ADVANCED OPTICAL MATERIALS

Supporting Information

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Efficient Super Broadband NIR $Ca_2LuZr_2Al_3O_{12}:Cr^{3+},Yb^{3+}$ Garnet Phosphor for pc-LED Light Source toward NIR Spectroscopy Applications

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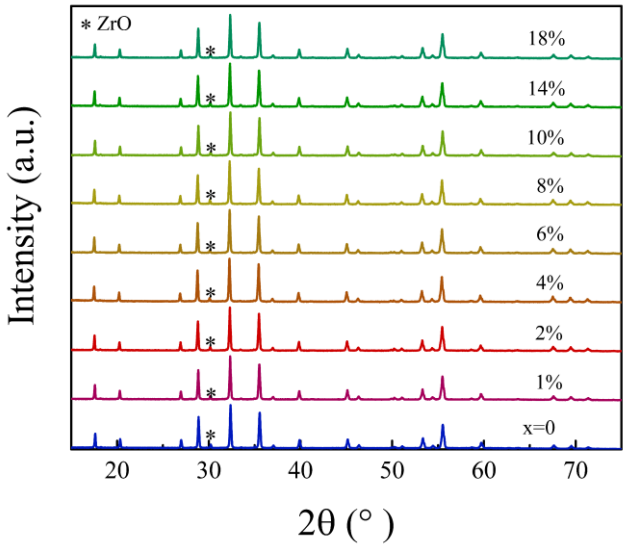

Figure S1. The XRD patterns of CLZA: 8%Cr, xYb (x= 0-0.18).

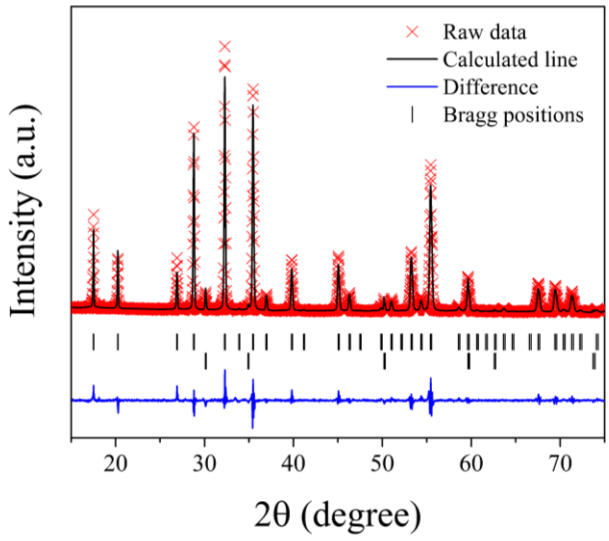

Figure S2. Rietveld refinement data of CLZA: 8%Cr, 4%Yb

Phase: 1 CLZA: 8%Cr, 4%Yb			
Space group: Ia$\bar{3}$d		**Crystal system Cubic**	
a = b = c: 12.39927	**Vol: 1906.285 (0.112)**	**Fract (%): 97.18 (1.16)**	
Rp: 6.64	**Rwp: 8.48**	**Rexp: 4.32**	**Chi2: 3.86**

Table S1. Rietveld refinement data of CLZA: 8%Cr, 4%Yb

NAME	X	Y	Z	B	OCC	MULT
CA1	0.25000	0.12500	0.00000	1.000	0.167	24
LU1	0.25000	0.12500	0.00000	1.000	0.080	24
ZR1	0.00000	0.00000	0.00000	1.000	0.142	16
AL2	0.25000	0.37500	0.00000	0.000	0.250	24
O1	0.03413	0.05509	0.65608	0.000	1.000	96
YB1	0.25000	0.12500	0.00000	1.000	0.003	24
CR1	0.00000	0.00000	0.00000	0.413	0.025	16

Table S2. Atomic parameters of CLZA: 8%Cr, 4%Yb

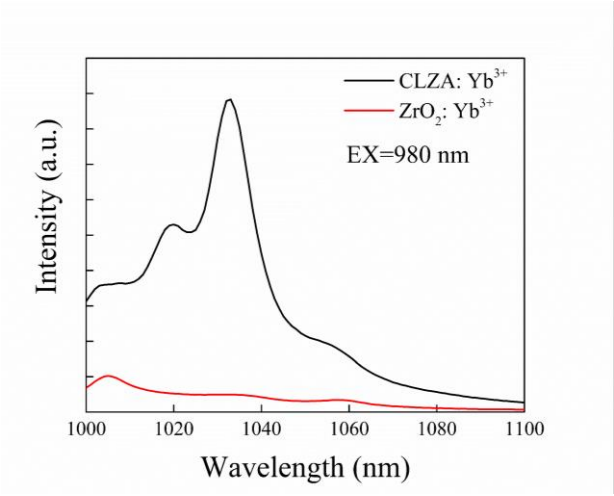

Figure S3. The PL spectra of CLZA: 1%Yb^{3+} and ZrO_2: 1%Yb^{3+}.

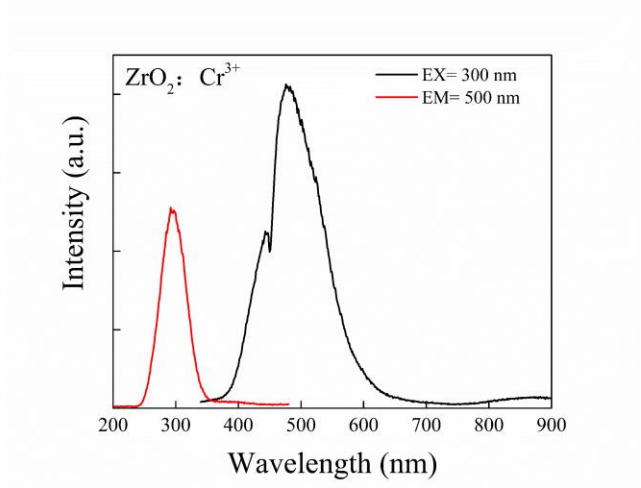

Figure S4. The PL and PLE spectra of ZrO_2:Cr^{3+}.

The XRD patterns of CLZA: Cr, xYb (x= 0-0.18) and the peaks of those diffract grams are shown in Figure S1. In general, the difference between radius of Lu^{3+} (0.977 Å) and Yb^{3+} (0.985 Å) is very small. So, we consider the Yb^{3+} mostly hold the site of Lu^{3+}. Although the Yb^{3+} may hold the site of Zr^{4+}, the XRD diffraction peaks did not show obvious shift with the increasing of Yb^{3+} concentration. To examine the effect of ZrO_2 impurity on the luminescence properties, we prepared ZrO_2:Yb^{3+} and ZrO_2:Cr^{3+}. Their PL spectra were measured and shown in the follow figures (added in SI). It can be seen the emission intensity of Yb^{3+} in ZrO_2: 1%Yb^{3+} was much lower than the emission intensity of Yb^{3+} in CLZA:1%Yb^{3+}. And the emission of Cr^{3+} in ZrO_2:Cr^{3+} was not be detected. For that, one possible reason may be hardly substation of Cr^{3+} for Zr^{4+}. The emission around 500 nm is originated from the host lattice of ZrO_2 with the excitation band at 300 nm. It indicated that the ZrO_2 cannot excited by the blue light around 455 nm. And the visible emission of ZrO_2 was not affect for the NIR emission. Hence, a small quantity of impurity phases negligibly affects the luminescence properties. However, trace unreacted ZrO_2

in the sample will decrease emission intensity, it is necessary to avoiding the ZrO_2 in preparation in the future.

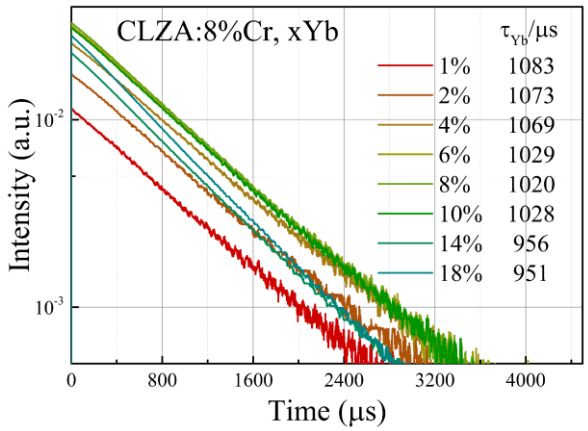

Figure S5. Decay curves of Yb^{3+} emission in the CLZA: 8%Cr, xYb (x= 0-0.18) phosphors after pulse excitation at 460 nm.

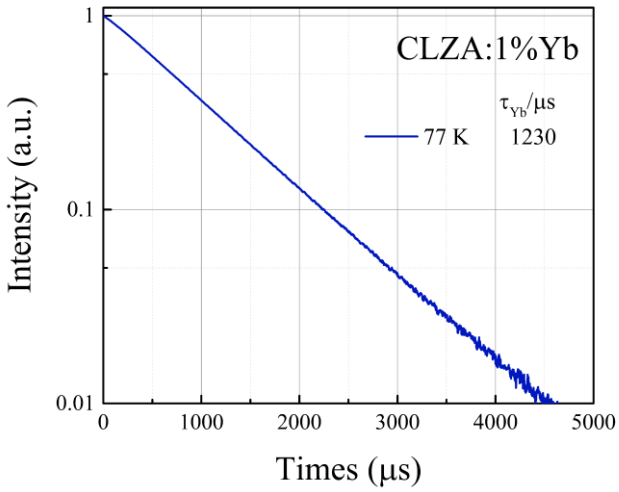

Figure S6. Decay curves of Yb^{3+} emission in the CLZA: 1%Yb phosphors at the 77 K after pulse excitation at 460 nm.

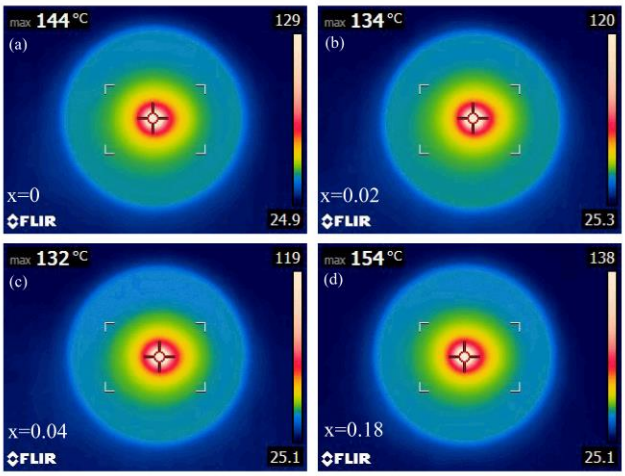

Figure S7. The images of the thermal imaging of the CLZA: 8%Cr, xYb (x= 0-0.18) phosphors under 455 nm excitation by LD.

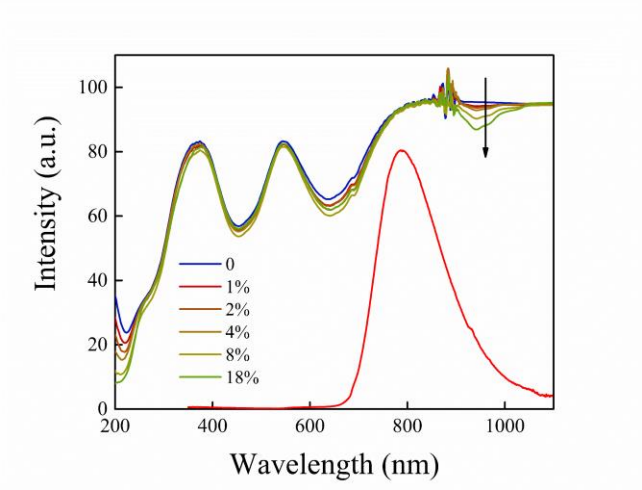

Figure S8. **The diffuse reflection spectra of the CLZA: 8%Cr, xYb (x= 0-0.18) phosphors and the PL spectrum of CLZA: 8%Cr.**

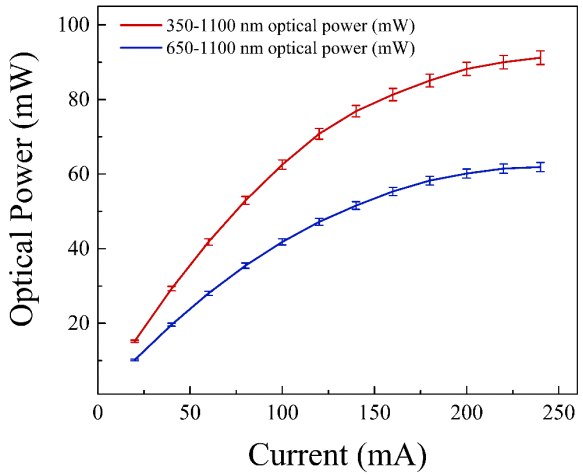

Figure S9. The errors bars for NIR output power of the NIR pc-LED

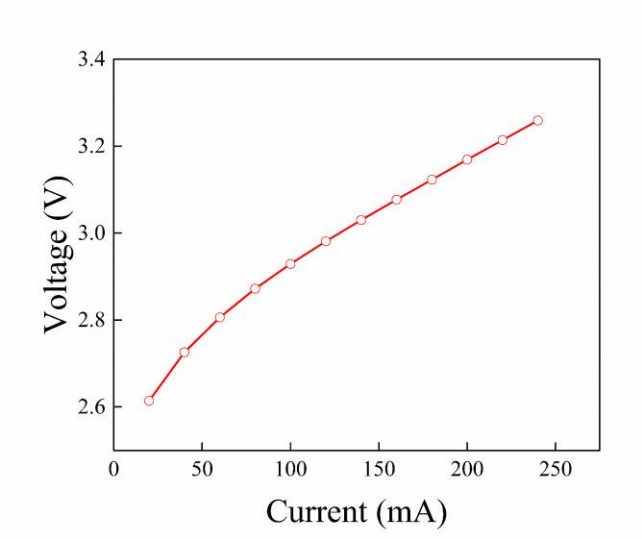

Figure S10. The current-voltage diagram of the NIR pc-LED

Note: There are two ways to calculate energy transfer efficiency --- by PL intensity and lifetime, respectively. The first one is calculated by PL intensity which is influenced merely by the ET process, the ET efficiency from Cr^{3+} to Yb^{3+}, can be calculated by [1-3]

$$\eta_{ET} = 1 - \frac{I_{Cr}}{I_{Cr_0}} \qquad \text{(S1)}$$

Where I_{Cr0} and I_{Cr} were the Cr emission intensity in the absence and in the presence of Yb^{3+}. The second one is calculating by the decreases of lifetime. The ET efficiency η'_{ET} from Cr^{3+} to Yb^{3+} can be calculated by the following equation:[4]

$$\eta'_{ET} = 1 - \frac{\tau_{Cr}}{\tau_{Cr_0}} \qquad \text{(S2)}$$

where τ_{Cr} represents the lifetime of Cr^{3+} with various Yb^{3+} concentration, and τ_{Cr_0} is the lifetime of Cr^{3+} in Cr^{3+} single-doped sample. It may be noticed that the values calculated by Equation (S2) are apparently smaller than those calculated by Equation (S1), which may be explained by experimental error from the measurement of the spectrum. So, we use the average values of the ET efficiency.

As shown in Figure 3b, η_{Yb} is the emission efficiency of the $^2F_{5/2}$ level of Yb^{3+} and η_{Cr_0} is the emission efficiency of Cr^{3+}. Hence, the Yb^{3+} and Cr^{3+} emission intensity in the co-doping phosphors can be evaluated respectively by

$$I_{Yb} = \eta_{ET} \cdot \eta_{Yb} \qquad \text{(S3)}$$

$$I_{Cr} = (1 - \eta_{ET}) \cdot \eta_{Cr_0} \qquad \text{(S4)}$$

Then, we have

$$\frac{I_{Yb}}{I_{Cr}} = \frac{\eta_{ET}}{1-\eta_{ET}} \cdot \frac{\eta_{Yb}}{\eta_{Cr_0}} \quad \text{(S5)}$$

As shown in Figure S2, τ_{Yb} is almost unchanged. Therefore, considering the η_{Yb} as constant. As the intrinsic emission efficiency of Cr^{3+}, the η_{Cr_0} is constant. Thus, a proportional relationship between $\bar{\eta}_{ET}/(1-\bar{\eta}_{ET})$ and I_{Yb}/I_{Cr} is obtained, as shown in Figure 3e.

References

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[2] Y. H. Song, E. K. Ji, B. W. Jeong, M. K. Jung, E. Y. Kim, D. H. Yoon, *Sci. Rep*. **2016**, *6*, 31206.

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[4] P. I. Paulose, G. Jose, V. Thomas, N. V. Unnikrishnan, M. K. R. Warrier, *J. Phys. Chem. Solids*. **2003**, *64*(5), 841-846.