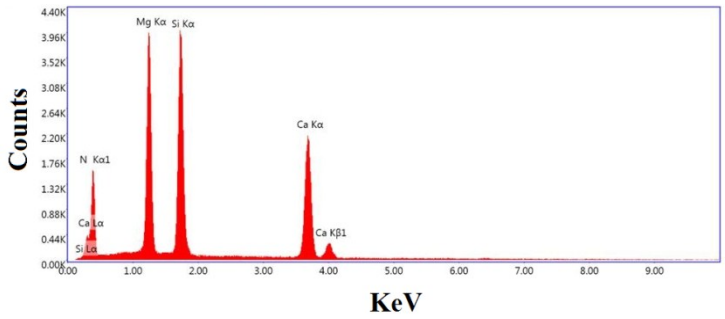

Fig. S1 The EDX spectrum of $Ca_8Mg_7Si_9N_{22}$.

Table S1 The EDX Results on Different Particles

Elements / No.	Ca%	Mg%	Si%	N%
1	15.15	15.43	15.48	53.94
2	16.39	16.5	15.52	51.59
3	14.48	15.87	14.53	55.12
4	14.85	16.71	15.63	52.81
5	15.93	16.98	15.98	51.11
Average	15.36	16.30	15.43	52.91

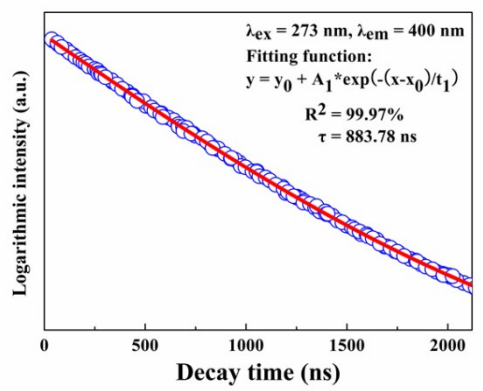

Fig. S2 The luminescence life decay curves of $Ca_{7.95}Mg_7Si_9N_{22}$:0.05Eu^{2+} phosphor monitored at λ_{ex} = 273 nm and λ_{em} = 400 nm.

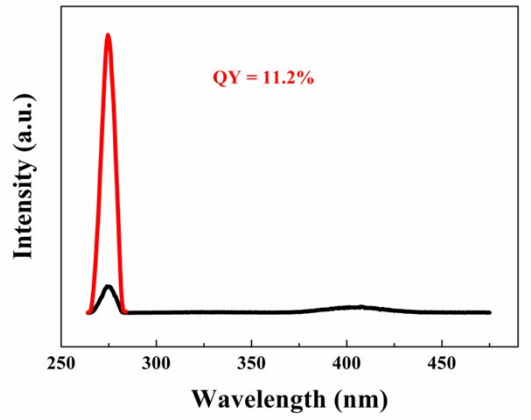

Fig. S3 The absolute quantum efficiency of the $Ca_{7.95}Mg_7Si_9N_{22}$:0.05Eu^{2+} phosphors.