Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supporting Information

A novel $Na_3La(PO_4)_2/LaPO_4$:Eu blue-red dual-emitting phosphor with high thermal stability for plant growth lighting

Mao Xia[a,b,c,&], Xianbo Wu[a,b,&], Yuan Zhong[a,b], Zhi Zhou*[a,b], Wai-Yeung Wong*[d]

a. College of Science, Hunan Agricultural University, Changsha, 410128, P.R. China.

b. Hunan Provincial Engineering Technology Research Center for Optical Agricultural, Hunan Agricultural University, Changsha, 410128, P.R. China.

c. State Key Laboratory of Powder Metallurgy, Central South University, Changsha, Hunan 410083, P.R. China

d. Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Hong Kong, P.R. China.

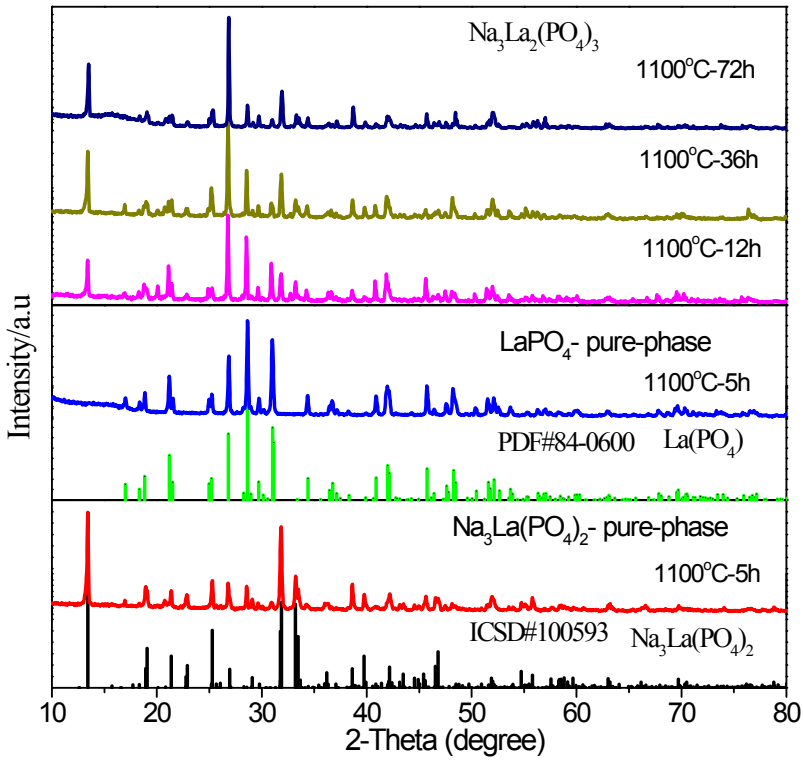

Fig.S1. XRD pattern of pure-phase $LaPO_4$, pure-phase $Na_3La(PO_4)_2$, and three samples of diphasic phosphors at different sintering time.

In order to obtain the pure-phase $Na_3La_2(PO4)_3$, we have tried other sintering

condition, including two-step method. First, to prepare pure-phase $Na_3La(PO_4)_2$ and $LaPO_4$, the reactions involved are as follows:

$3Na_2CO_3 + La_2O_3 + 4NH_4H_2PO_4 \rightarrow Na_3La(PO_4)_2 + 3CO_2 + 4NH_3 + 6H_2O$ (1)

$La_2O_3 + 2NH4H_2PO_4 \rightarrow 2LaPO_4 + 2NH_3 + 3H_2O$ (2)

Then, $Na_3La(PO_4)_2$ and $LaPO_4$ were mixed by stoichiometric ratio, boric acid acting as flux was added, and the mixture was sintered for 12 h, 36 h and 72 h. The XRD patterns are shown in Fig. S1. The three samples are all composed of $Na_3La(PO_4)_2$ and $LaPO_4$ phases. The crystallinity of samples changes with the increase of calcination time, but there was no new phase formed. Results indicates that the reaction (3) did not happen.

$Na_3La(PO_4)_3 + LaPO_4 \rightarrow Na_3La_2(PO_4)_3$ (nonreactive) (3)

Thus, we conclude that $Na_3La(PO_4)_2$ did not react with $LaPO_4$, and no $Na_3La_2(PO_4)_3$ phase was formed.

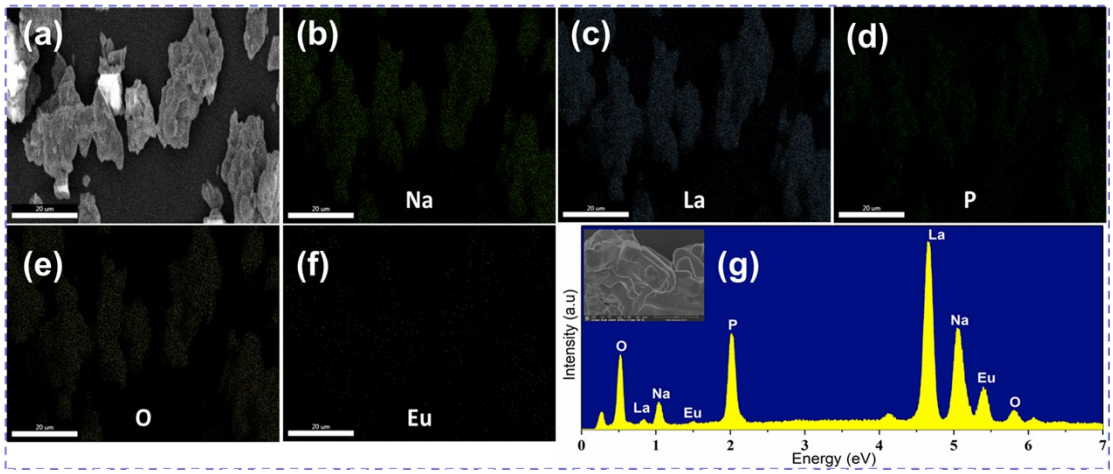

Fig. S2. (a) SEM image, (b-f) elemental mapping and (I) EDX spectrum of NLP:0.02Eu phosphors.

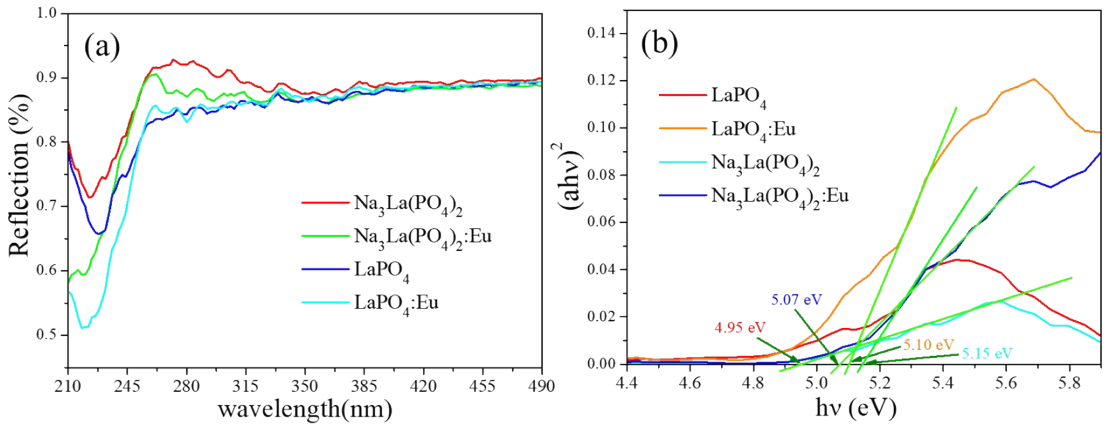

Fig. S3 (a) Diffuse reflection spectra of $LaPO_4$, $LaPO_4$:Eu, $Na_3La(PO_4)_2$ and $Na_3La(PO_4)_2$:Eu samples. (b) the plot of $(ahv)^2$ versus hv based on the samples.

According to the diffuse reflection spectra, the band gap of pure-phase $LaPO_4$, $LaPO_4$:Eu, $Na_3La(PO_4)_2$ and $Na_3La(PO_4)_2$:Eu samples were calculated to be 5.15, 5.10, 4.95 and 5.07 eV, respectively, as shown in **Fig. S3**. In pure-phase $LaPO_4$ and $Na_3La(PO_4)_2$, the band gap after Eu-doping showed little change ($LaPO_4$, reduce from 5.15 to 5.10 eV; $Na_3La(PO_4)_2$, increase from 4.95 to 5.07 eV)

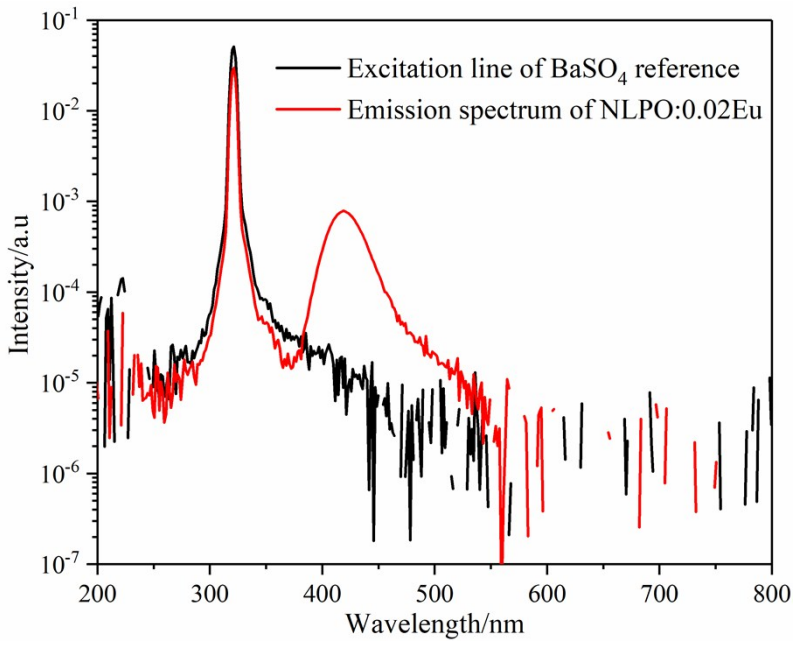

Fig. S4. Excitation line of $BaSO_4$ reference and emission spectrum of NLP:0.02Eu phosphor characterized by using an integrating sphere.

For photo-luminescence application, the importance of quantum efficiency (QE) should be considered. According to the method described by De Mello et al., QE can be calculated by the following equation:[1]

$$\eta = \frac{\int L_S}{\int E_R - \int E_S}$$

where L_S is the emission of the sample, E_S equals to the spectrum of the sample excited by the light, and E_R represents the spectrum of the excitation light without the sample. The results are listed in Fig. S3. Under 266 nm excitation, the calculated QE of NLP: 0.02Eu is 39.70%.

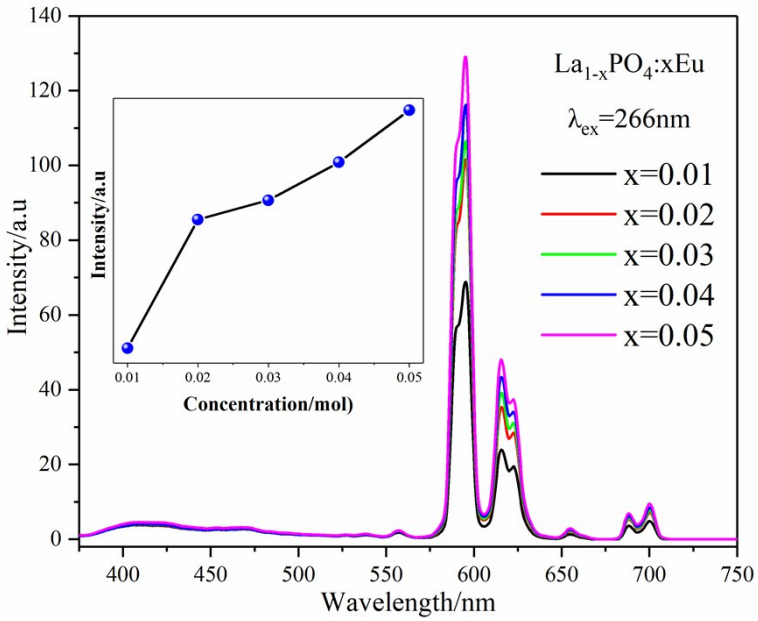

Fig. S5. Emission spectra (λ_{ex} = 266 nm) of $La_{1-x}PO_4$:xEu phosphors.

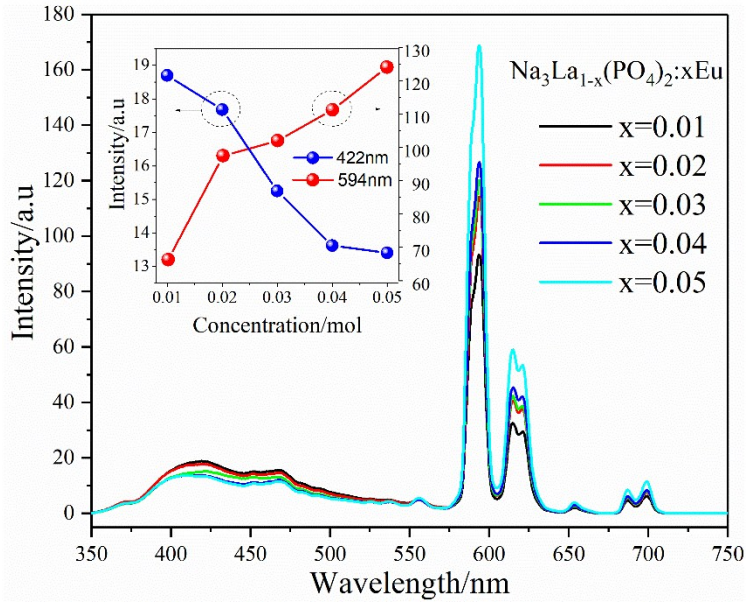

Fig. S6. Emission spectra (λ_{ex} = 266 nm) of $Na_3La_{2-x}(PO_4)_3$:xEu phosphors.

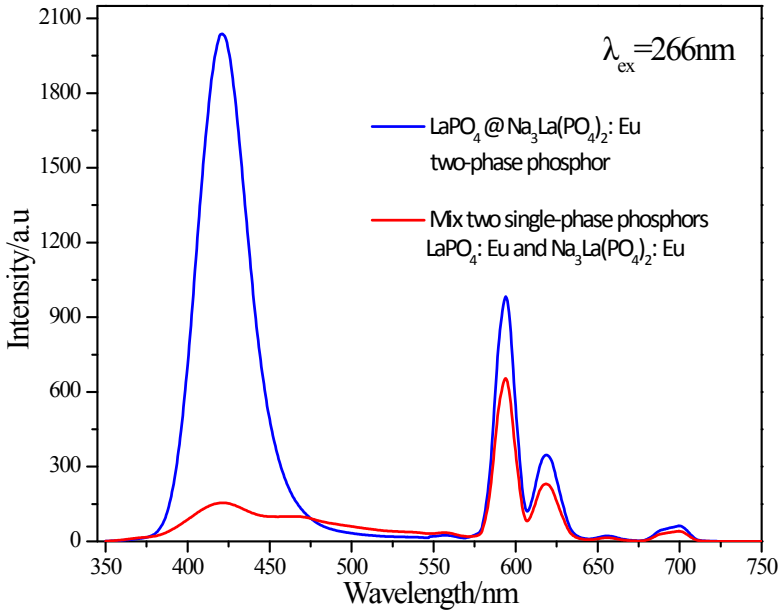

Fig. S7. The emission spectra of $LaPO_4$ @$Na_3La(PO_4)_2$:Eu two-phase phosphor (blue line) and mix the two single-phase phosphors $LaPO_4$:Eu and $Na_3La(PO_4)_2$:Eu (red line).

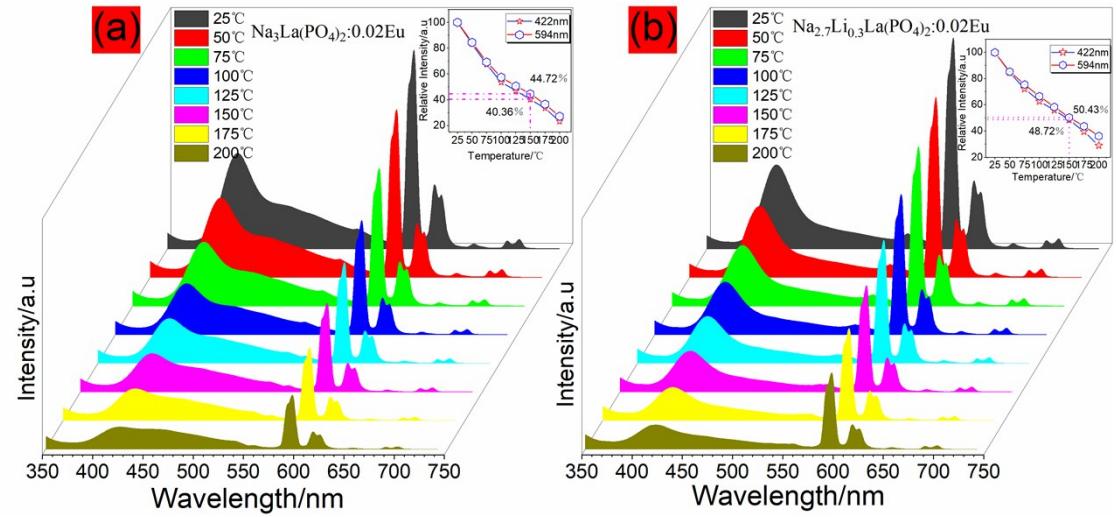

Fig. S8. The temperature dependent spectrum of (a) $Na_3La(PO_4)_2$:0.02Eu and (b) $Na_{2.7}Li_{0.3}La(PO_4)_2$:0.02Eu phosphor excited at 266 nm. The illustration shows the variety of relative luminescence intensity at 422 nm and 594 nm with temperature.

Notes and references

1. L.O. P.Lsson and A. P. Monkman, *Adv Mater*, 2002, **14**, 757-758.