Electronic Supplementary Information (ESI)

Fabrication of Amorphous Phase Encrusted Oxynitride Phosphor for White-light Emission via In-situ Penetration

Zhi-yong Mao,[a] Ying-chun Zhu,*[a] Lin Gan,[a] Fang-fang Xu,[a] Yang Wang[a] and Da-jian Wang*[b]

1. Experimental Procedure

1.1 Preparation

Amorphous phase encrusted oxynitride phosphor with white-light emission was prepared by two steps. Firstly, the yellow-emitting $Ca_{0.98}Si_9Al_3ON_{15}$: $0.02Eu^{2+}$ (denoted as Ca-SiAlON: Eu^{2+} in the manuscript) phosphor was synthesized by high temperature solid-state synthesis procedure. The stoichiometric amounts of starting materials α-Si_3N_4 (99.99%), AlN(99.99%), Eu_2O_3 (99.99%), $CaCO_3$ (99.99%) with the desired chemical formula and doped concentration were mixed properly in an agate mortar and then filled into BN crucible. The mixture of starting material was fired at 1700 ^{0}C for 4 h under N_2 atmosphere in a high-frequency induction furnace with a graphite heater. Secondly, blue-emitting amorphous phase was assembled on the surface of as-prepared Ca-SiAlON: Eu^{2+} yellow-emitting phosphor by a simple heat-treatment procedure, i.e. the Ca-SiAlON: Eu^{2+} yellow phosphor was mixed with SiO_2 nanopowder (99.9%, 15±5 nm) in a proportion of 3:1 in weight thoroughly then heated rapidly at different temperatures from 1200 ^{0}C to 1400 ^{0}C for 30 min under N_2 atmosphere in a high-frequency induction furnace with a graphite heater. The heating power was set to be the desired values directly in terms of the calibrated power-temperature relation (1200 ^{0}C ~ 6.5 KW, 1300 ^{0}C ~7 KW and 1400 ^{0}C ~7.5 KW) of this high-frequency induction furnace. Upon holding the sample at the goal temperature for 30 mins, the power of the furnace was cut off immediately and cools down naturally. In this way, the heating rate up to some desired holding temperature was roughly estimated to be around 250 ^{0}C /min while the cooling rate was estimated to be around 30^{0}C /min. For comparison, counterpart samples treated at the same temperatures without the addition of SiO_2 nanopowder were prepared in the same procedure.

1.2 Characterization

X-ray diffraction (XRD) patterns were recorded on a diffractometer (RINT 2200) to identify the phase component of as-prepared samples. SEM images and element analysis of as-obtained samples are obtained on a JSM-6700F field emission scanning electron microscope. FTIR analysis was carried out using KBr discs on a SHIMADZU (IR Prestige-21). HRTEM images and the SAED pattern are preformed on a JEM-2100F transmission electron microscope equipped with an X-ray EDS. The photoluminescence (PL) and photoluminescence of excitation (PLE) of our obtained luminescence materials were measured on FluoroMax®-4 fluorescence spectrometer. CIE chromaticity coordinates were traced on a PMS-80 Plus UV-Vis-Near IR Spectro-photocolorimeter (EVERINE, China) system with a phosphor excitation equipment. The photographs of the illuminated phosphor and their single-particle photo under UV radiation were taken using a digital camera (FinePix S1770, Japan) and a fluorescence microscope (DFM-40C， China) respectively.

2 XRD Patterns

The XRD patterns of as-prepared samples are demonstrated in Fig. ESI-1, which demonstrates Ca-SiAlON: Eu^{2+} sample possesses the dominated phase of α-SiAlON as identified with the JCPDS card (No.33-0261). SiO_2 induced sample at 1200 °C maintains the main phase of α-SiAlON. Distinct diffraction peaks of O-SiAlON and β-SiAlON phases occur for samples as obtained above 1200 °C. It is worthy to note that the diffraction intensity of SiO_2 induced samples lower than that of Ca-SiAlON: Eu^{2+} sample implies the decrease of crystallization. In other words, amorphous phase may present in SiO_2 induced samples. Impurity phases and decrease of diffraction intensity are not detected for those counterpart samples, revealing that impurity phases or/and amorphous phase have been introduced for SiO_2 induced samples with the addition of SiO_2.

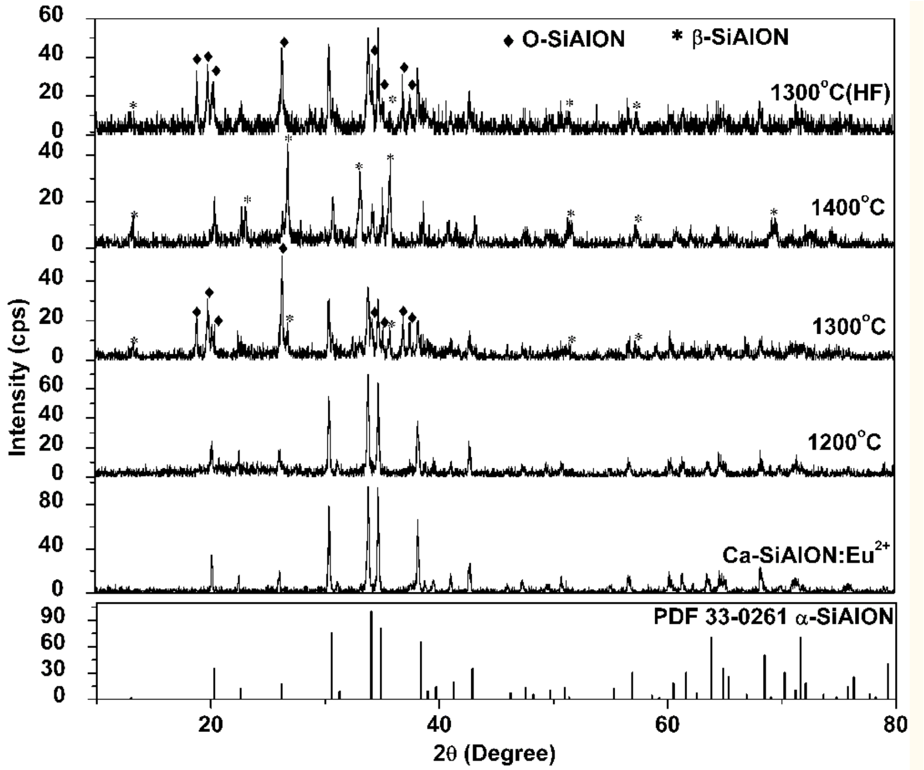

Fig. ESI-1. The XRD patterns of as-prepared samples and that of HF soaked sample.

3 FTIR spectra of Ca-SiAlON: Eu^{2+} sample and that of SiO_2 induced sample (1300 °C)

The absorption band from 700 to 1200 cm^{-1} is assigned to the Si-O stretching vibration (1090 cm^{-1}), overlapping that of the Si-N stretching vibration (860 cm^{-1}) of $[Si(O,N)_4]$-tetrahedra; Absorption peaks at 670, 560, 517, 480, 420 cm^{-1} are associated with the Al-N, Si-O, Al-O, Si-O, Ca-O bond respectively. The Si-O stretching vibration increases whereas Si-N stretching vibration decreases for SiO_2 induced sample compared with that of Ca-SiAlON: Eu^{2+} sample, indicating a partial replacement of Si-N bond in $[Si(O,N)_4]$-tetrahedra by incorporated Si-O bond. Meanwhile, those oxygen-related vibration modes in short wavenumber region show a strong absorption and shifts towards a smaller wavenumber compared with those for Ca-SiAlON: Eu^{2+} sample, probably indicating the incorporation of oxygen in Ca-SiAlON network. These shifts of O-related and N-related vibration modes provide evidence for the incorporation of SiO_2 in Ca-SiAlON network but not simply attached on the surface of Ca-SiAlON.

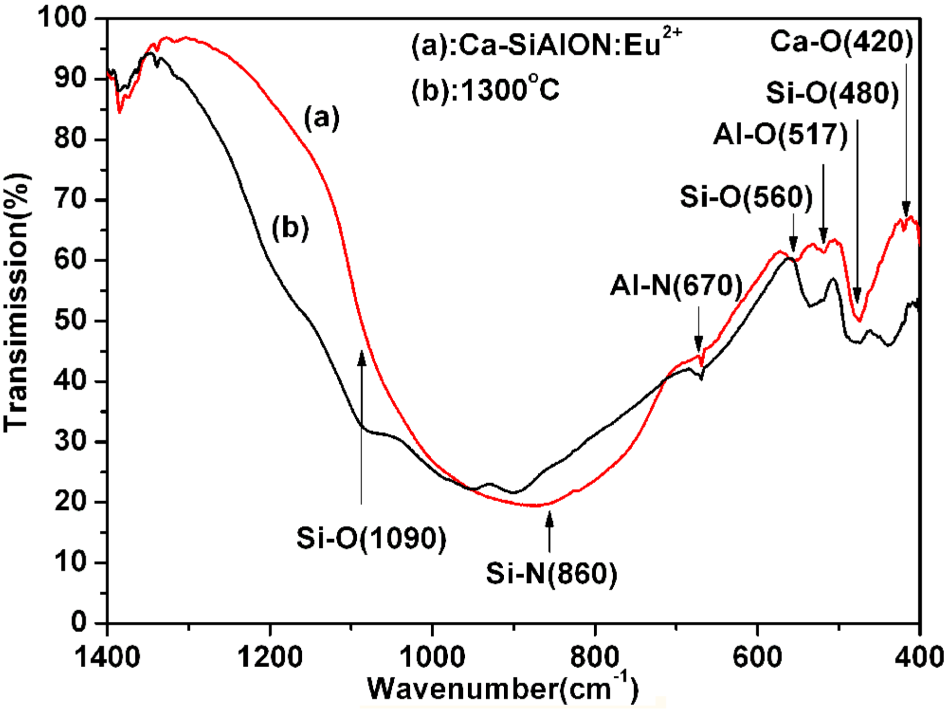

Fig. ESE-2 FTIR spectra of Ca-SiAlON: Eu^{2+} sample and SiO_2 induced sample at 1300 °C.

4 PLE spectrum

Figure S4 shows the PLE spectrum monitored at blue and yellow emission peaks for direct white light sample (1300 °C). It is observed that the yellow emission can be excited by UV-blue light (250 nm - 500 nm) whereas blue emission can be pumped by UV light (250 nm - 420 nm) efficiently. A compromising exists in the excitation diversity of blue and yellow emission and UV light in the wavelength range from 300 nm to 400 nm could be the optimal pump source for this phosphor to generate white light emission.

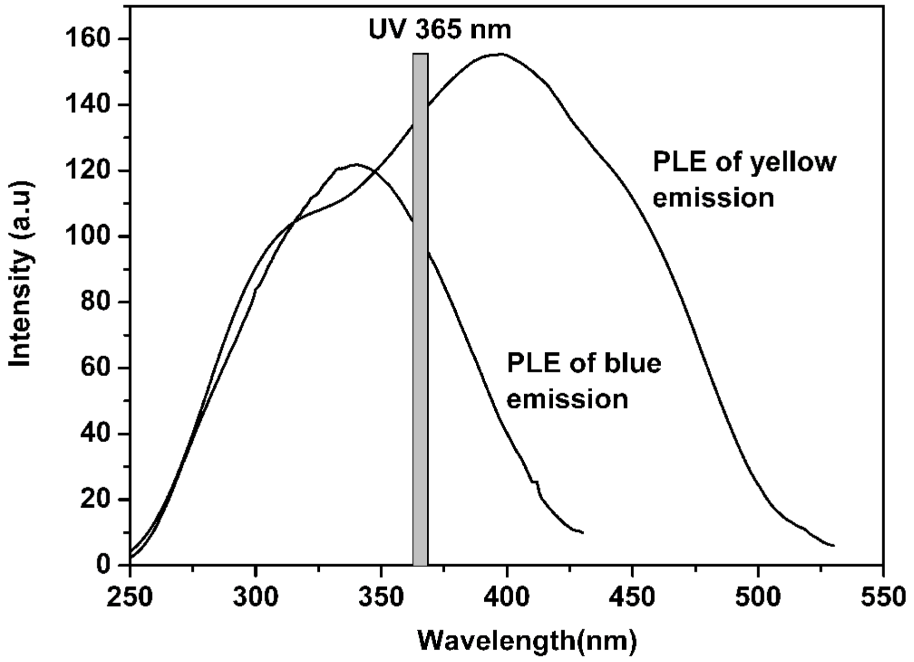

Fig. ESI-3 The PLE spectra monitored at blue and yellow emission peaks for SiO_2 induce sample at 1300°C.