

## Supporting Information

### [Zn<sup>2+</sup> - Ge<sup>4+</sup>] co-substitutes [Ga<sup>3+</sup> - Ga<sup>3+</sup>] to coordinately broaden the near-infrared emission of Cr<sup>3+</sup> in Ga<sub>2</sub>O<sub>3</sub> phosphors

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#### Raw materials and synthesis of samples

**Sample synthesis:** Ga<sub>2</sub>O<sub>3</sub> (99.99%, Aladdin), Cr<sub>2</sub>O<sub>3</sub> (99.95%, Aladdin), ZnO (99.99%, Aladdin) and GeO<sub>2</sub> (99.99%, Aladdin) are used as raw materials in a horizontal tube furnace using traditional The solid-phase synthesis reaction of Ga<sub>2</sub>O<sub>3</sub>: xCr<sup>3+</sup> and Ga<sub>1.98-y</sub>(Zn-Ge)<sub>y</sub>O<sub>3</sub>: 0.02Cr<sup>3+</sup> powder samples are synthesized. First, the stoichiometric raw materials are accurately weighed and mixed with a small amount of alcohol, then fully ground in an agate mortar. The mixed powder is placed in a horizontal tube furnace to sinter at 1500 °C for 2h with an air atmosphere. Finally, the sintered powder is taken out, cooled to room temperature and then ground. The prepared samples are used for subsequent studies.

**LED preparation:** A 460 nm LED chip is fixed in a substrate and the electrodes of the LED chip are attached to the substrate by gold thread. Then, mix an appropriate amount of the prepared phosphor with silica gel evenly, apply it on the commercially available LED chip, then install the fixed shell, and finally put it in an oven and heat it at 150 °C for 3 hours to get the pc - LED finished products.

#### Characterization and Calculation

##### Characterization:

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Phase data and crystal structures of previously prepared samples can be performed by using a Bruker Axs D2 PHASER diffractometer with Cu K $\alpha$  radiation ( $\lambda = 0.15405$  nm) at 30 kV and 10 mA. X-ray diffraction (XRD) patterns are measured under operating conditions in the  $10 \sim 80^\circ$  range with a step size of 0.0163 ( $2\theta$ ) and a count time of 0.1 s/step. The surface morphology and elemental composition of the powder samples are observed by field emission scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS), respectively. Diffuse reflectance spectra (DRS) of powder samples are detected and collected on an ultraviolet (UV) spectrophotometer (Shimadzu, UV-3600, Japan) using white powder BaSO<sub>4</sub> (99.99%, 1  $\mu$ m) as a calibrator. The decay curve of the luminescence lifetime is measured using a 460 nm LED pulsed Nd: YAG laser and a fl3-211 spectrofluorometric (HORIBA, JOBIN YVON, France). Emission and excitation spectra are measured using a modular fluorescence spectrometer (HORIBA, Quanta Master 8000, Canada). Temperature-dependent emission spectral properties are tested using a FL3-211 spectrofluorophotometer (HORIBA, JOBIN YVON, France) and TAP-02 (Orient KOJI), and the Quantaury-QY Plus C13534-11 (Hamamatsu Photonics, Japan) is used to obtain the Internal quantum efficiency (IQE), absorption efficiency (AE) and external quantum efficiency (EQE). LED photoelectric test system (Remote Photoelectric, HAAS-2000, China) is used to test the performance of packaged pc - LED.

**Calculation:** The XRD data is analyzed using the software TOPAS, and the Rietveld refinement of the phosphor is obtained.

Based on the density functional theory (DFT), the structural optimization and optoelectronic properties calculations are implemented by the Vienna ab initio simulation package (VASP) <sup>[1]</sup>. The projected augmented wave (PAW) method <sup>[2]</sup> is selected to deal with the electron-ion interactions and the Perdew-Burke-Ernzerh (PBE) functional <sup>[3]</sup> is selected to handle the electronic exchange energy. Furthermore, the photoelectric properties are obtained by the hybrid Heyd-Scuseria-Ernzerhof (HSE06) functional. The  $4 \times 4 \times 1$  k-point mesh is selected to examine the electronic

properties. For sufficient computational accuracy, we set cutoff energy to 450 eV with the convergence of energy and force with  $10^{-4}$  eV/Å and 0.01 eV, respectively. The out-of-plane dipole correction is adopted to meet the convergence criterion, and the band structure of Ga<sub>2</sub>O<sub>3</sub> crystal near Fermi level is drawn.

The definition of defect formation energy is:

$$\Delta H_f(\alpha, q) = E(\alpha, q) - E(\text{host}) - \sum_{\alpha} n_{\alpha} \mu_{\alpha} + q(\varepsilon_f + E_V)$$

where  $E(\text{host})$  is the total energy of the supercell;  $E(\alpha, q)$  is the total energy of the doped supercell ( $\alpha = \text{Zn, Ge or Ga}$ ).  $\mu_{\alpha}$  is the chemical potential of the atoms,  $n_{\alpha}$  is the number of atoms that are reduced ( $n_{\alpha} < 0$ ) or increased ( $n_{\alpha} > 0$ ) in the doped crystal, and  $q$  is the number of electron transfers.  $\varepsilon_f$  is the Fermi level of relative to the superunit cell band structure valence band top (VBM) energy  $E_V$ .

The atomic chemical potential  $\mu_{\alpha}$  depends on the growth conditions, and can be divided into two extreme cases: Ga-rich and O-rich. In this paper we consider the formation of ZnO, GeO<sub>2</sub> and Ga<sub>2</sub>O<sub>3</sub> from the direct combination of metals Zn, Ge, Ga and O<sub>2</sub>, and derive the chemical potential based on this assumption:

$$E(\text{ZnO}) = \mu_{\text{Zn}} + \mu_{\text{O}} = \mu_{\text{Zn}(\text{bulk})} + \mu_{\text{O}(\text{O}_2)} + \Delta H_f(\text{ZnO})$$

$$E(\text{Ga}_2\text{O}_3) = 2\mu_{\text{Ga}} + 3\mu_{\text{O}} = 2\mu_{\text{Ga}(\text{bulk})} + 3\mu_{\text{O}(\text{O}_2)} + \Delta H_f(\text{Ga}_2\text{O}_3)$$

**Rich - Ga:**

$$\mu_{\text{Zn}} = E(\text{ZnO}) - \frac{1}{3}E(\text{Ga}_2\text{O}_3) + \frac{2}{3}\mu_{\text{Ga}(\text{bulk})}$$

$$\mu_{\text{Ge}} = E(\text{GeO}_2) - \frac{2}{3}E(\text{Ga}_2\text{O}_3) + \frac{4}{3}\mu_{\text{Ga}(\text{bulk})}$$

$$\mu_{\text{Ga}} = \mu_{\text{Ga}(\text{bulk})}$$

**Rich - O:**

$$\mu_{\text{Zn}} = E(\text{ZnO}) - \mu_{\text{O}(\text{O}_2)}$$

$$\mu_{\text{Ge}} = E(\text{GeO}_2) - 2\mu_{\text{O}(\text{O}_2)}$$

$$\mu_{\text{Ga}} = \frac{1}{2}[E(\text{Ga}_2\text{O}_3) - 3\mu_{\text{O}(\text{O}_2)}]$$

The calculated formation energies for the extreme cases of Ga-rich and O-rich are shown in the table, where Zn occupies the Ga1 site, and Ge occupies the Ga2 site, the formation energy is the lowest, so this occupancy case is given priority.

Case		Raplace	Formation Energy (eV)
Rich - Ga	$\mu_{\text{Ga}} = -0.1102$	Zn-Ga1,Ge-Ga1	1.1423
	$\mu_{\text{Zn}} = 1.0085$	Zn-Ga1,Ge-Ga2	<b>0.5196</b>
	$\mu_{\text{Ge}} = 0.8085$	Zn-Ga2,Ge-Ga1	0.5693
		Zn-Ga2,Ge-Ga2	0.78
Rich - O	$\mu_{\text{Ga}} = -8.3329$	Zn-Ga1,Ge-Ga1	1.1423
	$\mu_{\text{Zn}} = -4.4733$	Zn-Ga1,Ge-Ga2	<b>0.5196</b>
	$\mu_{\text{Ge}} = -10.1551$	Zn-Ga2,Ge-Ga1	0.5693
		Zn-Ga2,Ge-Ga2	0.78

The IQE, AE and EQE of GZGOC phosphors were calculated by using the following equations [4,5]:

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

$$AE = \frac{\int E_R - \int E_S}{\int E_R}$$

$$EQE = AE \times IQE = \frac{\int L_S}{\int E_R}$$

where  $E_S$  stands for the spectrum of light used for exciting the phosphor,  $L_S$  represents the emission spectrum of the phosphor, and  $E_R$  is the spectrum of excitation light without phosphor in sphere. The specific calculation results of GZGOC phosphors are shown in **Figure S3** and **Table S3**.

## References:

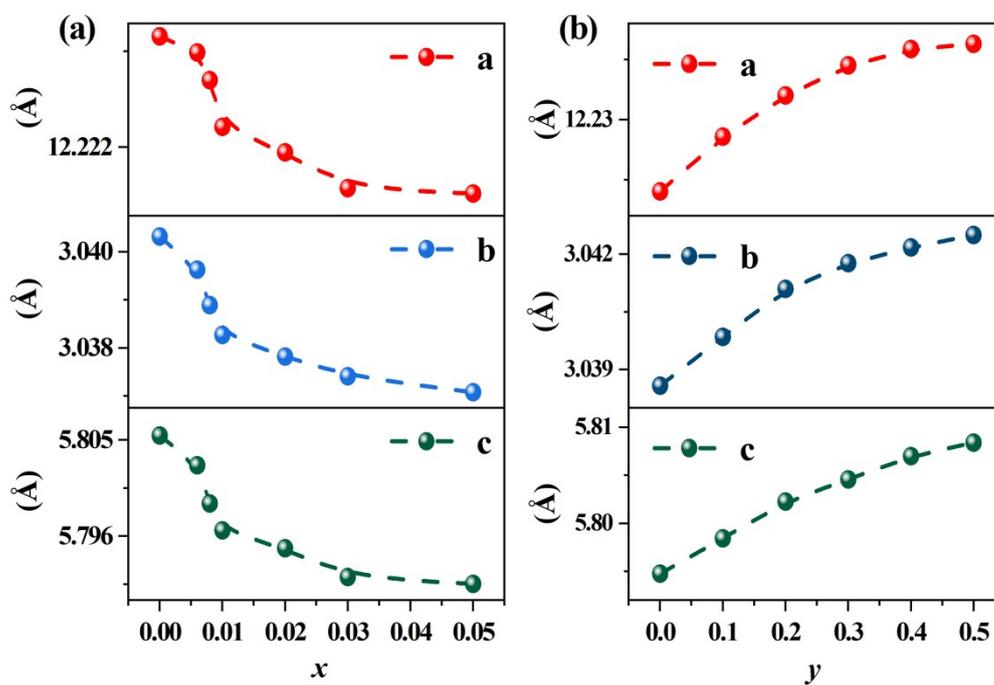
- [1] J. Hafner, Materials simulations using VASP—a quantum perspective to materials science, *Computer Physics Communications*, 177 (2007) 6-13.
- [2] J. Hafner, Ab-initio simulations of materials using VASP: Density-functional

theory and beyond, *Journal of Computational Chemistry*, 29 (2008) 2044-2078.

[3] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple, *Physical Review Letters*, 77 (1996) 3865-3868.

[4] E. Song, Y. Zhou, X.B. Yang, Z.F. Liao, W. Zhao, T. Deng, L.Y. Wang, Highly efficient and stable narrow-band red phosphor  $\text{Cs}_2\text{SiF}_6: \text{Mn}^{4+}$  for high-power warm white LED applications, *ACS Photonics*, 4 (2017) 2556–2565.

[5] H. Chen, Y.H. Wang, Photoluminescence and cathodoluminescence properties of novel rare-earth free narrow-band bright green-emitting  $\text{ZnB}_2\text{O}_4: \text{Mn}^{2+}$  phosphor for LEDs and FEDs, *Chemical Engineering Journal*, 361 (2019) 314-321.



**Figure S1** The refined lattice parameter of GOC (a) and GZGOC (b)

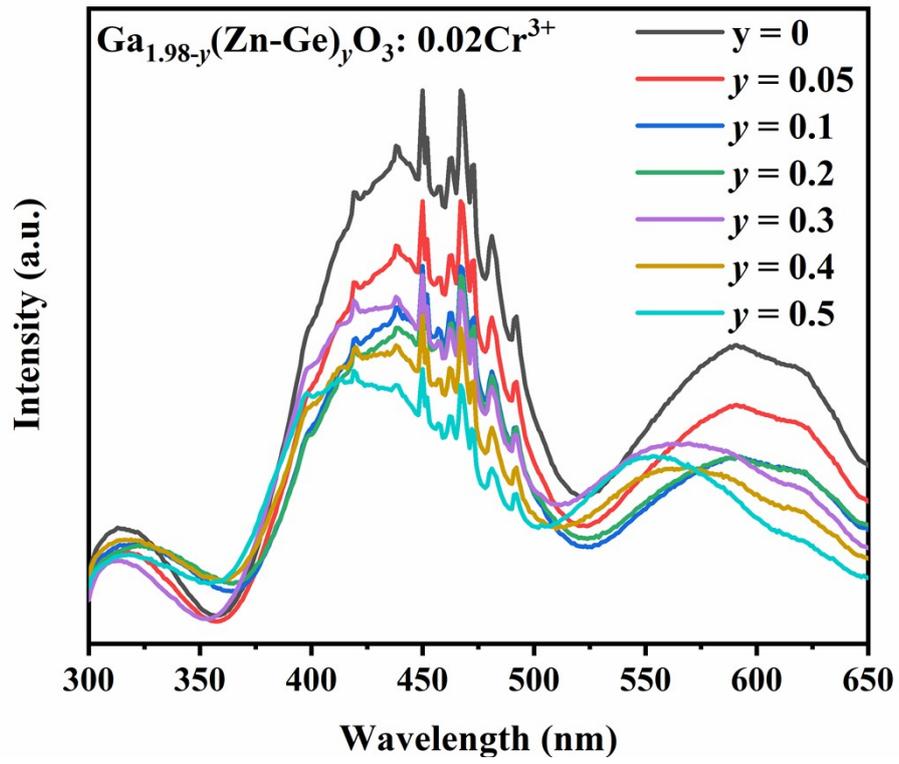


Figure S2 The excitation spectra of GZGOC.

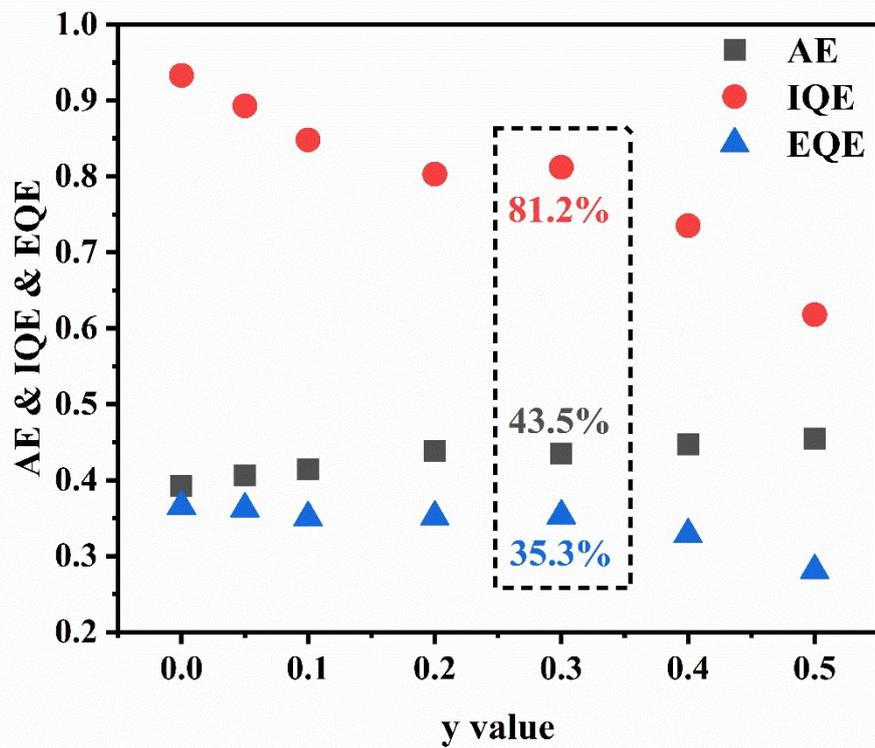
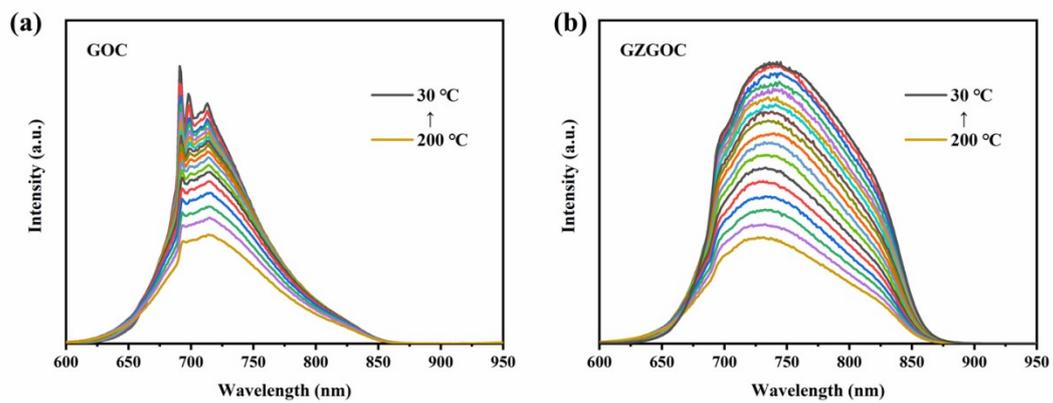


Figure S3 The IQE, AE and EQE of GZGOC.



**Figure S4** The variable temperature emission spectroscopy of GOC (a) and GZGOC (b)

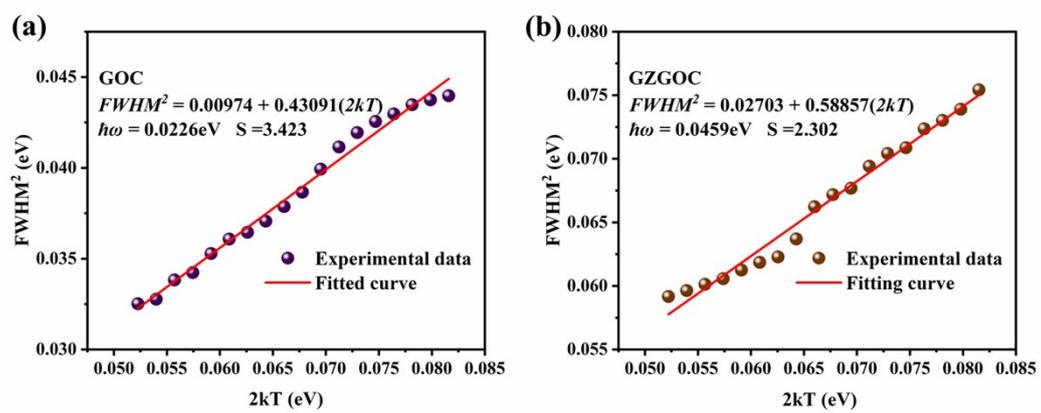
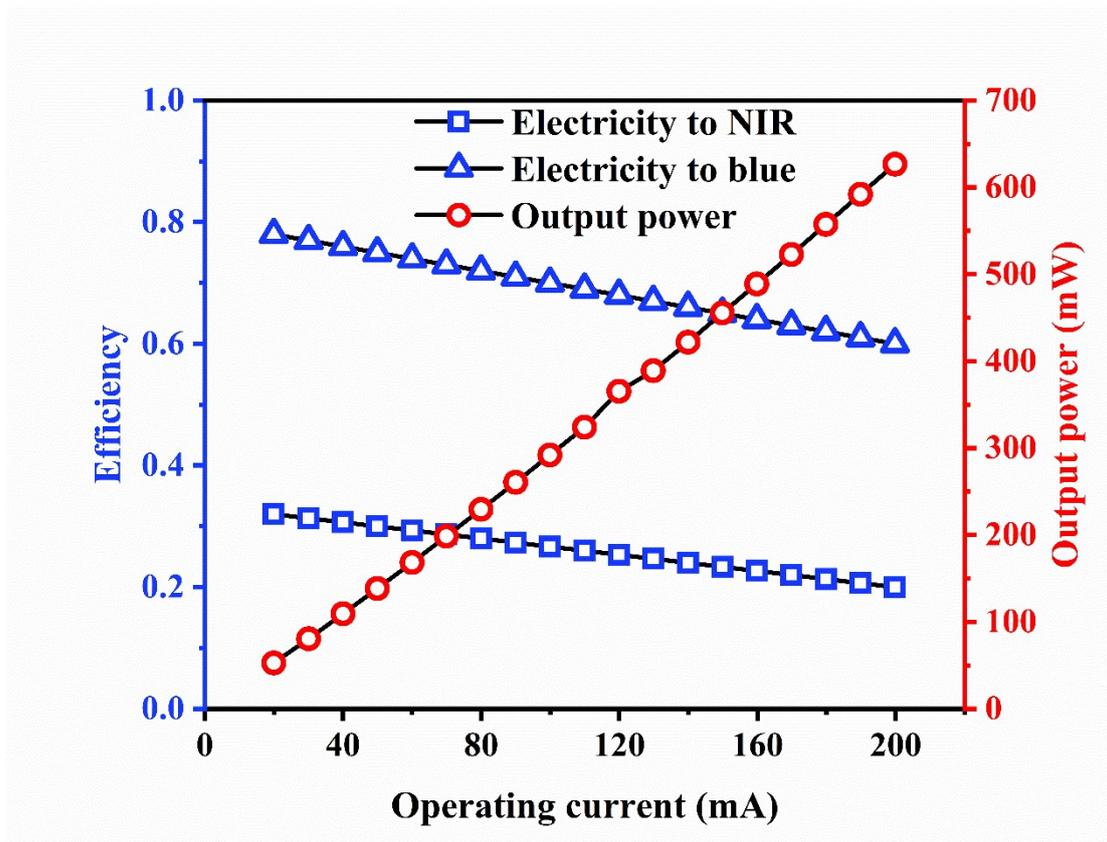


Figure S5 The function of  $2kT$  and  $FWHM^2$  of GOC (a) and GZGOC (b).



**Figure S6** The output power, electricity to blue light and electricity to NIR light power conversion efficiency under various operating current.

**Table S1** Refined Crystal Structure Data of Ga<sub>2</sub>O<sub>3</sub>

formula	Ga <sub>2</sub> O <sub>3</sub>
radiation type; $\lambda(\text{\AA})$	X-ray; 1.5405
temperature (K)	293 K
space group; <i>Z</i>	C2/m
<i>a</i> ( $\text{\AA}$ )	12.2300
<i>b</i> ( $\text{\AA}$ )	3.0400
<i>c</i> ( $\text{\AA}$ )	5.8000
$\beta$ (deg)	103.7
unit cell volume ( $\text{\AA}^3$ )	209.50423
expected factor, $R_{\text{exp}}$	6.19%
profile R-factor, $R_p$	8.21%
weighted profile R-factor, $R_{\text{wp}}$	10.11%

**Table S2** The refined atomic positions  $\text{Ga}_{1.68}(\text{Zn-Ge})_{0.3}\text{O}_3 : 0.02\text{Cr}^{3+}$ 

atom	Wyck. position	occ.	<i>x</i>	<i>y</i>	<i>z</i>
Ga1	<i>4i</i>	0.7	0.08863	0.0000	0.29865
Ga2	<i>4i</i>	0.7	0.34381	0.0000	0.18730
Zn1	<i>4i</i>	0.3	0.08863	0.0000	0.29865
Ge1	<i>4i</i>	0.3	0.34381	0.0000	0.18730
Cr1	<i>4i</i>	0.02	0.34381	0.0000	0.18730
O1	<i>4i</i>	1	0.15265	0.0000	0.60193
O2	<i>4i</i>	1	0.16498	0.0000	0.05772
O3	<i>4i</i>	1	0.50064	0.0000	0.25491

**Table S3** The IQE, AE and EQE of GZGOC phosphors

<i>y</i> value	<i>y</i> =0	<i>y</i> =0.05	<i>y</i> =0.1	<i>y</i> =0.2	<i>y</i> =0.3	<i>y</i> =0.4	<i>y</i> =0.5
IQE	93.3%	89.3%	84.8%	80.3%	81.2%	73.5%	61.8%
AE	39.2%	40.6%	41.4%	43.8%	43.5%	44.7%	45.5%
EQE	36.6%	36.3%	35.1%	35.2%	35.3%	32.9%	28.1%

**Table S4** The FWHM in the eV as the function of the temperature of GOC and GZGOC

2kT(eV)	GOC - FWHM <sup>2</sup> (eV)	GZGOC - FWHM <sup>2</sup> (eV)
0.05227	0.03252	0.05917
0.05399	0.03277	0.05963
0.05572	0.03383	0.06013
0.05744	0.03423	0.06056
0.05917	0.03528	0.06124
0.06089	0.03608	0.06185
0.06262	0.03646	0.06228
0.06434	0.03706	0.0637
0.06607	0.03786	0.06622
0.06779	0.03866	0.06717
0.06952	0.03993	0.06768
0.07124	0.04115	0.06941
0.07297	0.04194	0.07042
0.07469	0.04256	0.07087
0.07642	0.04298	0.07236
0.07814	0.04347	0.07302
0.07987	0.04374	0.07389
0.08159	0.04397	0.07543