SUPPORTING INFORMATION

Modiable NIR-persistent emmission intensity for Ti^{4+}/Cr^{3+} co-doped zinc gallogermanates and Enhanced luminescent mechanism

Yancen Liu[a], Jie Sun[a], Zhongqiao Sun[a], Hao Meng[a], Yide Han[a], Shulin Han[b], Lei Cai[b], Yu Zhang[c],Xia Zhang[a]*

[a]Department of Chemistry, College of Sciences, Northeastern University, Shenyang 110819, P. R. China.

[b]Shandong Province Key Laboratory of Medical Physics and Image Processing Technology, School of Physics and Electronics, Institute of Materials and Clean Energy, Shandong Normal University, Jinan 250014, P. R. China

[c]Hubei Key Laboratory of Energy Storage and Power Battery, and School of Mathematics, Physics and Optoelectronics Engineering, Hubei University of Automotive Technology, Shiyan 442002, China

*Corresponding author: X Zhang (Prof.)

Email: xzhang@mail.neu.edu.cn

Experimental

Materials

ZnO (99.00%), Ga_2O_3 (99.80%), GeO_2 (99.99%), Cr_2O_3 (99.00%), TiO_2 (99.00%) were of the analytical grade, and were purchased from Macklin (Shanghai, China).

Materials synthesis

The $Zn_3Ga_{1.9}Ge_2O_{10}:(Cr_x,Ti_y)_{0.1}$ (where x:y=1:0, 1:0.5, 1:1, 1:1.5, 1:2) NIR Long-persistent phosphor was prepared by using a solid state reaction routes. In a procedure, ZnO, Ga_2O_3, GeO_2, Cr_2O_3 and TiO_2 at definite amounts were placed in an agate mortar according to the corresponding stoichiometric ratio and fully mixed for 1 h, and then the mixture was put in a muffle furnace and heated from room temperature to 900 °C at a heating rate of 5 °C/min. After pre-sintered at 900 °C for 2 h, then the sample was grinded again, and re-put in the muffle furnace and annealed to 1150 °C for another 3 h at a heating rate of 5 °C/min. Finally, the sample was grinded and collected.

Characterization

X-ray diffraction (XRD) patterns were carried out by X'Pert Pro MRDDY 2094 diffractometer operating at 40 kV and of 40 mA equipped with Cu Kα radiation (λ = 1.54178 Å). Fieldemission scanning electron microscope (FE-SEM) were carried out by Hitachi SU8010. High-resolution transmission electron microscopy (HR-TEM) were carried out by a Tecnai G2 F-20 electron microscopy operated at 200 kV. Raman spectra were recorded using inVia Qontor Confocal Micro-Raman Spectrometer with 488 nm excitation. X-ray photoelectron spectroscopy (XPS) measurement was performed in a PHI ESCA-5000C electron spectrometer. The UV-vis diffusive

reflectance spectra (UV-vis DRS) was tested by a Lambda 750 UV-visible spectrophotometer with a wavelength range of 200–800 nm. The photoluminescence (PL) spectra was carried out using a FluoroMax-4 fluorescence spectrophotometer. Photoluminescence Excitation Spectroscopy (PLE), afterglow emission spectra and afterglow lifetime decay profiles were measured on an Edinburgh FLS1000 fluorescence spectrophotometer. Thermoluminescence (TL) spectra were measured by TOSL-3DS Type Optically Stimulated Luminescence 3D Spectrometer at a heatingrate of 5 K min-1. All photographs and videos were taken under ambient conditions using a Canon camera (EOS 80D) by a hand-hold UV lamp.

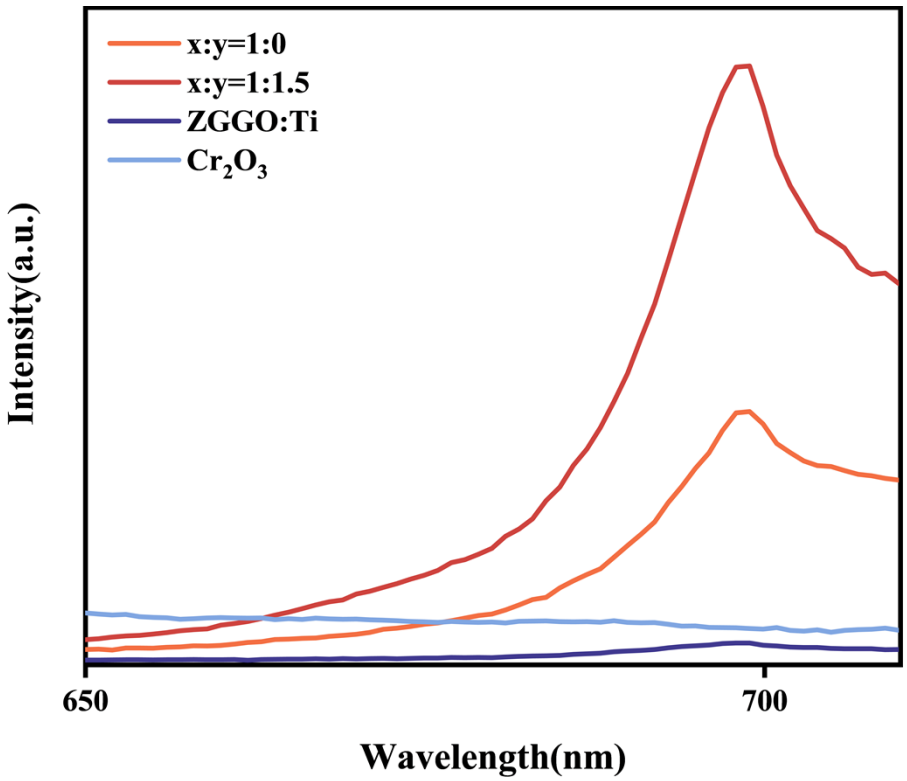

Figure S1 Photoluminescence spectra of ZGGO:Cr,Ti (x:y=1:0, 1:1.5), ZGGO:Ti and Cr_2O_3

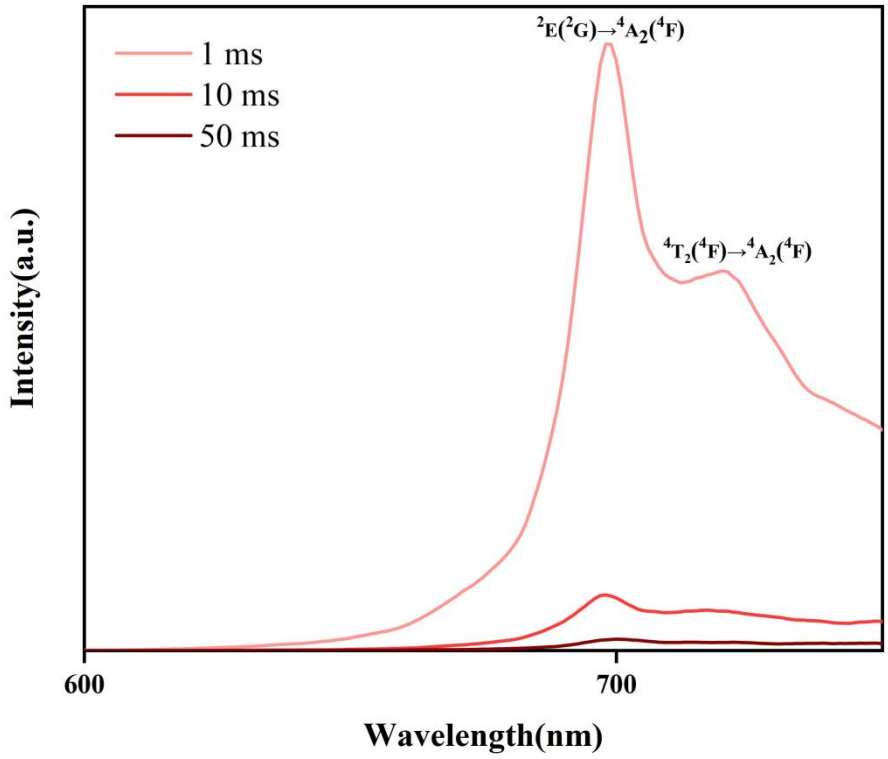

Figure S2 Afterglow emission spectra of ZGGO:Cr,Ti (x:y=1:1.5) under the excitation of 365 nm at room temperature

Table S1 The binding energies of the Zn $2p_{3/2}$ core-levels of ZGGO:Cr,Ti

	$Peak_1$		$Peak_2$	
Sample	BE (eV)	Area Percent	BE (eV)	Area Percent
x:y=1:0	1022.50	22.70	1021.84	77.30
x:y=1:1.5	1022.47	37.95	1021.69	62.05
x:y=1:2	1022.40	39.45	1021.67	60.55

Table S2 The binding energies of the Ga $2p_{3/2}$ core-levels of ZGGO:Cr,Ti

	$Peak_1$		$Peak_2$	
Sample	BE (eV)	Area Percent	BE (eV)	Area Percent
x:y=1:0	1118.36	74.53	1117.68	25.47
x:y=1:1.5	1118.5	66.54	1117.71	33.46
x:y=1:2	1118.5	62.89	1117.75	37.11

Table S3 The related spectral and crystal field parameters of ZGGO:Cr,Ti ,including absorption peak positions, corresponding transitions and the related crystal field parameters.

Type	Peak positions (nm)	Wavenumber (cm^{-1})	Transition	Crystal field parameters
d^3 (d^3–O_h)	ν_1=410	24390	$^4A_2(^4F)\rightarrow{}^4T_1(^4F)$	$Dq_{(Oh)}$=1773cm^{-1}
	ν_2=564	17730	$^4A_2(^4F)\rightarrow{}^4T_2(^4F)$	$B_{(Oh)}$=653 cm^{-1}
				$Dq/B_{(Oh)}$=2.72