## Tuning multicolor emission of Zn<sub>2</sub>GeO<sub>4</sub>:Mn phosphors by Li<sup>+</sup> doping for information encryption and anti-counterfeiting applications

Dangli Gao,\*a Kaiwei Ma, Peng Wang, Xiangyu Zhang, Qing Pang, Hong Xin,

Zihan Zhang<sup>c</sup> and Huan Jiao\*<sup>c</sup>

<sup>a</sup> College of Science, Xi'an University of Architecture and Technology, Xi'an 710055,

China

<sup>b</sup> College of Science, Chang'an University, Xi'an 710064, China

<sup>c</sup> School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an

710062, China

E-mails: gaodangli@163.com, gaodangli@xauat.edu.cn, jiaohuan@snnu.edu.cn.



**Fig. S1** XRD patterns of  $Zn_2GeO_4$ :Mn,x%Li (x=0 and 20),  $Zn_2GeO_4$ -NaLiGe<sub>4</sub>O<sub>9</sub>:Mn, x%Li (x=50 and 70) and NaLiGe<sub>4</sub>O<sub>9</sub>:Mn phosphors calcined at 900 °C. Note that the bottom of the panel is standard data for hexagonal  $Zn_2GeO_4$  (purple, PDF# 04-007-5691), and the top of the panel is orthorhombic NaLiGe<sub>4</sub>O<sub>9</sub>:0.25%Mn (green, PDF# 04-011-1336).



Fig. S2 XPS survey scan spectrum (a) and high-resolution XPS spectrum of Mn 2p (b) in  $Zn_2GeO_4$ -NaLiGe<sub>4</sub>O<sub>9</sub>:Mn, 70%Li sample.



Fig. S3 Li<sup>+</sup> doping concentration dependent PL spectra of  $Zn_2GeO_4$ -NaLiGe<sub>4</sub>O<sub>9</sub>:Mn, x%Li (x=50 and 70) and NaLiGe<sub>4</sub>O<sub>9</sub>:Mn phosphors under selective excitation with (a) 365 nm and (b) 468 nm, respectively. With the increase of Li<sup>+</sup> ion doping concentrations and excitation wavelengths, the red luminescence increases.



**Fig. S4** Li<sup>+</sup> doping concentration dependent PersL decay curves of  $Zn_2GeO_4$ -NaLiGe<sub>4</sub>O<sub>9</sub>:Mn, x%Li phosphors (*x*=50 and 70) phosphors monitored at 540 nm (a) and 664 nm (b) after irradiated by a 365 nm lamp for 5 min.



**Fig. S5** TL curves of Zn<sub>2</sub>GeO<sub>4</sub>-NaLiGe<sub>4</sub>O<sub>9</sub>:Mn,70%Li phosphor monitored at 540 nm emission over 30–140 °C. The sample has been pre-irradiated by 365 nm UV light for 8 min.



**Fig. S6** The proposed PL, PersL and PSL schematic diagram for green and red emissions of Mn<sup>2+</sup>/Mn<sup>4+</sup> in the Zn<sub>2</sub>GeO<sub>4</sub>-NaLiGe<sub>4</sub>O<sub>9</sub>:Mn phosphors. Therein, ① UV light excitation, ② energy (or electron) transfer processes, ③ trapping, ④ release and ⑤ recombination. The straight-line arrows and curved line arrows represent optical transitions and energy (or electron) transfer processes, respectively.