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Anomalous spontaneous-reduction of Mn^{7+}/Mn^{4+} to Mn^{2+} and luminescence properties in Zn_2GeO_4:Mn

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Table S1 The synthesis information of $Zn_{2-x}GeO_4$:$x$$Mn^{2+}$.

Mn source	synthetic temperature (°C)	Mn content (x)
$MnCO_3$	800/1000/1100/1200/1300 (6 h)	0.02
$MnCO_3$	1300(6 h)	0.005-0.07
$MnCO_3$/MnO_2/$KMnO_4$	800/1300(6 h)	0.03

Table S2 The synthesis information of other germanates.

Host	synthetic temperature (°C)	Mn source	Mn content (x)
Li_2ZnGeO_4	1200 (6 h)	$MnCO_3$/MnO_2/$KMnO_4$	0.01
Li_2MgGeO_4	1200 (6 h)	$MnCO_3$/MnO_2/$KMnO_4$	0.01
Na_2MgGeO_4	1100 (6 h)	$MnCO_3$/MnO_2/$KMnO_4$	0.01
Na_2ZnGeO_4	1100 (6 h)	$MnCO_3$/MnO_2/$KMnO_4$	0.01

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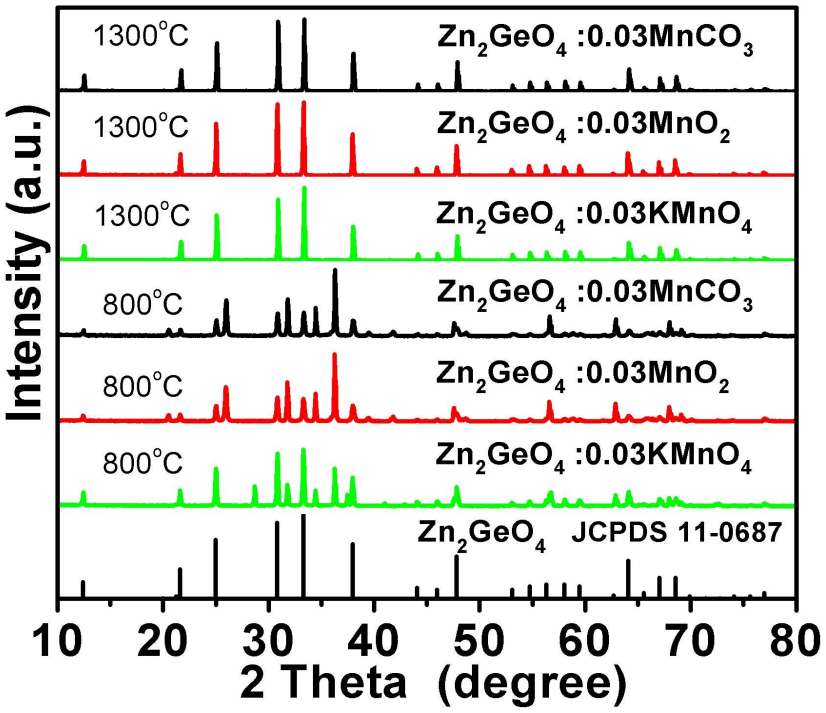

Fig. S1 The standard XRD pattern of Zn_2GeO_4 and measured XRD patterns of Zn_2GeO_4:0.03Mn^{2+} phosphor with different Mn-sources ($MnCO_3$, MnO_2 and $KMnO_4$) prepared at 1300 and 800 °C, respectively, for 6 h in air condition.

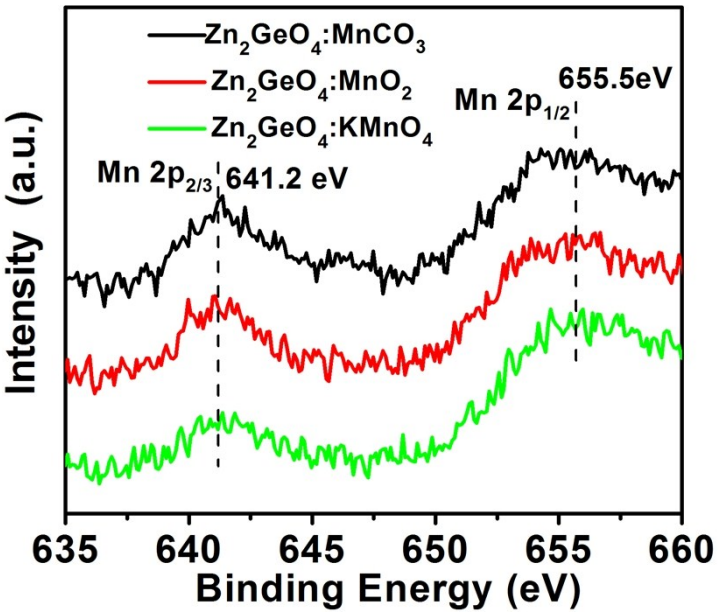

Fig. S2 XPS spectra for Mn 2p region in Zn_2GeO_4:Mn samples synthesized by using different Mn-sources ($MnCO_3$, MnO_2 and $KMnO_4$).

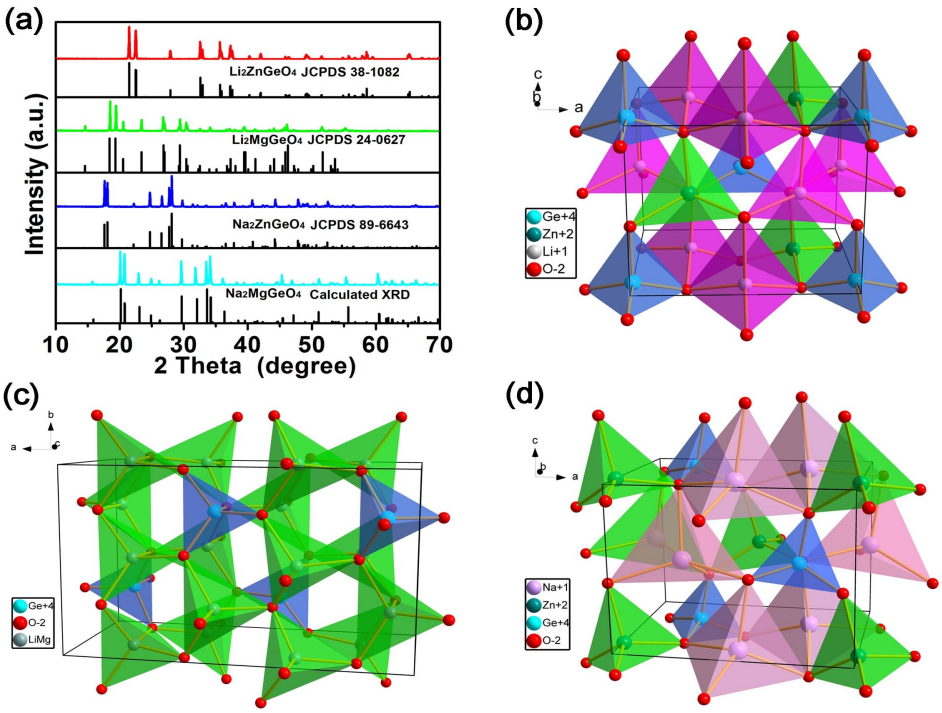

Fig. S3 (a) The standard XRD patterns of Li_2ZnGeO_4, Li_2MgGeO_4, Na_2ZnGeO_4, $Na_2MgGeO_4$and measured XRD patterns of the corresponding phosphors prepared *via* a high temperature solid-state reaction method. The crystal structures of (b) Li_2ZnGeO_4, (c) Li_2MgGeO_4, (d) Na_2ZnGeO_4, and Na_2MgGeO_4 have the same structure as Na_2ZnGeO_4.

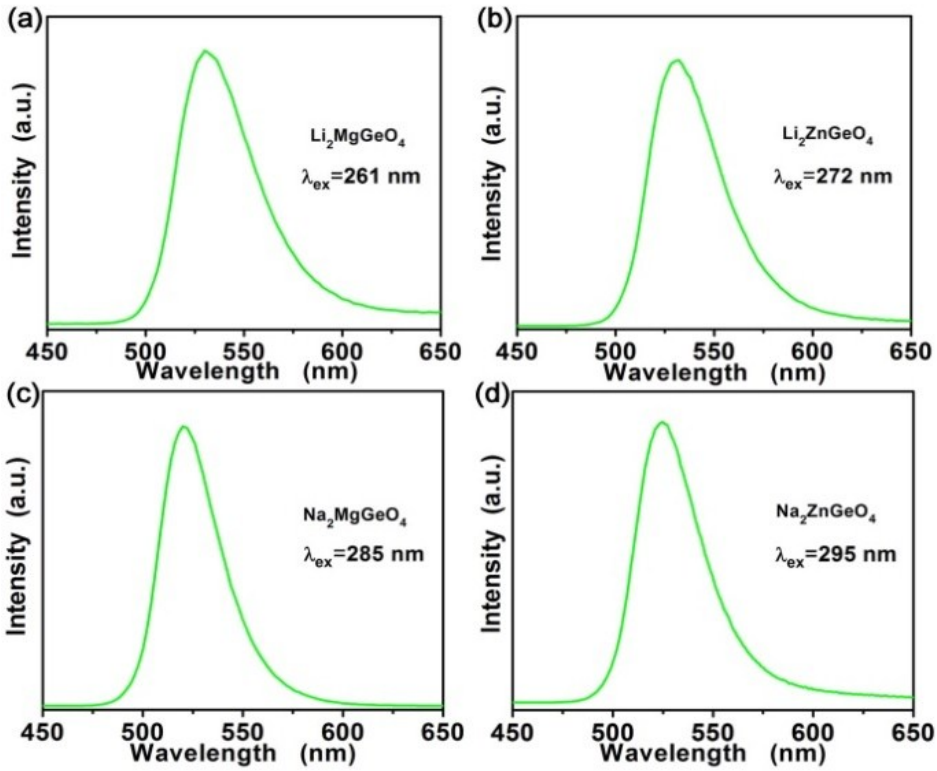

Fig. S4 PL spectra of (a) $Li_2ZnGeO_4:Mn^{2+}$, (b) $Li_2MgGeO_4:Mn^{2+}$, (c) $Na_2MgGeO_4:Mn^{2+}$, and (d) $Na_2ZnGeO_4:Mn^{2+}$ phosphors prepared by using $KMnO_4$ as Mn source.