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# A review on the structural dependent optical properties and energy transfer of $\text{Mn}^{4+}$ and multiple ion-codoped complex oxide phosphors

Meng Gao,<sup>a</sup> Yue Xiao Pan,<sup>a</sup> <sup>\*,a</sup> Yitian Jin<sup>a</sup> and Jun Lin <sup>\*,b</sup>

The tetravalent manganese  $\text{Mn}^{4+}$  ions with a  $3d^3$  electron configuration as luminescence centers in solid-state inorganic compounds have been widely investigated because they emit bright light in the red to far-red region when they are excited by light with a wavelength in the UV to blue light region. Herein, we present an overview of the recent developments of  $\text{Mn}^{4+}$  and multiple ion such as  $\text{Bi}^{3+}$  and rare earth ion  $\text{Dy}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Yb}^{3+}$ ,  $\text{Er}^{3+}$ ,  $\text{Ho}^{3+}$ , and  $\text{Tm}^{3+}$  codoped complex oxide phosphors. Most of the specified host lattices of these complex oxide phosphors possess multiple metallic cations, which provide possible substitutions with different codopants and form various luminescence centers with diverse spectra. The luminescence of  $\text{Mn}^{4+}$  and multiple ion-codoped materials spans almost the whole visible light to near infrared (NIR) region. The crystal structures of complex oxide phosphors, the spectroscopic properties of  $\text{Mn}^{4+}$ , and the energy transfer between  $\text{Mn}^{4+}$  and multiple ions are introduced and summarized in detail with regard to their practical applications. This review provides an insight into the optical properties of  $\text{Mn}^{4+}$  and the energy transfer process in multiple ion-codoped luminescence materials, which will be helpful in the development of novel excellent materials for applications in the lighting industry.

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## 1. Introduction

The optical properties based on the structures of host lattices and the energy transfer between  $\text{Mn}^{4+}$  and multiple ion-codoped complex oxide phosphors described in this review make the identified luminescence materials promising for application in solar energy cells, white light-emitting diodes (WLEDs), indoor lighting for plant cultivation, and temperature sensors, as illustrated in Fig. 1.

Solar energy cells and WLEDs are considered as alternative approaches to relieve the energy crisis with the increasing global energy consumption. Solar energy cells using crystalline silicon solar cells have occupied majority of the solar cell market owing to their well-developed techniques and low cost; however, their conversion efficiency should be improved further for their wide commercial applications. It is well known that most of the energy of the solar spectrum is concentrated at wavelengths beyond 900 nm including UV-visible (UV-vis) and NIR light, which cannot be absorbed by the current crystalline silicon solar cells with high efficiency.<sup>1–4</sup>

Converting the energy of the solar spectrum at wavelengths beyond 900 nm into the range located 900–1100 nm, which matches the maximum spectral response of the absorption of crystalline silicon, is an important alternative approach to improve the energy conversion efficiency of crystalline silicon solar cells. Recently, much attention has been paid to developing  $\text{Mn}^{4+}$ -doped phosphors because  $\text{Mn}^{4+}$  usually shows sharp line emissions in the red-infrared (IR) region due to its unique  $3d^3$  electron configurations. It has been observed that  $\text{Mn}^{4+}$  shows red to far-red photoluminescence, which is assigned to the spin-forbidden  ${}^2\text{E}_g \rightarrow {}^4\text{A}_{2g}$  transition under the excitation of UV or blue light owing to its high effective positive charge and the influence of a strong local crystal-field.<sup>5–12</sup> The reversible conversion of UV-vis into NIR, and NIR into visible light with dual-mode luminescence can be realized by codoping multiple ions such as  $\text{Nd}^{3+}/\text{Er}^{3+}/\text{Yb}^{3+}$  into  $\text{Mn}^{4+}$  ion-doped luminescence materials. The red emission of  $\text{Mn}^{4+}$  can be obtained when it is excited by 980 nm due to the energy transfer from  $\text{Nd}^{3+}/\text{Er}^{3+}/\text{Yb}^{3+}$  to  $\text{Mn}^{4+}$  ions.<sup>13</sup> The NIR photoluminescence maxima at 1064, 1537, and 980 nm originating from  $\text{Nd}^{3+}/\text{Er}^{3+}/\text{Yb}^{3+}$  ions can be sensitized by  $\text{Mn}^{4+}$  with excitation in the UV-vis region (200–500 nm).<sup>13–16</sup> The conversion of UV-vis light into NIR light at about 1064 nm through energy transfer from  $\text{Mn}^{4+}$  to multiple ions is desirable to improve the conversion efficiency of solar cells by coating the phosphor layer on the surface of a crystalline Si layer.

WLEDs have received extensive attention due to their high energy efficiency, long lifetime, and environmental friendliness.

<sup>a</sup>Key Laboratory of Carbon Materials of Zhejiang Province, College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325035, P. R. China. E-mail: yxpan@wzu.edu.cn; Fax: +86-577-88373017; Tel: +86-577-88373017

<sup>b</sup>State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China. E-mail: jlin@ciac.ac.cn; Fax: +86-431-85698041; Tel: +86-431-85262031



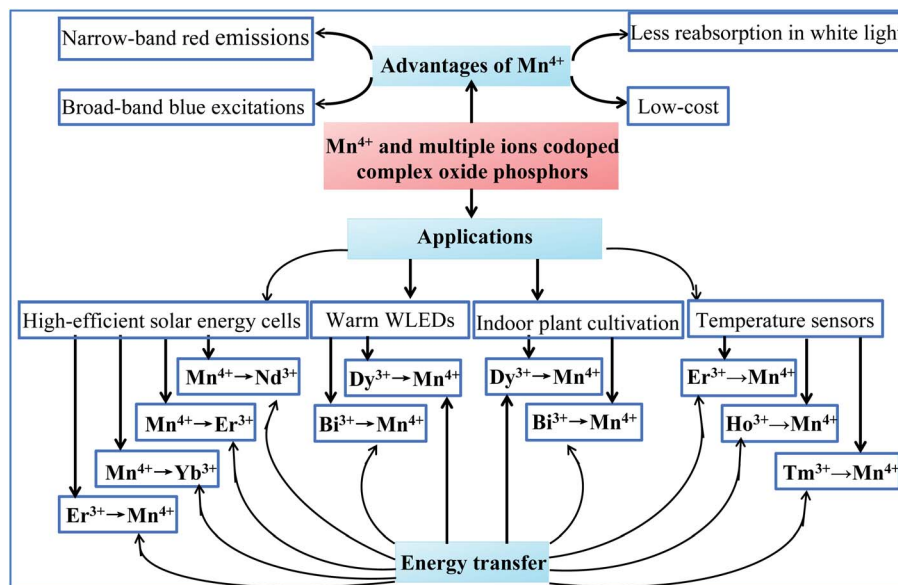


Fig. 1 Optical properties, energy transfer, and potential application of  $\text{Mn}^{4+}$  and multiple ion-codoped complex oxide phosphors described in this review.

The WLEDs fabricated with blue semiconductor GaN chips and yellow phosphor  $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$  (YAG:Ce) can produce cold white light because the red component in their spectra is weak. To meet the requirement for indoor illumination, warm white light with a high color rendering index ( $\text{CRI} > 80$ ) and a low correlated color temperature ( $\text{CCT} < 4000 \text{ K}$ ) is necessary.<sup>17,18</sup> Accordingly, phosphors with strong absorption in the blue light region and intense emission in the red light region should be co-coated on blue semiconductor GaN chips to produce warm white light.  $\text{Mn}^{4+}$  ions located at octahedral crystallographic sites are favorable luminescent centers and promising for blue GaN-excited warm WLED applications because they have narrow-band red emissions, broad-band blue excitations, and no reabsorption in white light, while being free of expensive rare earth metals.<sup>5–12</sup> Thus, much attention has been paid to developing red phosphors to provide alternatives to the commercial nitride phosphors. In particular, the interest in  $\text{Mn}^{4+}$ -doped inorganic phosphors has increased because the  $\text{Mn}^{4+}$  luminescence center usually shows sharp line emissions in the red region with high color purity due to the sharp feature of its emission spectrum.<sup>5–12</sup>

Recently, indoor plant cultivation has attracted considerable attention because this advanced technology can exclude the unfavorable influence of the climate and natural damage. To meet the requirement in lighting for indoor plant cultivation, blue-violet light in wavelength range of 420–500 nm is indispensable for chlorophyll A and chlorophyll B, and red-far red light in wavelength range of 640–750 nm is indispensable for phytochrome PR and phytochrome PFR.<sup>19–24</sup> The fabrication of red  $\text{Mn}^{4+}$ -doped phosphors in blue LED chip results in a superior performance in lighting for indoor plant cultivation due to the blue light from LED chips and red light from  $\text{Mn}^{4+}$ -doped luminescence materials excited by blue light. This type of light device is a promising light source for large scale industrial

application because of the energy saving and long working time of LEDs, and low cost of  $\text{Mn}^{4+}$ -doped luminescence materials.  $\text{Bi}^{3+}$  and  $\text{Mn}^{4+}$  codoped oxide phosphors, which emit dual blue and red light upon excitation by near UV (NUV) LEDs, are alternative candidates for application in the agricultural industry to improve the efficiency of photosynthesis. To maintain the electroneutrality of the compound, excess metal ion vacancies and  $\text{O}^{2-}$  ions in the lattices of complex oxides may be formed for charge compensation.<sup>25–30</sup>

The upconverted NIR luminescence of  $\text{Mn}^{4+}$  was realized with the aid of the efficient energy transfer of  $\text{Yb}^{3+} \rightarrow \text{Ln}^{3+} \rightarrow \text{Mn}^{4+}$  in the specially prepared  $\text{Yb}^{3+}/\text{Ln}^{3+}/\text{Mn}^{4+}$  ( $\text{Ln} = \text{Er}, \text{Ho}, \text{Tm}$ ) codoped  $\text{YAlO}_3$  and its energy transfer efficiency was systematically clarified by its steady-state and time-resolved upconverted emission spectra.<sup>31</sup> The dual emission based on  $\text{Mn}^{4+}$  and multiple ion (such as  $\text{Yb}^{3+}$ ,  $\text{Ln}^{3+}$ , and  $\text{Mn}^{4+}$ ) codoped phosphors is promising for accurate temperature sensors due to the fact that the thermal quenching mechanisms of  $\text{Mn}^{4+}$  and  $\text{Ln}^{3+}$  are different.<sup>32</sup> Fig. 2 presents a summary of the energy transfer between  $\text{Mn}^{4+}$  and multiple ions, the emission wavelengths, and corresponding electronic transitions of both the donor and acceptor. The octahedral environment-coordinated  $\text{Mn}^{4+}$  ions emit red to far-red emissions in the region of 600 to 700 nm. Thus, tunable spectral emissions from the visible to NIR region can be realized by codoping  $\text{Mn}^{4+}$  and multiple ions.

In all the host lattice of complex oxides, as summarized in Table 1,  $\text{Mn}^{4+}$  ions perfectly substitute the sites in the centers of the octahedral environment coordinated with six oxygen atoms due to their similar radius and valence, such as  $\text{Ga}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Ta}^{5+}$ , and  $\text{Mg}^{2+}$ – $\text{Te}^{6+}$  pairs, and  $\text{Nb}^{5+}$  ions. Multiple cation sites in the complex oxide host lattice provide the possibility for codoping  $\text{Mn}^{4+}$  ions and  $\text{Bi}^{3+}$  or trivalent rare earth ions. The optical characteristics of  $\text{Mn}^{4+}$  and other ions are strongly dependent on the structural symmetry of the host materials.



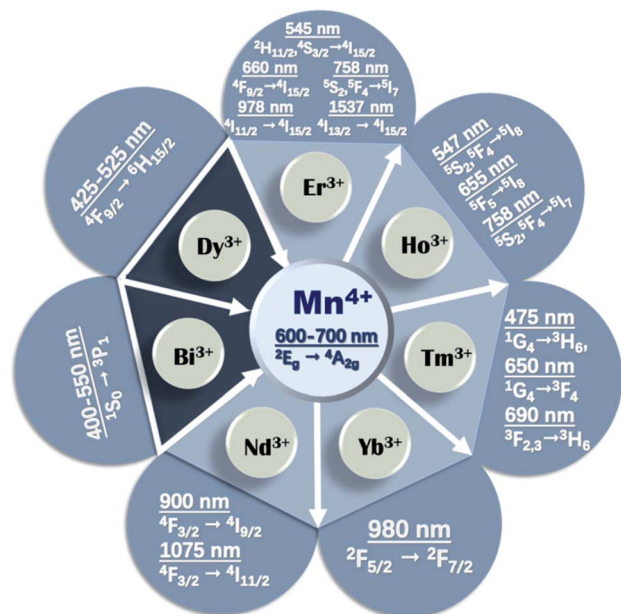


Fig. 2 Summary of the energy transfer between  $\text{Mn}^{4+}$  and rare earth ions.

This review aims to comprehensively present the structural-dependent optical properties based on the energy transfer between  $\text{Mn}^{4+}$  and multiple ions in codoped complex oxide phosphors for potential applications in high-efficient solar energy cells, warm WLEDs, indoor plant cultivation, and temperature sensors.

$\text{Mn}^{4+}$  is isoelectronic with  $\text{Cr}^{3+}$ , but the crystal field at the higher charged  $\text{Mn}^{4+}$  ions is stronger than that of  $\text{Cr}^{3+}$  and the vibronic emission  ${}^2\text{E}_g \rightarrow {}^4\text{A}_{2g}$  of  $\text{Mn}^{4+}$  is more intense than that of  $\text{Cr}^{3+}$ . The Tanabe–Sugano energy diagram presents the energy splitting of the  $\text{Mn}^{4+}$  ion with an octahedral coordination dependent on the crystal field strength (Fig. 3a).<sup>5–12,38,40</sup> The Stokes shift and the features of the photoluminescence emission and excitation (PL and PLE) spectra of  $\text{Mn}^{4+}$  ions are known to be tunable by changing the crystal-field of the host. The

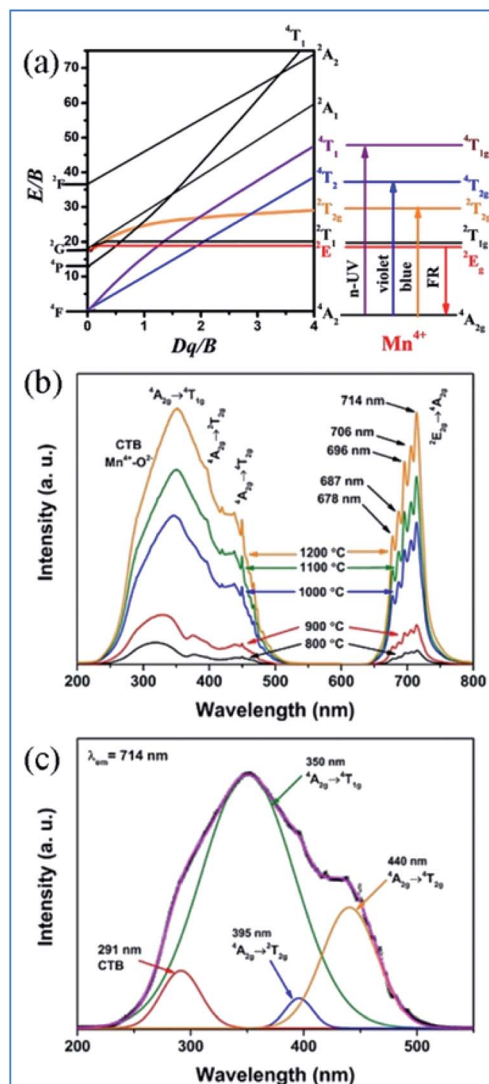


Fig. 3 (a) Tanabe–Sugano diagram for  $\text{Mn}^{4+}$  dependent on the crystal field in complex oxides, (b) typical PLE and PL spectra, and (c) Gaussian curves of PLE spectra of  $\text{Mn}^{4+}$  in  $\text{Ca}_{14}\text{Zn}_6\text{Ga}_{10}\text{O}_{35}$  phosphors. Reprinted with permission from ref. 39, Copyright 2017, The Royal Society of Chemistry.

Table 1 Summary of the substituted sites for  $\text{Mn}^{4+}$  and rare earth (RE) ions, and the PLE and PL position of  $\text{Mn}^{4+}$  in various host lattices

	$\text{Mn}^{4+}$ doping octahedral centers	RE doping	Excitation of $\text{Mn}^{4+}$ at 200–500 nm (maximum band)	Emission of $\text{Mn}^{4+}$ at 650–800 nm (maximum peak)	Ref.
$\text{Ca}_{14}\text{Zn}_6\text{Ga}_{10}\text{O}_{35}$	$\text{Ga}^{3+}$	$\text{Ca}^{2+}$	313 nm	712 nm	13, 46, 51 and 61–63
$\text{Ca}_{14}\text{Zn}_6\text{Al}_{10}\text{O}_{35}$	$\text{Al}^{3+}$	$\text{Ca}^{2+}$	460 nm	710 nm	14, 15, 54, 65 and 66
$\text{Ca}_3\text{ZnAl}_4\text{O}_{10}$	$\text{Al}^{3+}$	$\text{Ca}^{2+}$	467 nm	715 nm	18
$\text{Gd}_2\text{ZnTiO}_6$	$\text{Ti}^{4+}$	$\text{Gd}^{3+}$	365 nm	704 nm	33, 74 and 75
$\text{La}_2\text{LiTaO}_6$	$\text{TaO}_6$	$\text{La}^{3+}$	495 nm	709 nm	34
$\text{NaMgLaTeO}_6$	$\text{Mg}^{2+}$ and $\text{Te}^{6+}$	$\text{La}^{3+}$	365 nm	705 nm	16
$\text{La}_2\text{MgTiO}_6$	$\text{Ti}^{4+}$	$\text{La}^{3+}$	355 nm	710 nm	35, 79 and 80
$\text{Ba}_2\text{LaNbO}_6$	$\text{Nb}^{5+}$	$\text{La}^{3+}$	352 nm	677 nm	35
$\text{CaAl}_{12}\text{O}_{19}$	$\text{Al}^{3+}$	$\text{Ca}^{2+}$	400 nm	654 nm	36, 116 and 117
$\text{Mg}_2\text{TiO}_4$	$\text{Ti}^{4+}$	$\text{Mg}^{2+}$	475 nm	657 nm	37
$\text{La}_2\text{ZnTiO}_6$	$\text{Ti}^{4+}$	$\text{La}^{3+}$	345 nm	710 nm	38
$\text{MgAl}_2\text{Si}_2\text{O}_8$	$\text{Si}^{4+}$	$\text{Mg}^{2+}$	258 nm	710 nm	39 and 145–147
$\text{YAlO}_3$	$\text{Al}^{3+}$	$\text{Y}^{3+}$	414 nm	714 nm	32

spectral position of  $\text{Mn}^{4+}$  ions can be easily tuned over a wide range from 620 nm to 723 nm by modifying the crystal field environment.<sup>8,41</sup>  $\text{Mn}^{4+}$  ions are inclined to form  $\text{Mn}^{4+}\text{--Mn}^{4+}$  pairs due to the  $\text{O}^{2-}$  impurities in oxides, which significantly influence the excited state dynamics and reduce the luminescence efficiency of  $\text{Mn}^{4+}$ .<sup>36,42</sup>

## 2. Luminescent properties of $\text{Mn}^{4+}$ in complex oxide phosphors

$\text{Mn}^{4+}$  ions generally occupy octahedral sites coordinated by eight oxygens in complex oxide phosphors, and the PLE and PL spectra of  $\text{Mn}^{4+}$  ions are located in the range of 200–500 nm and 600–700 nm, respectively. As shown in Fig. 3b and c, the excitation bands located at 350 and 440 nm in the PLE spectrum of  $\text{Mn}^{4+}$  in  $\text{Ca}_{14}\text{Zn}_6\text{Ga}_{10}\text{O}_{35}$  (CZGO) are assigned to the spin-allowed transitions of  $\text{Mn}^{4+}$ . The three Gaussian peaks at 313, 356, and 462 nm are attributed to the  ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$ ,  ${}^4\text{A}_{2g} \rightarrow {}^2\text{T}_{2g}$ , and  ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$  of  $\text{Mn}^{4+}$  transitions, respectively. The broad band at 291 nm in the PLE spectrum of  $\text{Mn}^{4+}$  is ascribed to both the charge transfer transitions of  $\text{Mn}^{4+} \rightarrow \text{O}^{2-}$  and  ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$  transitions of  $\text{Mn}^{4+}$  ions. Under excitation at 310 nm, the intense red emission is composed of some distinguishable sharp R lines and Stokes/anti-Stokes side-peaks located at 676, 684, 695, 704 and 713 nm due to the different vibrational modes for the  $3d^3$  electrons when  $\text{Mn}^{4+}$  is in the  $[\text{MnO}_6]^{8-}$  octahedral complex, which correspond to the vibronic sidebands of the  ${}^2\text{E}_g \rightarrow {}^4\text{A}_{2g}$  transition of the  $\text{Mn}^{4+}$  ions.<sup>43</sup>

## 3. NIR emission of $\text{Nd}^{3+}$ , $\text{Yb}^{3+}$ , $\text{Er}^{3+}$ , $\text{Ho}^{3+}$ , and $\text{Tm}^{3+}$ sensitized by $\text{Mn}^{4+}$

### 3.1 $\text{Ca}_{14}\text{Zn}_6\text{Ga}_{10}\text{O}_{35}$ as host lattice for $\text{Mn}^{4+}$ and multiple ion codoping

**3.1.1 Formation of tunable color luminescence centers in  $\text{Ca}_{14}\text{Zn}_6\text{Ga}_{10}\text{O}_{35}$ .** Fig. 4a shows that when viewed from the  $^{100}$  plane, the unit cells for the crystal structure of  $\text{Ca}_{14}\text{Zn}_6\text{Ga}_{10}\text{O}_{35}$  (CZGO) possess a cubic structure with the space group  $F23$  (196) and lattice parameters  $a = 15.0794 \text{ \AA}$  and  $V = 3428.88 \text{ \AA}^3$ . According to Pauling's rules, one of these empty containers is

filled with octahedral  $(\text{Ga,Zn})\text{O}_6^-$ , while the others are half occupied by four corner-linked tetrahedral  $\text{ZnO}_4$  sharing a common oxygen atom.<sup>45</sup> All the edges are shared by various Ca polyhedra. Thus, there are three independent  $\text{Ca}^{2+}$  sites in CZGO, where two of them have an octahedral geometry and the third is in a seven-coordinated polyhedron. Moreover, the effective ionic radii of the six-coordinated  $\text{Ga}^{3+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Ca}^{2+}$  ions are 0.62, 0.74, and 1.00  $\text{\AA}$ , respectively. The specific crystal structure of CZGO makes doping multiple ions and forming tunable color luminescence centers possible.<sup>46</sup>

Based on the effective ionic radii of cations with different coordination numbers (CN),<sup>47</sup> trivalent rare earth ions are expected to randomly occupy six- and seven-coordinated  $\text{Ca}^{2+}$  (CN = 6,  $r = 1.00 \text{ \AA}$  and CN = 7,  $r = 1.06 \text{ \AA}$ ) sites, and  $\text{Mn}^{4+}$  (CN = 6,  $r = 0.53 \text{ \AA}$ ) ions are preferentially accommodated at the  $\text{Ga}^{3+}$  (CN = 5,  $r = 0.62 \text{ \AA}$ ) sites with an octahedral coordination in the crystal structure.<sup>41</sup> Electroneutrality in the  $\text{Mn}^{4+}$  and multiple ion-codoped CAZO phosphors can be easily achieved due to some defects such as the formation of  $\text{Ca}^{2+}$  vacancies and excess  $\text{O}^{2-}$  ligands for charge compensation.<sup>48</sup>

**3.1.2 Dual mode energy transfer between  $\text{Mn}^{4+}$  and  $\text{Nd}^{3+}/\text{Er}^{3+}/\text{Yb}^{3+}$  in CZGO.** The energy transfer efficiency depends on the matching of the energy levels between the excitation wavelength of the acceptor and donor emission frequency.<sup>50,51</sup> Fig. 5a–c depict the spectral overlap between the emission spectrum of  $\text{Mn}^{4+}$  and the excitation spectra of  $\text{Nd}^{3+}/\text{Er}^{3+}/\text{Yb}^{3+}$ , which demonstrates that the  $\text{Mn}^{4+}$  ion has a strong possibility of being an effective sensitizer for NIR emission of  $\text{Nd}^{3+}/\text{Er}^{3+}/\text{Yb}^{3+}$  through a non-radiative resonant energy transfer process.<sup>49</sup>

Fig. 5e–g show the emission spectra of  $\text{Mn}^{4+}$  and multiple ions  $\text{Nd}^{3+}/\text{Er}^{3+}/\text{Yb}^{3+}$  codoped CZGO with different doping concentrations of  $\text{Ln}^{3+}$  ions, respectively. Upon excitation at 313 nm, the NIR emissions of  $\text{Nd}^{3+}/\text{Er}^{3+}/\text{Yb}^{3+}$  such as the emission peaks at 900 and 1075 nm are assigned to the  ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{9/2}$  and  ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{11/2}$  transitions of  $\text{Nd}^{3+}$ , that at 978 and 1537 nm are ascribed to the  ${}^4\text{I}_{11/2} \rightarrow {}^4\text{I}_{15/2}$  and  ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$  transitions of  $\text{Er}^{3+}$ , and that at 980 nm is caused by the  ${}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$  transition of  $\text{Yb}^{3+}$ . The emission intensity of  $\text{Mn}^{4+}$  monotonously decreases with an increase in the content of  $\text{Ln}^{3+}$ , which indicates energy transfer occurs from  $\text{Mn}^{4+}$  to  $\text{Nd}^{3+}/\text{Er}^{3+}/\text{Yb}^{3+}$ .

The energy transfer process from  $\text{Mn}^{4+}$  to multiple ions,  $\text{Nd}^{3+}/\text{Er}^{3+}/\text{Yb}^{3+}$ , in CZGO is illustrated in Fig. 6a. Under excitation of NUV to visible light ranging from 250 to 550 nm, the  $\text{Mn}^{4+}$  ions are excited into their charge transfer or excited states of  ${}^4\text{T}_{1g}$  and  ${}^4\text{T}_{2g}$ , which then rapidly relax to the metastable state of  ${}^2\text{E}_g$  of the  $\text{Mn}^{4+}$  ions. The energy transfer occurs via  $\text{Mn}^{4+}: {}^2\text{E}_g + \text{Nd}^{3+}: {}^4\text{I}_{9/2} \rightarrow \text{Mn}^{4+}: {}^4\text{A}_{2g} + \text{Nd}^{3+}: {}^4\text{F}_{9/2}$ ,  ${}^4\text{F}_{7/2}$ ,  ${}^4\text{S}_{3/2}$  or  $\text{Mn}^{4+}: {}^2\text{E}_g + \text{Yb}^{3+}: {}^2\text{F}_{7/2} \rightarrow \text{Mn}^{4+}: {}^4\text{A}_{2g} + \text{Yb}^{3+}: {}^2\text{F}_{5/2}$ . The NIR emissions at 896 and 1064, 1540, and 980 nm are generated by the radiative transitions of the  $\text{Nd}^{3+}: {}^4\text{F}_{3/2}$ ,  $\text{Er}^{3+}: {}^4\text{I}_{13/2}$  and  $\text{Yb}^{3+}: {}^2\text{F}_{5/2}$  levels, respectively.<sup>52</sup>

Under 980 nm light excitation, green upconverted emission peaks at 551 and 561 nm attributed to the  ${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2}$  and  ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$  transitions of  $\text{Er}^{3+}$  are produced, as shown in Fig. 6b. Therefore, the red emission centered at 712 nm of  $\text{Mn}^{4+}$

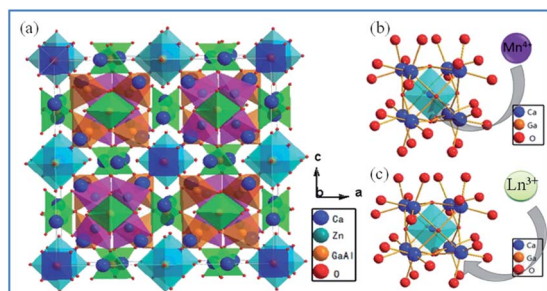


Fig. 4 (a) Crystal structure of  $\text{Ca}_{14}\text{Zn}_6\text{Ga}_{10}\text{O}_{35}$ , (b) schematic diagram of  $\text{Mn}^{4+}$  ions occupying the octahedral lattice sites of  $\text{Ga}^{3+}$ , and (c)  $\text{Ln}^{3+}$  ions occupying the  $\text{Ca}^{2+}$  ion sites in the  $\text{Ca}_{14}\text{Zn}_6\text{Ga}_{10}\text{O}_{35}$  host. Reprinted with permission from ref. 44, Copyright 2017, The Royal Society of Chemistry.



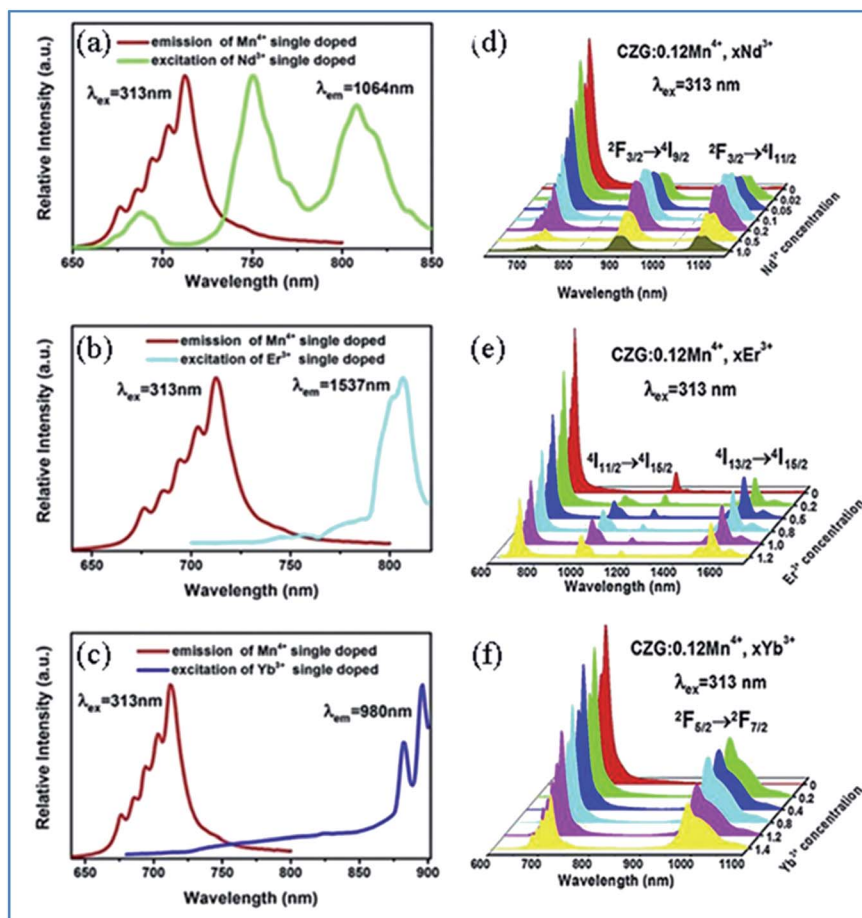


Fig. 5 (a–c) Overlap between the PL spectrum of  $\text{Ca}_{14}\text{Zn}_6\text{Ga}_{10}\text{O}_{35}:\text{Mn}^{4+}$  and PLE spectra of  $\text{Ca}_{14}\text{Zn}_6\text{Ga}_{10}\text{O}_{35}:\text{Ln}^{3+}$  ( $\text{Ln} = \text{Nd}, \text{Er}, \text{and Yb}$ ), respectively. (d–f) Changes in the PL spectra of  $\text{Mn}^{4+}$  and multiple ion  $\text{Nd}^{3+}/\text{Er}^{3+}/\text{Yb}^{3+}$  codoped  $\text{Ca}_{14}\text{Zn}_6\text{Ga}_{10}\text{O}_{35}$  with a change in the concentration of  $\text{Nd}^{3+}/\text{Er}^{3+}/\text{Yb}^{3+}$ , respectively. Reprinted with permission from ref. 49, Copyright 2019, Elsevier BV.

and  $\text{Er}^{3+}$  codoped CZGO phosphor produced by excitation at 980 nm is ascribed to the energy transfer from  $\text{Er}^{3+}$  to  $\text{Mn}^{4+}$ .

The green and red emission centered at 551 (561) and 661 nm can be ascribed to the transitions of  $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$  ( $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ ) and  $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$  of  $\text{Er}^{3+}$ , respectively, *via* the multiple non-radiative multiphonon relaxations from the  $^4\text{F}_{7/2}$  to  $\text{H}_{11/2}$ ,  $^4\text{S}_{3/2}$  and  $^4\text{F}_{9/2}$  levels.<sup>53</sup> The deep red emission ascribed to the transition of  $^2\text{E}_g \rightarrow ^4\text{A}_{2g}$  of  $\text{Mn}^{4+}$  is attributed to the energy transfer from  $\text{Er}^{3+}$  to  $\text{Mn}^{4+}$ , as illustrated in the corresponding mechanism diagram in Fig. 6c. The spectral overlap observed between the emission spectrum of  $\text{Er}^{3+}$  and the excitation spectrum of  $\text{Mn}^{4+}$  makes the reversal energy transfer from  $\text{Er}^{3+}$  to  $\text{Mn}^{4+}$  possible, as presented in Fig. 6d.

### 3.2 $\text{Ca}_{14}\text{Zn}_6\text{Al}_{10}\text{O}_{35}$ as host lattice for $\text{Mn}^{4+}$ and multiple ion codoping

**3.2.1 Formation of tunable color luminescence centers in  $\text{Ca}_{14}\text{Zn}_6\text{Al}_{10}\text{O}_{35}$ .** Fig. 7 shows the unit cell structure and the coordination environment of the cation sites of a typical  $\text{Ca}_{14}\text{Zn}_6\text{Al}_{10}\text{O}_{35}$  (CZAO) compound. CZAO has a cubic structure with the space group  $F23$ . In the crystal structure of CZAO,  $\text{Ca}^{2+}$  has three different coordination environments, where two of them

are coordinated to six oxygen atoms, forming a distorted octahedron, while the third is in a seven-coordinated polyhedron and the average Ca–O distance is equal to 2.498 Å.<sup>54,55</sup> In addition, four of the five independent positions occupied by Zn and Al are in the tetrahedral coordination, with the average Zn–O distance of 1.951 Å and average Al–O distances of 1.719, 1.794 and 1.891 Å, respectively. The positions are in an octahedron coordination, and the one-fifth positions occupied by Al and Zn are octahedral coordinations.<sup>56–59</sup> The  $\text{Ca}^{2+}$  site is likely to be replaced by a small amount of  $\text{Nd}^{3+}/\text{Yb}^{3+}$  ions without significant structural changes due to the similar ion radii between  $\text{Ca}^{2+}$  and  $\text{Nd}^{3+}/\text{Yb}^{3+}$  ( $\text{Ca}^{2+}$ :  $r = 0.100$  nm;  $\text{Nd}^{3+}$ :  $r = 0.098$  nm; and  $\text{Yb}^{3+}$ :  $r = 0.086$  nm).

**3.2.2 Energy transfer between  $\text{Mn}^{4+}$  and  $\text{Nd}^{3+}/\text{Er}^{3+}/\text{Yb}^{3+}$  in CZAO.** Under excitation by UV to visible light from 250 to 550 nm, intense NIR emissions are produced at 900 and 1060 nm originating from the  $\text{Nd}^{3+}$ :  $^4\text{F}_{3/2}/^4\text{I}_{9/2}$  and  $\text{Nd}^{3+}$ :  $^4\text{F}_{3/2}/^4\text{I}_{11/2}$  in  $\text{Mn}^{4+}$  and  $\text{Nd}^{3+}$ -codoped phosphors. The emission at 980 nm in the  $\text{Mn}^{4+}$ ,  $\text{Yb}^{3+}$  codoped samples is ascribed to the  $\text{Yb}^{3+}$ :  $^2\text{F}_{5/2}/^2\text{F}_{7/2}$  transitions.<sup>60</sup> The energy transfer based on the strong absorption of  $\text{Mn}^{4+}$  and spin-allowed transitions of  $\text{Nd}^{3+}/\text{Yb}^{3+}$  through dipole–dipole interaction is illustrated in Fig. 8. The shapes of the PLE



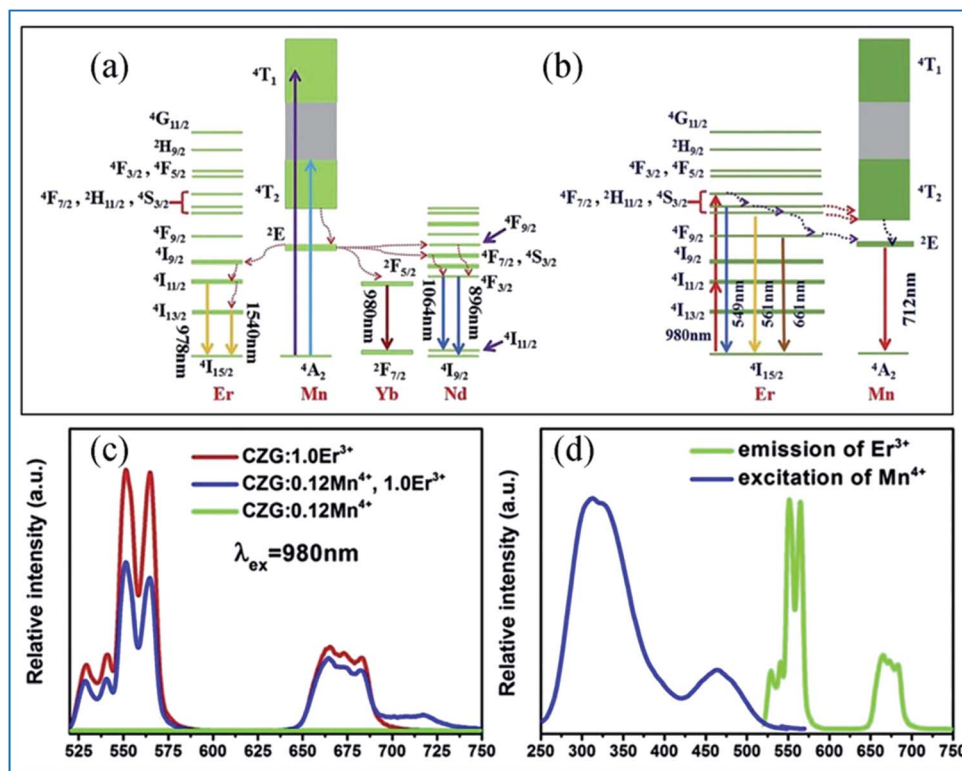


Fig. 6 (a) Excitation/emission and energy transfer mechanism of Mn<sup>4+</sup> to Ln<sup>3+</sup> in Ca<sub>14</sub>Zn<sub>6</sub>Ga<sub>10</sub>O<sub>35</sub>:Mn<sup>4+</sup>,Ln<sup>3+</sup> (Ln = Nd, Er, and Yb) phosphors. (b) Mechanism of the up-conversion of Er<sup>3+</sup> and energy transfer from Er<sup>3+</sup> to Mn<sup>4+</sup>. (c) Emission spectra of Mn<sup>4+</sup> and Er<sup>3+</sup> codoped Ca<sub>14</sub>Zn<sub>6</sub>Ga<sub>10</sub>O<sub>35</sub> upon 980 nm excitation and (d) spectral overlap between the emission of Er<sup>3+</sup> and excitation of Mn<sup>4+</sup>. Reprinted with permission from ref. 49, Copyright 2019, Elsevier BV.

spectra of both the Mn<sup>4+</sup>/Nd<sup>3+</sup> and Mn<sup>4+</sup>/Yb<sup>3+</sup> codoped samples monitored at 1060 nm and 980 nm, respectively, are quite similar to that of the Mn<sup>4+</sup> single-doped sample (Fig. 8a–c). Only weak and discrete PLE peaks in the visible region caused by the f–f transitions of Nd<sup>3+</sup> appear in the Nd<sup>3+</sup> single-doped sample and no PLE peak in the visible region is observed in the Yb<sup>3+</sup> single-doped sample (Fig. 8a and b), respectively. Thus, the

characteristics of the above PLE spectra demonstrate that the NIR luminescence of Nd<sup>3+</sup>/Yb<sup>3+</sup> in Mn<sup>4+</sup> and multiple ion Nd<sup>3+</sup>/Yb<sup>3+</sup> codoped CZAO is generated by the energy transfer from Mn<sup>4+</sup> to Nd<sup>3+</sup>/Yb<sup>3+</sup> ions.<sup>61–63</sup>

The energy transfer efficiency depends on the spectral matching of the excitation of the acceptor and emission spectra of the donor. As shown in Fig. 8d, good spectral overlap can be

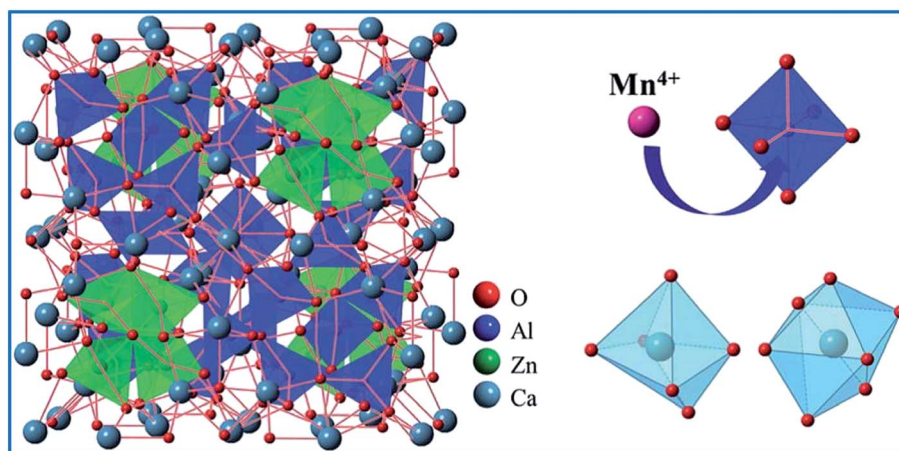


Fig. 7 Schematic of the crystal structure of Ca<sub>14</sub>Zn<sub>6</sub>Al<sub>10</sub>O<sub>35</sub>. Reprinted with permission from ref. 14, Copyright 2016, The Royal Society of Chemistry.

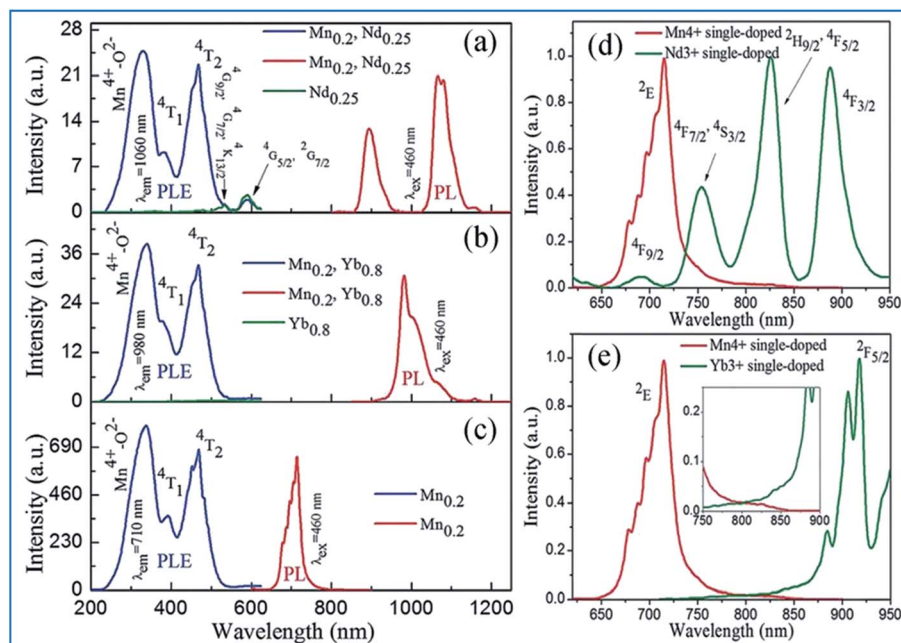


Fig. 8 (Left) PLE spectra and/or (right) PL spectra for (a)  $\text{Ca}_{13.75}\text{Zn}_6\text{Al}_{9.8}\text{O}_{35}:\text{Mn}_{0.2}, \text{Nd}_{0.25}$  and  $\text{Ca}_{13.75}\text{Zn}_6\text{Al}_{10}\text{O}_{35}:\text{Nd}_{0.25}$ , (b)  $\text{Ca}_{13.2}\text{Zn}_6\text{Al}_{9.8}\text{O}_{35}:\text{Mn}_{0.2}, \text{Yb}_{0.8}$  and  $\text{Ca}_{13.2}\text{Zn}_6\text{Al}_{10}\text{O}_{35}:\text{Yb}_{0.8}$ , and (c)  $\text{Ca}_{14}\text{Zn}_6\text{Al}_{9.8}\text{O}_{35}:\text{Mn}_{0.2}$ . Spectral overlap between the emission spectrum of  $\text{Mn}^{4+}$  and the excitation spectrum of (d)  $\text{Nd}^{3+}$  monitored at 1060 nm and (e)  $\text{Yb}^{3+}$  monitored at 980 nm. Reprinted with permission from ref. 14, Copyright 2016, The Royal Society of Chemistry.

observed between the  ${}^2\text{E}_g$  emission of  $\text{Mn}^{4+}$  and the  ${}^4\text{F}_{9/2}$ ,  ${}^4\text{F}_{7/2}$ , and  ${}^4\text{S}_{3/2}$  excitations of  $\text{Nd}^{3+}$ . It can be seen from Fig. 8e that although there is a relatively large energy gap between the excited state  ${}^2\text{E}_g$  of  $\text{Mn}^{4+}$  and  ${}^2\text{F}_{5/2}$  of  $\text{Yb}^{3+}$ , an efficient energy transfer from  $\text{Mn}^{4+}$  to  $\text{Yb}^{3+}$  can still occur in the  $\text{Mn}^{4+}$  and  $\text{Yb}^{3+}$  codoped samples with strong electron-phonon coupling.<sup>64</sup> Therefore, the NIR luminescence of  $\text{Yb}^{3+}$  may be mainly generated by phonon-assisted energy transfer from  $\text{Mn}^{4+}$  to  $\text{Yb}^{3+}$ . The excitation/emission and energy transfer pathways for the  $\text{Mn}^{4+}$  and codoped  $\text{Nd}^{3+}/\text{Yb}^{3+}$  ion couples in CZAO are quite similar to that in the host lattice of CZGO.<sup>14,49</sup>

NIR emissions from  $\text{Nd}^{3+}/\text{Yb}^{3+}$  have been observed in  $\text{Mn}^{4+}$  and  $\text{Nd}^{3+}/\text{Yb}^{3+}$  codoped CZAO phosphors. The intensity of the NIR emissions of  $\text{Nd}^{3+}/\text{Yb}^{3+}$  increases initially with an increase in the content of rare earth ions  $\text{Nd}^{3+}/\text{Yb}^{3+}$ , and then decreases gradually as a result of concentration quenching.<sup>62</sup> The NIR luminescence intensity is enhanced by 338 times at 1060 nm for  $\text{Ca}_{13.75}\text{Zn}_6\text{Al}_{9.4}\text{O}_{35}:\text{Mn}_{0.6}, \text{Nd}_{0.25}$  and 306 times at 980 nm for  $\text{Ca}_{13.2}\text{Zn}_6\text{Al}_{9.4}\text{O}_{35}:\text{Mn}_{0.6}, \text{Yb}_{0.8}$ , respectively, which is attributed to the efficient energy transfer from  $\text{Mn}^{4+}$  to the  $\text{Nd}^{3+}/\text{Yb}^{3+}$  ions, respectively.<sup>65,66</sup> Fig. 9a and b illustrate the excitation spectra of  $\text{Mn}^{4+}$  and emission spectra of  $\text{Er}^{3+}$  in  $\text{Mn}^{4+}$  and/or  $\text{Er}^{3+}$  codoped samples with various doping concentrations. The two broad and intense excitation bands (monitored at  $\text{Mn}^{4+}$  710 nm emission) correspond to the spin-allowed transitions  ${}^4\text{A}_g \rightarrow {}^4\text{T}_g$  and  ${}^4\text{A}_g \rightarrow {}^4\text{T}_g$  of  $\text{Mn}^{4+}$  (Fig. 9a). The weak and discrete excitation peaks (monitored at  $\text{Er}^{3+}$  1540 nm emission) are ascribed to the transitions from  ${}^4\text{I}_{15/2}$  to  ${}^4\text{G}_{11/2}$ ,  ${}^4\text{F}_{5/2}$ ,  ${}^4\text{F}_{7/2}$ ,  ${}^2\text{H}_{11/2}$ , and  ${}^4\text{S}_{3/2}$  of  $\text{Er}^{3+}$ . From the excitation spectrum of the  $\text{Mn}^{4+}$  and  $\text{Er}^{3+}$  codoped sample monitored at the 1540 nm emission of  $\text{Er}^{3+}$  in Fig. 9b, it can be seen that not only broad and intense excitation bands

ascribed to  $\text{Mn}^{4+}$  ions but also the superimposed excitation peaks assigned to the  ${}^4\text{I}_{15/2}$  to  ${}^2\text{H}_{11/2}$  and  ${}^4\text{S}_{3/2}$  transitions of  $\text{Er}^{3+}$  appear, indicating the energy transfer from  $\text{Mn}^{4+}$  to  $\text{Er}^{3+}$ .

### 3.3 Complex hexoxides as host lattices for $\text{Mn}^{4+}$ and multiple ion codoping

As shown in Fig. 10a,<sup>65</sup>  $\text{Gd}_2\text{ZnTiO}_6$  (GZT) crystallizes in a double-perovskite monoclinic structure with the space group  $P2_1/n$ , with the cell parameters of  $a = 5.3664(9)$  Å,  $b = 5.6631(9)$  Å,  $c =$

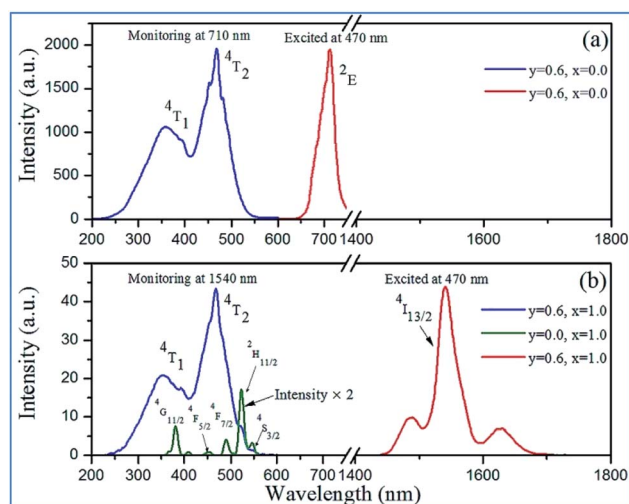


Fig. 9 Excitation and emission spectra of  $\text{Ca}_{14-x}\text{Zn}_6\text{Al}_{10-y}\text{O}_{35}:\text{Mn}_y, \text{Er}_x$  ( $y = 0.0, 0.6$ ;  $x = 0.0, 1.0$ ) in (a) NIR and (b) IR regions. Reprinted with permission from ref. 4, Copyright 2016, The Royal Society of Chemistry.



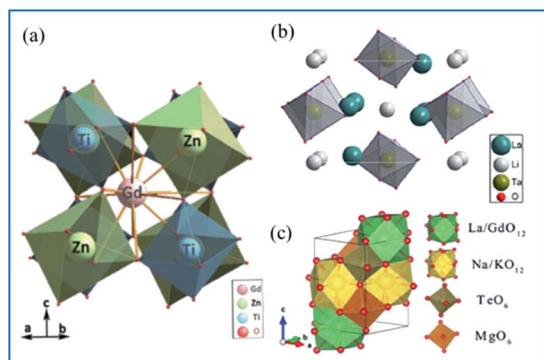


Fig. 10 Crystal structure of (a)  $\text{Gd}_2\text{ZnTiO}_6$ . Reprinted with permission from ref. 65, Copyright 2014, The Chemical Society of Japan. (b)  $\text{La}_2\text{LiTaO}_6$ . Reprinted with permission from ref. 34, Copyright 2014, Springer Nature. (c)  $\text{NaMgLaTeO}_6$ . Reprinted with permission from ref. 16, Copyright 2018, The Royal Society of Chemistry.

7.6847(9) Å and  $\beta = 90.294(2)^\circ$ . In the crystal structure of GZT, the  $\text{Zn}^{2+}$  and  $\text{Ti}^{4+}$  ion centers are at two slantwise octahedral sites surrounded by six oxygen atoms, and the  $\text{Gd}^{3+}$  ion occupies the decahedron site coordinated with twelve oxygen atoms.  $\text{La}_2\text{LiTaO}_6$  is built up of alternating strands of  $\text{LiO}_6$  and slightly disordered  $\text{TaO}_6$  with  $\text{La}^{3+}$  located in the cavities of the interconnected network of octahedral sites, as shown in Fig. 10b.<sup>67–70</sup>

According to the doping rule that with a similar radius and the same valence of the dopants and host cationic ions,  $\text{Mn}^{4+}$  ions perfectly enter the centers of the octahedral environment coordinated with six oxygen atoms and the trivalent rare earth ions can occupy the  $\text{Gd}^{3+}$  and/or  $\text{La}^{3+}$  sites in the host lattices of complex hexoxides, respectively.  $\text{NaMgLaTeO}_6$  crystallizes in a monoclinic system with the  $P12_1/m1(11)$  space group, as depicted in Fig. 10c.<sup>16,71,72</sup> Both  $\text{Mg}^{2+}$  and  $\text{Te}^{6+}$  are located at the six-fold sites to form  $\text{MgO}_6$  and  $\text{TeO}_6$  octahedra with a shared oxygen atom, respectively. Moreover, the La/Gd and Na/K atoms are coordinated with twelve oxygen atoms to form polyhedral La/GdO<sub>12</sub> and Na/KO<sub>12</sub>. These four types of polyhedra connect closely to construct the space framework of this crystal structure.<sup>73</sup> The  $\text{Mg}^{2+}$  and  $\text{Te}^{6+}$  sites at the centers of the octahedra are expected to be substituted by  $\text{Mn}^{4+}$  ions and red luminescence centers of  $\text{Mn}^{4+}$  are formed. In the  $\text{Mn}^{4+}$  and  $\text{Er}^{3+}$  codoped GZT sample, efficient energy transfer from  $\text{Mn}^{4+}$  to  $\text{Er}^{3+}$  was observed, and the mechanism is quite similar to that in  $\text{Mn}^{4+}$  and  $\text{Er}^{3+}$  codoped CZAO.<sup>14</sup>

It can be seen from Fig. 11a that the emission spectrum of  $\text{Gd}_2\text{ZnTiO}_6:\text{yMn}^{4+},0.02\text{Er}^{3+}$  ( $y = 0, 0.002$ ) is excited at 335 nm, corresponding to the  $^4\text{A}_{2g} \rightarrow ^4\text{T}_{1g}$  of  $\text{Mn}^{4+}$ , and in that of  $\text{Gd}_2\text{ZnTiO}_6:0.002\text{Mn}^{4+},2x\text{Er}^{3+}$  ( $x = 0, 0.005$ ) are excited at 379 nm, corresponding to  $^4\text{A}_{2g} \rightarrow ^4\text{T}_{1g}$  of  $\text{Mn}^{4+}$  and  $^4\text{I}_{15/2} \rightarrow ^4\text{G}_{11/2}$  of  $\text{Er}^{3+}$ .<sup>75</sup> Only the characteristic emission peaks ( $^2\text{E}_g$ ) of  $\text{Mn}^{4+}$  can be observed and no characteristic visible emission peaks ( $^2\text{H}_{11/2}/^4\text{S}_{3/2}$ ) of  $\text{Er}^{3+}$  for the GZT:0.002 $\text{Mn}^{4+}$ ,0.02 $\text{Er}^{3+}$  sample in the emission excited at 335 nm. Spectral overlap exists between the emission for  $\text{Er}^{3+}$  ( $^2\text{H}_{11/2}/^4\text{S}_{3/2}$ ) and the absorption for  $\text{Mn}^{4+}$  ( $^4\text{A}_{2g}$ ), which provides a possible energy transfer pathway from  $\text{Mn}^{4+}$  to  $\text{Er}^{3+}$ .<sup>76</sup> The emission intensity of  $^2\text{E}_g$  of  $\text{Mn}^{4+}$  upon the codoping of  $\text{Er}^{3+}$  in

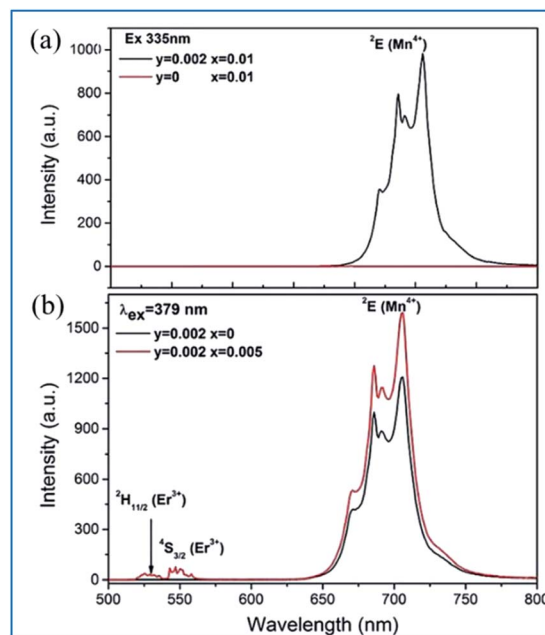


Fig. 11 (a) Emission spectra of  $\text{Gd}_2\text{ZnTiO}_6:\text{yMn}^{4+},0.02\text{Er}^{3+}$  ( $y = 0, 0.002$ ) excited at 335 nm, and (b)  $\text{Gd}_2\text{ZnTiO}_6:0.002\text{Mn}^{4+},2x\text{Er}^{3+}$  ( $x = 0, 0.005$ ) excited at 379 nm. Reprinted with permission from ref. 74, Copyright 2017, The Royal Society of Chemistry.

GZT is much stronger than that of  $\text{Mn}^{4+}$  single-doped GZT under the common excitation wavelength of 379 nm, which indicates that energy back transfer occurs from  $\text{Er}^{3+}$  ( $^2\text{H}_{11/2}/^4\text{S}_{3/2}$ ) to  $\text{Mn}^{4+}$  ( $^4\text{A}_2$ ) under the common excitation wavelength of 379 nm (see Fig. 11b).

The IR emission at 1529 nm is ascribed to the  $^4\text{F}_{9/2}$  ( $^4\text{I}_{9/2}$ )  $\rightarrow$   $^4\text{I}_{13/2}$  transition of  $\text{Er}^{3+}$  through energy transfer from  $\text{Mn}^{4+}$  in the  $\text{Mn}^{4+}$  and  $\text{Er}^{3+}$  codoped GZT phosphor and the corresponding mechanism is illustrated in Fig. 12a. The  $\text{Mn}^{4+}$  ions are excited into their excite states under irradiation by short-wavelength light in the region of 250–550 nm, and then the energy transfer of  $^2\text{E}(\text{Mn}^{4+}) \rightarrow ^4\text{F}_{9/2}, ^4\text{I}_{9/2}(\text{Er}^{3+})$  happens between the  $\text{Mn}^{4+}$  and  $\text{Er}^{3+}$  ions to populate the  $^4\text{F}_{9/2}$  and  $^4\text{I}_{9/2}$  levels of  $\text{Er}^{3+}$  followed by nonradiative relaxation to  $^4\text{I}_{13/2}$ . Finally, IR emission at 1529 nm is produced by radiative transition from  $^4\text{I}_{13/2}$  to  $^4\text{I}_{15/2}$  of  $\text{Er}^{3+}$ .

Far-red (FR) and near-infrared (NIR) double-wavelength emissions have been observed in the  $\text{Mn}^{4+}$  and  $\text{Yb}^{3+}$  codoped GZT phosphor, which are expected to application in LEDs towards plant cultivation.<sup>77–79</sup> The PLE and PL spectra of the  $\text{Mn}^{4+}$  and  $\text{Yb}^{3+}$  codoped samples are shown in Fig. 12b–d. The shapes and positions of both PLE spectra (Fig. 12b) monitored at emission 704 nm from the  $^2\text{E}_g \rightarrow ^4\text{A}_{2g}$  transition of  $\text{Mn}^{4+}$  and that at 980 nm from the  $\text{Yb}^{3+}$  transition  $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$  are similar to that of  $\text{Mn}^{4+}$  singly doped GZT, which indicates that energy transfer between  $\text{Mn}^{4+}$  and  $\text{Yb}^{3+}$  occurs in the codoping systems. Under the excitation of 365 nm light, both FR emission from  $\text{Mn}^{4+}$  and NIR emission from  $\text{Yb}^{3+}$  are observed in Fig. 12c and d. The FR emission intensity of  $\text{Mn}^{4+}$  gradually decreases with an increase in the content of  $\text{Yb}^{3+}$ , whereas the NIR emission intensity first increases and then decreases due to the





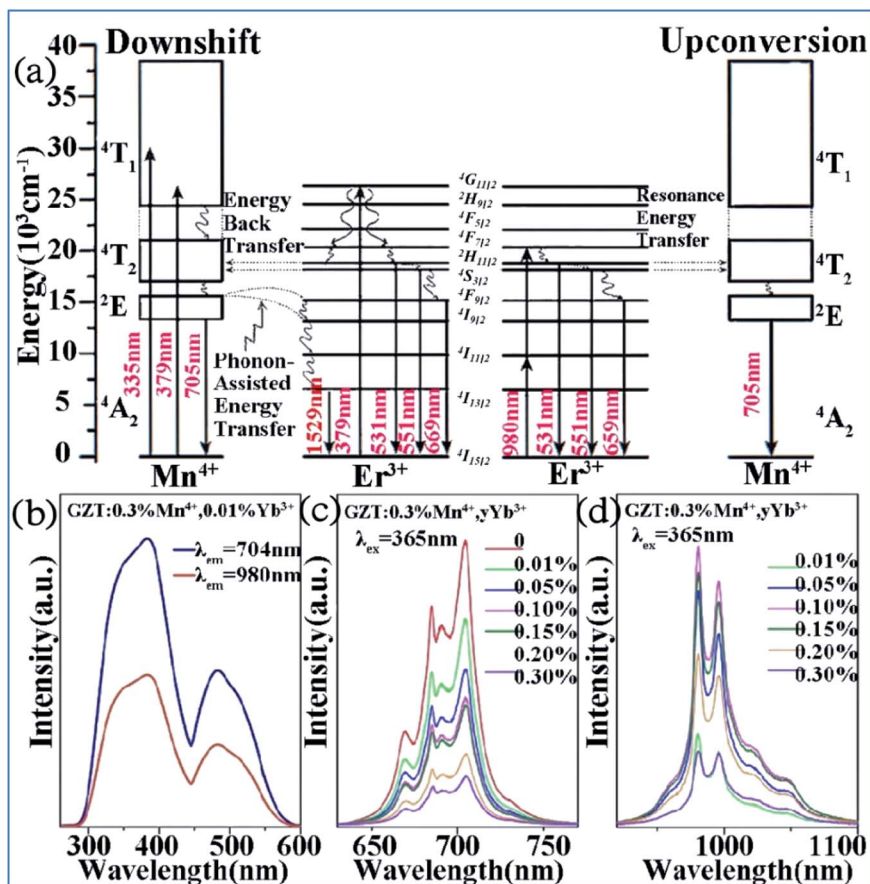


Fig. 12 (a) Electron transitions and mutual sensitized energy transfer scheme between Mn<sup>4+</sup> and Er<sup>3+</sup> in the Gd<sub>2</sub>ZnTiO<sub>6</sub> matrix. Reprinted with permission from ref. 74, Copyright 2017, The Royal Society of Chemistry. (b) PLE, (c) visible, and (d) NIR spectra of Gd<sub>2</sub>ZnTiO<sub>6</sub>:0.3%Mn<sup>4+</sup>,yYb<sup>3+</sup>. Reprinted with permission from ref. 33, Copyright 2018, Elsevier BV.

concentration quenching effect, which further prove the occurrence of energy transfer from Mn<sup>4+</sup> to Yb<sup>3+</sup>.

The similar energy transfer from Mn<sup>4+</sup> to Yb<sup>3+</sup> has been also observed in Mn<sup>4+</sup> and Yb<sup>3+</sup> codoped La<sub>2</sub>MgTiO<sub>6</sub> samples. Broad excitation bands from 250 nm to 550 nm corresponding to the absorptions involving the <sup>4</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>1g</sub>, and <sup>4</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>2g</sub> transitions of Mn<sup>4+</sup> monitored at 710 nm and Yb<sup>3+</sup> ions monitored at 980 nm were observed in the PLE of La<sub>1.91</sub>MgTi<sub>0.998</sub>O<sub>6</sub>:Mn<sub>0.002</sub>,Yb<sub>0.09</sub> sample, as shown in Fig. 13a.<sup>36,80,81</sup> The excitation spectrum monitored at 980 nm of Yb<sup>3+</sup> emission is similar to that monitored at 710 nm of the Mn<sup>4+</sup> emission in the La<sub>1.91</sub>MgTi<sub>0.998</sub>O<sub>6</sub>:Mn<sub>0.002</sub>,Yb<sub>0.09</sub> sample, which clearly proves that energy transfer from Mn<sup>4+</sup> to Yb<sup>3+</sup> takes place in the Mn<sup>4+</sup> and Yb<sup>3+</sup> codoped La<sub>2</sub>MgTiO<sub>6</sub> samples when the Mn<sup>4+</sup> ions are excited.

Fig. 13b and c exhibit the emission spectra of the La<sub>2-x</sub>MgTi<sub>1-y</sub>O<sub>6</sub>:Mn<sub>y</sub>,Yb<sub>x</sub> and La<sub>2-x</sub>MgTi<sub>1-y</sub>O<sub>6</sub>:Mn<sub>y</sub>,Yb<sub>x</sub> samples pumped by 460 nm light. The NIR emission band with the highest peak at 990 nm is from the <sup>2</sup>F<sub>5/2</sub> → <sup>2</sup>F<sub>7/2</sub> transition of Yb<sup>3+</sup> ions and its emission is strongly dependent the concentrations of Yb<sup>3+</sup> ions.<sup>35,82,83</sup> The integrated intensity of the NIR emission band centered at 990 nm increases initially with an increase in the concentration of Yb<sup>3+</sup> ions.

Energy transfer from Mn<sup>4+</sup> to Yb<sup>3+</sup> occurs in the Mn<sup>4+</sup> and Yb<sup>3+</sup> codoped Ba<sub>2</sub>LaNbO<sub>6</sub> (BLNO) samples, as illustrated in Fig. 14.<sup>35</sup> The spectral shapes and positions of the excitation spectra monitored at 677 nm (Mn<sup>4+</sup> emission) and 998 nm (Yb<sup>3+</sup> emission) remain the same, but their intensities are different, which indicates that energy transfer from Mn<sup>4+</sup> to Yb<sup>3+</sup> occurs in the Mn<sup>4+</sup> and Yb<sup>3+</sup> codoped BLNO, as show in Fig. 14a and b. The emission centered at 998 nm is consistent with the infrared light needed for bacterial chlorophyll.<sup>22,84</sup> The intensity of the Mn<sup>4+</sup> emission at 677 nm decreases, while that of the Yb<sup>3+</sup> emission at 998 nm increases due to the transfer of energy from Mn<sup>4+</sup> to Yb<sup>3+</sup>.

Fig. 14c shows the decay lifetimes of BLNO:0.003Mn<sup>4+</sup>,yYb<sup>3+</sup>, which decrease with an increase in the Yb<sup>3+</sup> concentration, thus proving the occurrence of energy transfer from Mn<sup>4+</sup> to Yb<sup>3+</sup> in the phosphor. According to the mechanism of energy transfer of Mn<sup>4+</sup> and Yb<sup>3+</sup> based on Fig. 14d,<sup>35,85,86</sup> the Mn<sup>4+</sup> ions are excited from the ground state (<sup>4</sup>A<sub>2g</sub>) to excited states (<sup>4</sup>T<sub>1g</sub>, <sup>2</sup>T<sub>2g</sub>, and <sup>4</sup>T<sub>2g</sub>) under UV light excitation, and then relax to the <sup>2</sup>E<sub>g</sub> state. The energy can be transferred from the <sup>2</sup>E<sub>g</sub> state of Mn<sup>4+</sup> to the <sup>2</sup>F<sub>5/2</sub> level of Yb<sup>3+</sup> through nonradiative transition, thereby producing the NIR emission observed at 998 nm.

The energy transfer from Mn<sup>4+</sup> to Nd<sup>3+</sup> occurs in the Mn<sup>4+</sup> and Nd<sup>3+</sup> codoped (Na,K)Mg(La,Gd)TeO<sub>6</sub> samples, as illustrated



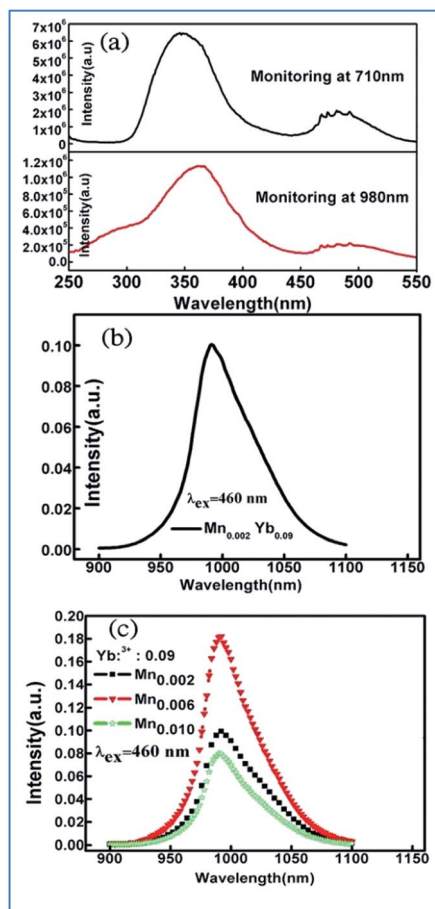


Fig. 13 (a) Excitation spectra of Mn<sup>4+</sup> monitored at 710 nm and Yb<sup>3+</sup> monitored at 980 nm in La<sub>1.91</sub>MgTi<sub>0.99</sub>O<sub>6</sub>:Mn<sub>0.002</sub>Yb<sub>0.09</sub> sample, emission spectra of (b) La<sub>2-x</sub>MgTi<sub>1-y</sub>O<sub>6</sub>:Mn<sub>0.002</sub>Yb<sub>0.09</sub> samples pumped by 460 nm light. Reprinted with permission from ref. 35, Copyright 2018, Elsevier BV.

in Fig. 15.<sup>16</sup> Upon excitation at 365 nm UV, both emissions from Mn<sup>4+</sup> and Nd<sup>3+</sup> are observed, and the Mn<sup>4+</sup> emission intensity and the corresponding decay time of Mn<sup>4+</sup> at 705 nm decrease monotonously with an increase in Nd<sup>3+</sup> concentration, which strongly confirms the efficient energy transfer from the Mn<sup>4+</sup> to Nd<sup>3+</sup> ions in these samples.<sup>87,88</sup>

The energy transfer processes of Mn<sup>4+</sup> → Nd<sup>3+</sup> → Yb<sup>3+</sup> occurring in the Mn<sup>4+</sup>, Nd<sup>3+</sup> and Yb<sup>3+</sup> codoped NaMgLaTeO<sub>6</sub> (NMLTO) samples are illustrated in Fig. 16.<sup>16</sup> The emission spectra of NML:0.02Mn<sup>4+</sup>,0.30Yb<sup>3+</sup> excited at 365 nm contains both the Mn<sup>4+</sup> emission band at around 705 nm due to the Mn<sup>4+</sup> <sup>2</sup>E<sub>g</sub> → <sup>4</sup>A<sub>2g</sub> transition, and the Yb<sup>3+</sup> emission band with a maximum at around 1003 nm attributed to the Yb<sup>3+</sup> <sup>2</sup>F<sub>5/2</sub> → <sup>2</sup>F<sub>7/2</sub> transition. The excitation spectrum (200–900 nm) monitored at 1003 nm clearly contains the Mn<sup>4+</sup> absorption band, suggesting energy transfer from Mn<sup>4+</sup> to Yb<sup>3+</sup> ions.<sup>89–91</sup> In the Mn<sup>4+</sup>, Nd<sup>3+</sup>, and Yb<sup>3+</sup> codoped NMLTO sample, the emission spectra of the obviously present bands from all three ions Mn<sup>4+</sup>, Nd<sup>3+</sup>, and Yb<sup>3+</sup> in the range of 600–1300 nm upon 365 nm UV excitation.<sup>92,93</sup> The emission intensity of Nd<sup>3+</sup> decreases monotonously with an increase in Yb<sup>3+</sup> concentration, which

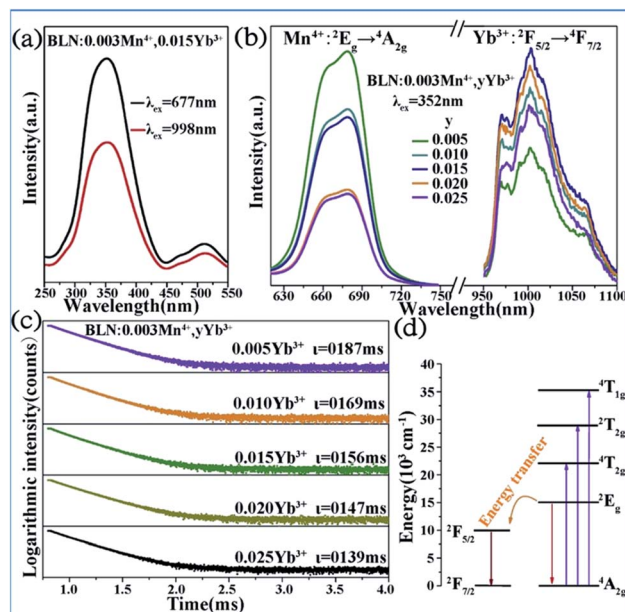


Fig. 14 (a) PLE and (b) PL spectra of Ba<sub>2</sub>LaNbO<sub>6</sub>:Mn<sup>4+</sup>,Yb<sup>3+</sup> phosphors. (c) Decay curves of Ba<sub>2</sub>LaNbO<sub>6</sub>:Mn<sup>4+</sup>,Yb<sup>3+</sup>. (d) Energy transfer schematic diagram of Mn<sup>4+</sup> and Yb<sup>3+</sup> codoped system. Reprinted with permission from ref. 35, Copyright 2019, Elsevier BV.

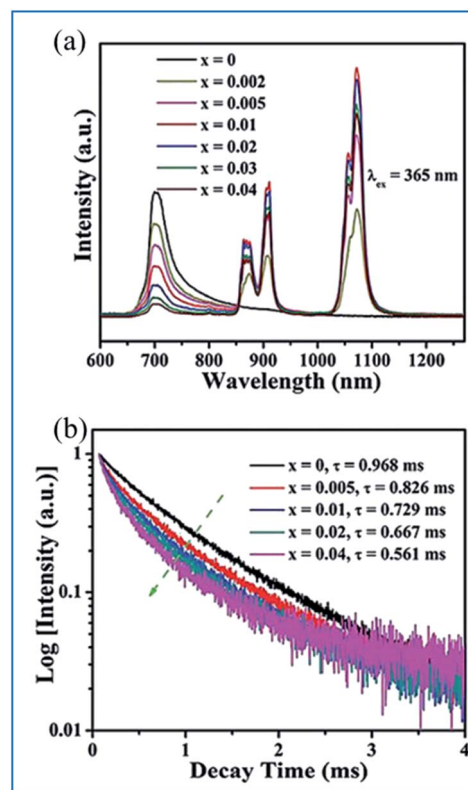


Fig. 15 (a) PL emission spectra ( $\lambda_{\text{ex}} = 365$  nm) of NaMgLaTeO<sub>6</sub>:0.02Mn<sup>4+</sup>,xNd<sup>3+</sup> and (b) corresponding decay curves for NaMgLaTeO<sub>6</sub>:0.02Mn<sup>4+</sup>,xNd<sup>3+</sup> ( $\lambda_{\text{ex}} = 365$  nm,  $\lambda_{\text{em}} = 705$  nm). Reprinted with permission from ref. 16, Copyright 2018, The Royal Society of Chemistry.

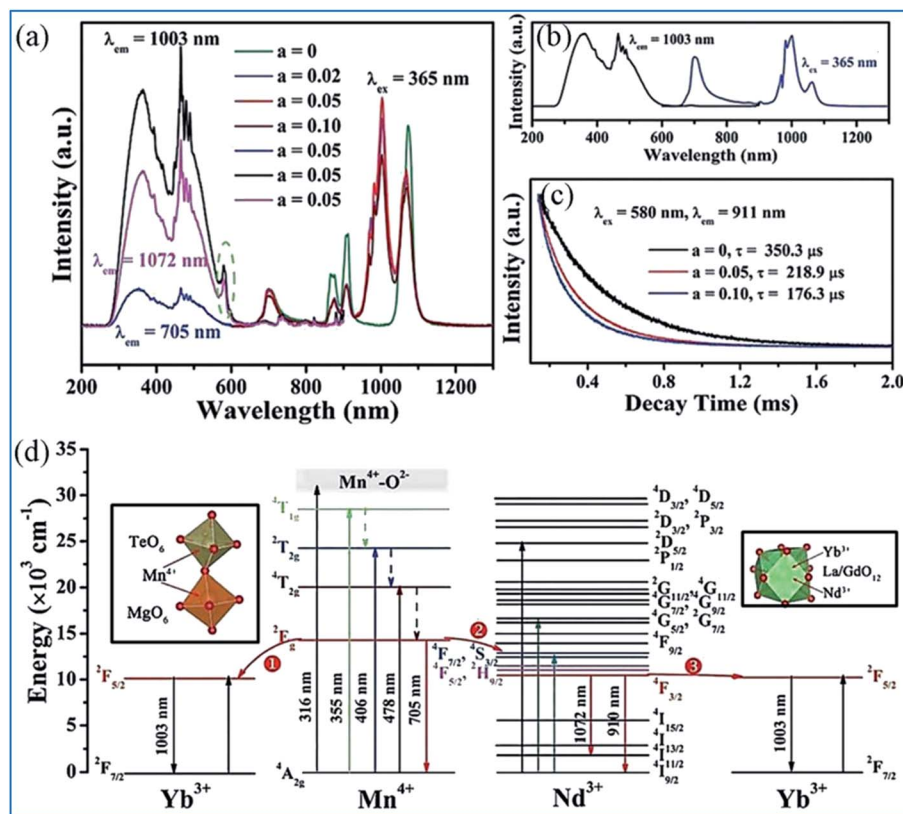


Fig. 16 PL excitation and emission spectra of (a) NaMgLaTeO<sub>6</sub>:0.02Mn<sup>4+</sup>,0.30Yb<sup>3+</sup>, (b) NaMgLaTeO<sub>6</sub>:0.02Mn<sup>4+</sup>,0.01Nd<sup>3+</sup>,aYb<sup>3+</sup>, and (c) decay curves of NaMgLaTeO<sub>6</sub>:0.02Mn<sup>4+</sup>,0.01Nd<sup>3+</sup>,aYb<sup>3+</sup> (λ<sub>ex</sub> = 580 nm, λ<sub>em</sub> = 911 nm). (d) Partial coordination environment in the NaMgLaTeO<sub>6</sub> structure and schematic energy-level diagram illustrating the possible energy transfer processes in the NaMgLaTeO<sub>6</sub>:Mn<sup>4+</sup>,Nd<sup>3+</sup>,Yb<sup>3+</sup> materials. Reprinted with permission from ref. 16, Copyright 2018, The Royal Society of Chemistry.

illustrates the possibility of energy transfer from the Nd<sup>3+</sup> to Yb<sup>3+</sup> ions as shown in Fig. 16a–c.

Fig. 16d shows an overview of the partial electronic energy level diagram of Mn<sup>4+</sup>, Nd<sup>3+</sup>, and Yb<sup>3+</sup> in NMLTO and a schematic diagram illustrating the possible energy transfer processes occurring in Mn<sup>4+</sup>, Nd<sup>3+</sup>, and Yb<sup>3+</sup> codoped NMLTO.<sup>16</sup> The energy at the Mn<sup>4+</sup> excited state <sup>2</sup>E<sub>g</sub> can be transferred to the Nd<sup>3+</sup> levels <sup>4</sup>F<sub>7/2</sub> and <sup>4</sup>S<sub>3/2</sub> via the Forster resonant energy transfer process to produce the emissions at 910 and 1072 nm.<sup>90,94</sup>

The NIR emissions of Nd<sup>3+</sup> at 910 and 1072 nm from the <sup>4</sup>F<sub>7/2</sub> and <sup>4</sup>S<sub>3/2</sub> levels, respectively, increases and the red emission of Mn<sup>4+</sup> at 705 nm from the <sup>2</sup>E<sub>g</sub> excited state decreases with an increase in the concentration of Mn<sup>4+</sup>, which indicates the energy transfer from Mn<sup>4+</sup> to Nd<sup>3+</sup>.<sup>68,95</sup> Then the excited <sup>4</sup>F<sub>7/2</sub> and <sup>4</sup>S<sub>3/2</sub> energy levels of Nd<sup>3+</sup> can relax nonradiatively to the <sup>4</sup>F<sub>5/2</sub> and <sup>2</sup>H<sub>9/2</sub> Nd<sup>3+</sup> energy levels, and transfer the energy to the <sup>2</sup>F<sub>5/2</sub> Yb<sup>3+</sup> excited state and enhance the Yb<sup>3+</sup> emission.

As can be seen in Fig. 17, the excitation spectra of the Mn<sup>4+</sup>, Nd<sup>3+</sup> and Yb<sup>3+</sup> codoped NMLTO samples match well with the solar spectrum in the UV and visible regions, and the emission bands are located at the ideal 930–1100 nm region for excellent response for crystal silicon solar energy cells.<sup>68,96</sup> Thus, the Mn<sup>4+</sup>, Nd<sup>3+</sup> and Yb<sup>3+</sup> codoped NMLTO sample has potential for

the effective broadband spectral conversion of UV/visible light to the NIR band utilizing the energy transfer processes of Mn<sup>4+</sup> → Nd<sup>3+</sup> → Yb<sup>3+</sup>.

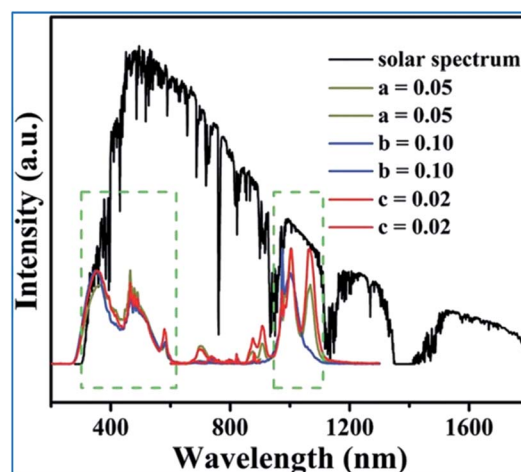


Fig. 17 Solar spectrum and PL excitation and emission spectra of NaMgLaTeO<sub>6</sub>:0.02Mn<sup>4+</sup>,0.01Nd<sup>3+</sup>,aYb<sup>3+</sup>, NaMgGdTeO<sub>6</sub>:0.01-Mn<sup>4+</sup>,0.02Nd<sup>3+</sup>,bYb<sup>3+</sup> and KMgLaTeO<sub>6</sub>:0.006Mn<sup>4+</sup>,0.03Nd<sup>3+</sup>,cYb<sup>3+</sup>. Reprinted with permission from ref. 16, Copyright 2018, The Royal Society of Chemistry.





## 4. Tunable multiple emissions via energy transfer in a single host lattice

### 4.1 Energy transfer between $\text{Dy}^{3+}$ and $\text{Mn}^{4+}$

As displayed in Fig. 18a, the PLE spectrum of the  $\text{Ca}_{13.88}\text{Al}_{10}\text{Zn}_6\text{O}_{35}:0.12\text{Dy}^{3+}$  phosphor monitored at 576 nm consists of a series of sharp peaks with the strongest absorption at 351 nm due to the  $^6\text{H}_{15/2} \rightarrow ^6\text{P}_{7/2}$  transition of  $\text{Dy}^{3+}$ . Under excitation at 351 nm, the PL spectrum consists of two dominant peaks at around 482 nm (blue) and 576 nm (yellow), corresponding to the  $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$  and  $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$  transitions of  $\text{Dy}^{3+}$ , respectively.<sup>97–99</sup> As shown in Fig. 18b, significant spectral overlap was observed between the PLE of  $\text{Mn}^{4+}$  and PL of  $\text{Dy}^{3+}$ ,

indicating that effective energy transfer from  $\text{Dy}^{3+}$  to  $\text{Mn}^{4+}$  is expected.

The energy transfer process from  $\text{Dy}^{3+}$  to  $\text{Mn}^{4+}$  is elucidated according to the schematic energy level diagram in Fig. 18c. In the cross-relaxation processes, the  $\text{Dy}^{3+}$  ions at the  $^4\text{F}_{9/2}$  level can be de-excited to the  $^6\text{F}_{9/2}/^6\text{H}_{7/2}$ ,  $^6\text{H}_{9/2}/^6\text{F}_{11/2}$ , or  $^6\text{F}_{1/2}$  level, while the ions at the  $^6\text{H}_{15/2}$  ground state will accept the energies excited simultaneously to the  $^6\text{F}_{3/2}$ ,  $^6\text{F}_{5/2}$ , and  $^6\text{H}_{9/2}/^6\text{F}_{11/2}$  levels. Although the energy level  $^4\text{F}_{9/2}$  of  $\text{Dy}^{3+}$  (20 747  $\text{cm}^{-1}$ ) is higher than the  $^2\text{E}_g$  energy level of  $\text{Mn}^{4+}$  (14 025  $\text{cm}^{-1}$ ), the energy transfer from the  $^4\text{F}_{9/2}$  level of  $\text{Dy}^{3+}$  to the  $^2\text{E}$  level of  $\text{Mn}^{4+}$  may be realized *via* the assistance of phonons.<sup>97,100–104</sup>

The PL spectra of  $\text{Ca}_{13.88}\text{Al}_{10-y}\text{Zn}_6\text{O}_{35}:0.12\text{Dy}^{3+}, y\text{Mn}^{4+}$  ( $y = 0, 0.01, 0.05, 0.10, 0.15, 0.20$ , and  $0.25$ ) upon excitation at 351 nm and the change in the emission intensities of  $\text{Dy}^{3+}$  and  $\text{Mn}^{4+}$  with the concentration of  $\text{Mn}^{4+}$  are presented in Fig. 19.<sup>97</sup> The emissions at 482 and 576 nm are due to the  $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{j/2}$  ( $j = 15, 13$ ) transitions of  $\text{Dy}^{3+}$ , and the red emission with a multi-peak structure in the wavelength range of 650 to 750 nm corresponds to the vibronic emission  $^2\text{E}_g \rightarrow ^4\text{A}_{2g}$  of  $\text{Mn}^{4+}$ . The emission intensity of  $\text{Mn}^{4+}$  increases, whereas that of  $\text{Dy}^{3+}$  is simultaneously found to decrease monotonically with an increase in concentration of  $\text{Mn}^{4+}$ , indicating that the energy transfer from  $\text{Dy}^{3+}$  to  $\text{Mn}^{4+}$  is efficient.<sup>105–108</sup>

### 4.2 Tunable dual emissions for $\text{Bi}^{3+}$ and $\text{Mn}^{4+}$ codoped phosphors

It was found that both the blue light from  $\text{Bi}^{3+}$  and red light from  $\text{Mn}^{4+}$  are produced in all the  $\text{Bi}^{3+}$  and  $\text{Mn}^{4+}$  codoped CZAO samples, as illustrated in Fig. 20a. The emission band from 400 nm to 550 nm with a maximum at 410 nm is ascribed to the  $^3\text{P}_1 \rightarrow ^1\text{S}_0$  transition of the  $\text{Bi}^{3+}$  ions, while that from 650 nm to 750 nm is ascribed to the  $^2\text{E}_g \rightarrow ^4\text{A}_{2g}$  emission of the  $\text{Mn}^{4+}$  ions.<sup>25,109</sup> The intensity of the blue emission decreases and that of the red emission increases with an increase in the  $\text{Mn}^{4+}$  concentration, as shown in Fig. 20b, which indicates the occurrence of energy transfer from  $\text{Bi}^{3+}$  to  $\text{Mn}^{4+}$ . The dual-emission color can be tuned by changing the  $\text{Bi}^{3+}/\text{Mn}^{4+}$  ratio.

A similar energy transfer from  $\text{Bi}^{3+}$  to  $\text{Mn}^{4+}$  was also observed in the  $\text{Bi}^{3+}$  and  $\text{Mn}^{4+}$  codoped CZAO phosphor due to the

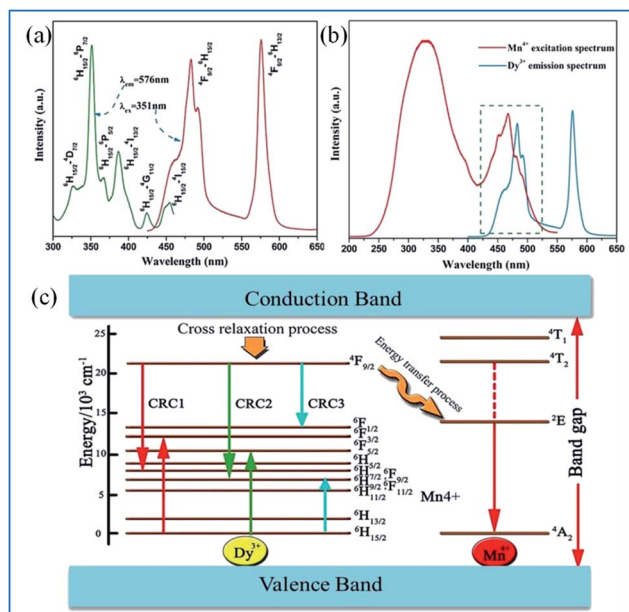


Fig. 18 (a) PLE and PL spectra of  $\text{Ca}_{13.88}\text{Al}_{10}\text{Zn}_6\text{O}_{35}:0.12\text{Dy}^{3+}$ , (b) spectral overlap between the PLE of  $\text{Mn}^{4+}$  and the PL of  $\text{Dy}^{3+}$ , (c) schematic level diagram for the cross-relaxation process and energy transfer process from  $\text{Dy}^{3+}$  to  $\text{Mn}^{4+}$ . Reprinted with permission from ref. 97, Copyright 2016, Kluwer Academic Publishers.

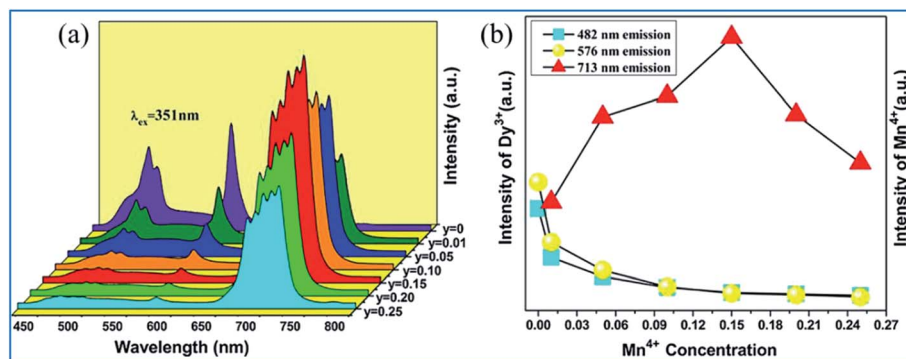


Fig. 19 (a) PL spectra of  $\text{Ca}_{13.88}\text{Al}_{10-y}\text{Zn}_6\text{O}_{35}:0.12\text{Dy}^{3+}, y\text{Mn}^{4+}$  ( $y = 0, 0.01, 0.05, 0.10, 0.15, 0.20$ , and  $0.25$ ) under the excitation at 351 nm and (b) emission intensities of  $\text{Dy}^{3+}$  and  $\text{Mn}^{4+}$  as a function of the concentration of  $\text{Mn}^{4+}$ . Reprinted with permission from ref. 97, Copyright 2016, Kluwer Academic Publishers.

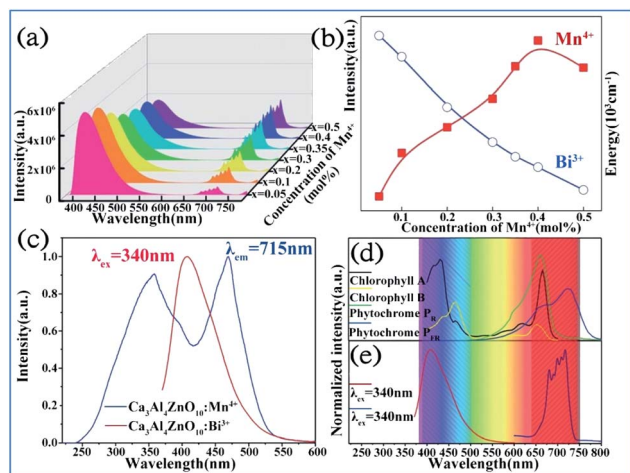


Fig. 20 (a) Emission spectra ( $\lambda_{\text{ex}} = 351$  nm) of samples of  $\text{Ca}_{14}\text{Zn}_6\text{-Al}_{10}\text{O}_{35}:0.5\% \text{Bi}^{3+}, x\% \text{Mn}^{4+}$  ( $x = 0.05, 0.1, 0.2, 0.3, 0.35, 0.4$  or  $0.5$ ) and (b) dependence of the luminescence intensities of the red emission from  $\text{Mn}^{4+}$  and blue emission from  $\text{Bi}^{3+}$  on the  $\text{Mn}^{4+}$  doping concentrations. Reprinted with permission from ref. 25, Copyright 2017, The Royal Society of Chemistry. (c) PLE spectrum of  $\text{Ca}_3\text{ZnAl}_4\text{-O}_{10}:0.008\text{Mn}^{4+}$  and PL spectrum of the  $\text{Ca}_3\text{ZnAl}_4\text{O}_{10}:0.008\text{Bi}^{3+}$  phosphor. (d) Absorption spectra of chlorophyll A, chlorophyll B, and phytochromes PR and PPR, and (e) PL spectra of  $\text{Bi}^{3+}$  and  $\text{Mn}^{4+}$  in  $\text{Ca}_3\text{ZnAl}_4\text{O}_{10}$ . Reprinted with permission from ref. 26, Copyright 2018, The Royal Society of Chemistry.

spectral overlap in the PLE of  $\text{Mn}^{4+}$  and PL of  $\text{CZAO}:0.008\text{Bi}^{3+}$ , as shown in Fig. 20c. Under the same excitation source,  $\text{Bi}^{3+}$  and  $\text{Mn}^{4+}$  codoped CZAO phosphors show dual emissions, where the blue-violet emission is mainly from the  $^3\text{P}_1 \rightarrow ^1\text{S}_0$  transition of  $\text{Bi}^{3+}$  and the far red emission is attributed to the  $^2\text{E}_g \rightarrow ^4\text{A}_{2g}$  transition of  $\text{Mn}^{4+}$ .<sup>26,110,111</sup> As presented in Fig. 20d and e, the blue emission of  $\text{Bi}^{3+}$  matches the absorption spectra of chlorophyll A and chlorophyll B, while the red emission from  $\text{Mn}^{4+}$  matches the absorption spectra of phytochrome PR and phytochrome PFR, which indicate that the phosphor has potential for application in plant growth LED lighting.

The energy transfer process from  $\text{Bi}^{3+}$  to  $\text{Mn}^{4+}$  realized in  $\text{Bi}^{3+}$  and  $\text{Mn}^{4+}$  codoped  $\text{La}_2\text{MgTiO}_6$  (LMT) phosphors is illustrated in Fig. 21. The absorption bands from 275 to 375 nm in the PLE spectra for  $\text{LMT}:0.005\text{Bi}^{3+}$  in Fig. 21a are ascribed to the  $^1\text{S}_0 \rightarrow ^1\text{P}_1$  and  $^1\text{S}_0 \rightarrow ^3\text{P}_1$  transitions of  $\text{Bi}^{3+}$ . A blue emission (375–500 nm) with a maximum at 417 nm of  $\text{Bi}^{3+}$  is detected, which is due to the  $^3\text{P}_1 \rightarrow ^1\text{S}_0$  transitions. The strong red emission band from 650 to 750 nm with an emission peak at 710 nm is observed owing to the  $^2\text{E}_g \rightarrow ^4\text{A}_{2g}$  transition of  $\text{Mn}^{4+}$ . The spectral overlap between the emission spectrum of  $\text{Bi}^{3+}$  and the excitation spectra of  $\text{Mn}^{4+}$  provides strong evidence for the energy transfer between  $\text{Bi}^{3+}$  and  $\text{Mn}^{4+}$ . The emission intensity of  $\text{Bi}^{3+}$  gradually decreases and that of  $\text{Mn}^{4+}$  presents a monotonous increase with an increase in the  $\text{Mn}^{4+}$  doping concentration, which indicates that energy transfer occurs in the  $\text{Bi}^{3+}$  and  $\text{Mn}^{4+}$  codoped LMT phosphors, as shown in Fig. 21b.

The electronic transitions and the energy transfer process in the  $\text{Bi}^{3+}$  and  $\text{Mn}^{4+}$  codoped phosphors are illustrated the schematic energy level diagram shown in Fig. 21c.<sup>26</sup> The  $\text{Bi}^{3+}$  ions are

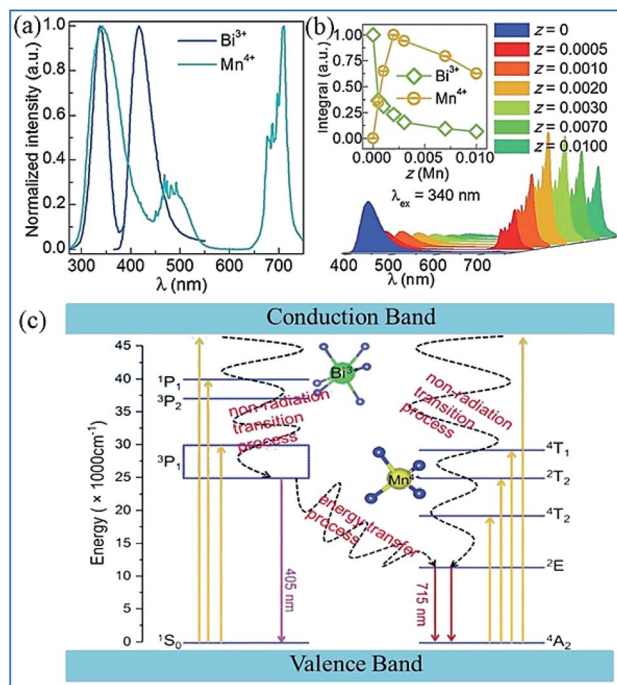


Fig. 21 (a) PLE and PL spectra of  $\text{La}_2\text{MgTiO}_6:0.005\text{Bi}^{3+}$  (blue) and  $\text{La}_2\text{MgTiO}_6:0.002\text{Mn}^{4+}$  (cyan). (b) PL spectra of  $\text{La}_2\text{MgTiO}_6:0.005\text{Bi}^{3+}, z\text{Mn}^{4+}$  ( $0 \leq z \leq 0.01$ ). The inset shows the integrated intensity of the  $\text{Bi}^{3+}$  and  $\text{Mn}^{4+}$  emission as a function of the concentration of  $\text{Mn}^{4+}$ . Reprinted with permission from ref. 112, Copyright 2018, The Royal Society of Chemistry. (c) Schematic illustration of the electronic transitions and energy transfer process in  $\text{Ca}_3\text{ZnAl}_4\text{O}_{10}:\text{Bi}^{3+}, \text{Mn}^{4+}$ . Reprinted with permission from ref. 26, Copyright 2018, The Royal Society of Chemistry.

initially excited from the ground state  $^1\text{S}_0$  to the excited state  $^3\text{P}_1$ ,  $^3\text{P}_2$ , and  $^1\text{P}_1$  or even the conduction bands under the irradiation of UV light. Then, the  $\text{Bi}^{3+}$  ions relax to the lowest excited state of  $^3\text{P}_1$  and return to the  $^1\text{S}_0$  ground state through radiative transition and yield blue emission. Simultaneously, the  $\text{Bi}^{3+}$  ions in the  $^3\text{P}_1$  state can also transfer their energy to the adjacent  $\text{Mn}^{4+}$  ions and promote the  $\text{Mn}^{4+}$  ions from the  $^4\text{A}_{2g}$  ground state to the  $^4\text{T}_{2g}$ ,  $^2\text{T}_{2g}$ , and  $^4\text{T}_{1g}$  energy levels and relax to the  $^2\text{E}_g$  level through a nonradiative transition and then produce red emission when they return to the  $^4\text{A}_{2g}$  ground state.<sup>113–115</sup> The energy transfer occurring between  $\text{Bi}^{3+}$  and  $\text{Mn}^{4+}$  eventually lead to an enhancement in the far-red emission of  $\text{Mn}^{4+}$ .

## 5. Red emitting phosphors for plant growth LED lights

### 5.1 Enhanced red emission of $\text{Mn}^{4+}$ by codoping rare earth ions

The  $\text{Dy}^{3+}$  and  $\text{Mn}^{4+}$  codoped  $\text{Ca}_{14}\text{Ga}_{10-m}\text{Al}_m\text{Zn}_6\text{O}_{35}$  ( $\text{CGAZO}:\text{Dy}^{3+}, \text{Mn}^{4+}$ ) phosphor can exhibit strong far-red emission, which has potential application for plant growth LED lighting.<sup>44</sup> As shown in Fig. 22a, the three absorption bands A (200–290 nm), B (290–420 nm), and C (420–550 nm) of the phosphors in the



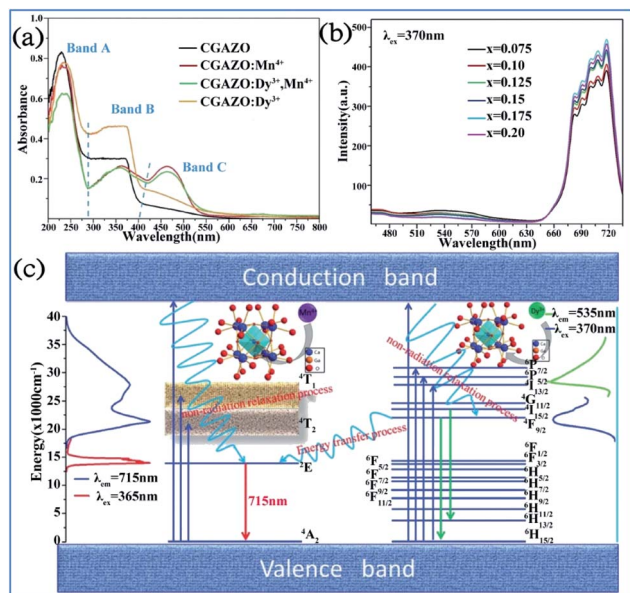


Fig. 22 UV-vis absorption spectra of (a) Ca<sub>14</sub>Ga<sub>10-m</sub>Al<sub>m</sub>Zn<sub>6</sub>O<sub>35</sub> with different dopants. (b) PL spectra of Ca<sub>14</sub>Ga<sub>10-m</sub>Al<sub>m</sub>Zn<sub>6</sub>O<sub>35</sub>:0.12Dy<sup>3+</sup>,xMn<sup>4+</sup> phosphor. (c) Energy level, electron transitions and energy transfer schematic diagram of Dy<sup>3+</sup>, Mn<sup>4+</sup> in Ca<sub>14</sub>Ga<sub>10-m</sub>Al<sub>m</sub>Zn<sub>6</sub>O<sub>35</sub> matrix. Reprinted with permission from ref. 44, Copyright 2017, The Royal Society of Chemistry.

UV-vis absorption spectra can be attributed to the host lattice absorption, charge transfer transition of Mn<sup>4+</sup>-O<sup>2-</sup>, and spin-allowed transitions <sup>4</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>1g</sub> and <sup>4</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>2g</sub> of the Mn<sup>4+</sup> ions, respectively.<sup>116</sup> The absorption intensity of bands A and C decrease, but that of band B is enhanced with elevated Al<sup>3+</sup> concentrations, which indicates that the absorption intensity of the phosphor powder is enhanced in the ultraviolet light range, but reduced slightly in the blue light range.

As shown in Fig. 22b, the PL intensity of the Mn<sup>4+</sup> activator increased, whereas that of the Dy<sup>3+</sup> sensitizer simultaneously decreased monotonically with an increase in the concentration of Mn<sup>4+</sup> ions, which demonstrates that energy transfer from Dy<sup>3+</sup> to Mn<sup>4+</sup> occurred in the Dy<sup>3+</sup> and Mn<sup>4+</sup>-co-activated CGAZO, as described using Fig. 22c. The Dy<sup>3+</sup> ions are excited to their <sup>6</sup>P<sub>7/2</sub> or <sup>6</sup>P<sub>5/2</sub> or <sup>4</sup>I<sub>13/2</sub> excited states or conduction band under irradiation of near UV light and nonradiatively relax to their <sup>4</sup>F<sub>9/2</sub> state. The energy transfer process between the Dy<sup>3+</sup> and Mn<sup>4+</sup> ions occurs via <sup>4</sup>F<sub>9/2</sub> (Dy<sup>3+</sup>) → <sup>2</sup>E<sub>g</sub> (Mn<sup>4+</sup>) and the Mn<sup>4+</sup> ions return from the lowest excited level <sup>2</sup>E<sub>g</sub> (Mn<sup>4+</sup>) to the <sup>4</sup>A<sub>2g</sub> ground state (Mn<sup>4+</sup>) through a radiative transition, which produces the far-red light emission at 715 nm.

## 5.2 Enhanced red emission of Mn<sup>4+</sup> by codoping Bi<sup>3+</sup>

The red emission of the Mn<sup>4+</sup> ions in the phosphors based on the CaAl<sub>12</sub>O<sub>19</sub>,<sup>117,118</sup> Mg<sub>2</sub>TiO<sub>4</sub>,<sup>37,119–121</sup> and La<sub>2</sub>ATiO<sub>6</sub> (ref. 112) (A = Mg, Zn) host lattices can be dramatically enhanced by the incorporation of Bi<sup>3+</sup> codopant. The spectral profiles of the excitation and emission spectra of Mn<sup>4+</sup> with or without codoping Bi<sup>3+</sup> ions in these Mn<sup>4+</sup> doped phosphors are quite similar. Therefore, it can be speculated that the synergetic effect

of codoping Bi<sup>3+</sup> plays a key role in the modification of the crystal structure and the luminescence efficiency of Mn<sup>4+</sup>. Thus, the strategy for enhancing the luminescence performance of Mn<sup>4+</sup> plays a pivotal role in the development of highly efficient red-emitting phosphors.<sup>122–125</sup>

## 6. Luminescent thermometers based on Mn<sup>4+</sup> and multiple ion-doped materials

By employing the highly temperature-sensitive Mn<sup>4+</sup> luminescence as the temperature detecting signal, while the temperature-insensitive rare earth ion (Eu<sup>3+</sup>, Tb<sup>3+</sup> or Dy<sup>3+</sup>) emission was used as a reference signal, Mn<sup>4+</sup> and multiple rare earth ion codoped phosphors exhibited an excellent temperature sensing performance with absolute and relative sensitivities as high as 0.114–0.441 K<sup>-1</sup> and 2.32–4.81% K<sup>-1</sup>, respectively, which indicate their potential application in luminescent thermometers.<sup>126–128</sup>

In Fig. 23a and b, the bright red luminescence of the Eu<sup>3+</sup> and Mn<sup>4+</sup> codoped YAG samples originated from both the

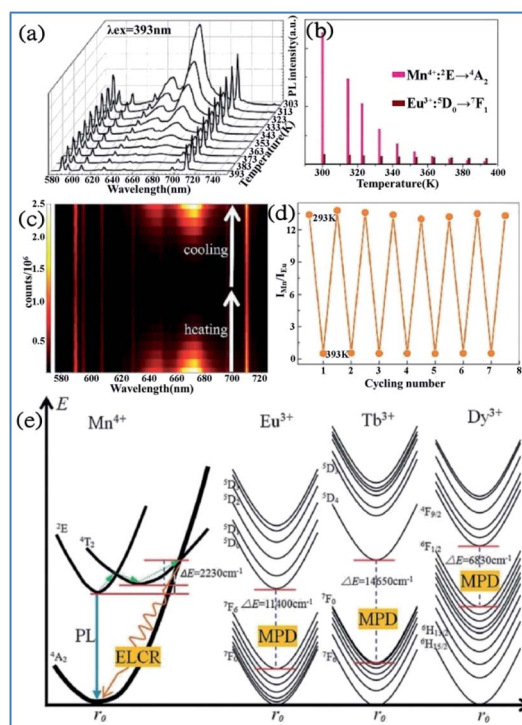


Fig. 23 Temperature-dependent (a) PL spectra of a Mn<sup>4+</sup>/Eu<sup>3+</sup>:YAG sample recorded from 303 K to 393 K. (b) PL intensities of Mn<sup>4+</sup> and Eu<sup>3+</sup>. (c) Emission mapping upon the cycling process of heating and cooling. (d) Temperature-induced switching of FIR between Mn<sup>4+</sup> and Eu<sup>3+</sup> (alternating between 293 K and 393 K). Reprinted with permission from ref. 122, Copyright 2016, The Royal Society of Chemistry. (e) Configurational coordinate diagrams of the Mn<sup>4+</sup>/Eu<sup>3+</sup>/Tb<sup>3+</sup>/Dy<sup>3+</sup> emitting centers in the Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> host, showing the energy-level crossing relaxation (ELCR) quenching mechanism for the Mn<sup>4+</sup> activator and the multi-phonon de-excitation (MPD) quenching mechanism for the Eu<sup>3+</sup>/Tb<sup>3+</sup>/Dy<sup>3+</sup> centers. Reprinted with permission from ref. 129, Copyright 2016, The Royal Society of Chemistry.



transitions  $^5D_0 \rightarrow ^7F_J$  of  $\text{Eu}^{3+}$  and  $^2E_g \rightarrow ^4A_{2g}$  of  $\text{Mn}^{4+}$ . With an increase in temperature, the luminescence of  $\text{Mn}^{4+}$  weakens quickly, whereas that of  $\text{Eu}^{3+}$  exhibits a slight decrease. As shown in Fig. 23c, the remarkable change in  $I_{\text{Mn}}/I_{\text{Eu}}$  with a variation in temperature measured on the cycling process of heating-cooling can almost be restored to the original states after the heating-cooling cycle.<sup>130–134</sup> As confirmed in Fig. 23d, this temperature-dependent  $I_{\text{Mn}}/I_{\text{Eu}}$  is repeatable and reversible after several cycling experiments. Therefore, a highly sensitive temperature determination can be expected if the  $\text{Mn}^{4+}$  emission is employed as the detection signal of temperature, while the  $\text{Eu}^{3+}$  emission is used as the reference signal.

The photon generation and energy transfer between  $\text{Mn}^{4+}$  and rare earth ions in  $\text{Mn}^{3+}$ ,  $\text{Mn}^{4+}$ , and  $\text{Nd}^{3+}$  codoped YAG nanocrystals can be illustrated by an energy level diagram, as presented in Fig. 23e. The  $\text{Mn}^{4+}$  ions are excited from the  $^4A_{2g}$  ground state to the  $^4T_2$  excited state, followed by nonradiative multiphonon relaxation, leading to population of the  $^2E_g$  state, and then emit red emission at 670 nm, which is ascribed to the radiative electronic  $^2E_g \rightarrow ^4A_{2g}$  transition of  $\text{Mn}^{4+}$ . The appearance of an intersection point between the  $^4T_2$  parabola and the  $^4A_{2g}$  parabola at  $\Delta E$  (activation energy, in this case  $\Delta E_1 = 2506 \text{ cm}^{-1}$ ) is due to the strong electron-phonon coupling. The value of  $\Delta E_1$  is associated with the distortion of the  $\text{Mn}^{4+}$  energy states, which is strongly dependent on the crystal field. With an increase in the temperature, the population of higher vibrational states gradually increases up to the moment when the provided thermal energy is sufficiently high to overcome the intersection point ( $\Delta E_1$ ), above which electrons from the  $^2E_g$  level are transferred through  $^4T_{2g}$  to the  $^4A_{2g}$  ground state *via* nonradiative multiphonon relaxation. In contrast, rare earth ions are expected to be less affected by luminescence temperature quenching because their energy diagram usually consist of numerous f energy states due to low electron-phonon coupling. Therefore,  $\text{Mn}^{4+}$  and rare earth ions codoped in a single host lattice can be applied in a luminescent thermometer.<sup>135–138</sup>

The structural coordinate diagram in Fig. 23e proposes a possible mechanism for elucidating the high temperature sensitivity of  $\text{Mn}^{4+}$  and rare earth ion (such as  $\text{Eu}^{3+}/\text{Tb}^{3+}$  and  $\text{Dy}^{3+}$ ) codoped samples. The  $\text{Mn}^{4+}$  luminescence is easily thermally quenched through an energy-level crossing relaxation (ELCR) between the  $^4T_{2g}$  excited state and the  $^4A_{2g}$  ground state due to the role of strong electron-phonon coupling. The thermal quenching of rare earth ions is completely different to that of  $\text{Mn}^{4+}$  since there is no crossing point between the excited states and the ground state of rare earth ions because their 4f orbitals are shielded from the surroundings by the filled  $5s_2$  and  $5p_6$  orbitals,<sup>139,140</sup> and consequently the multi-phonon deexcitation (MPD) mode is the dominant mechanism responsible for the thermal-quenching of rare earth ions. The thermal-quenching probability of  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ , and  $\text{Dy}^{3+}$  luminescence is quite low because the required phonon numbers to bridge the energy gaps of  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$  and  $\text{Dy}^{3+}$  are 16, 21 and 10, respectively.

The representative thermal evolution of the emission spectra of  $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Mn}^{3+}$ ,  $\text{Mn}^{4+}$ ,  $\text{Nd}^{3+}$  nanocrystals presented in Fig. 24a

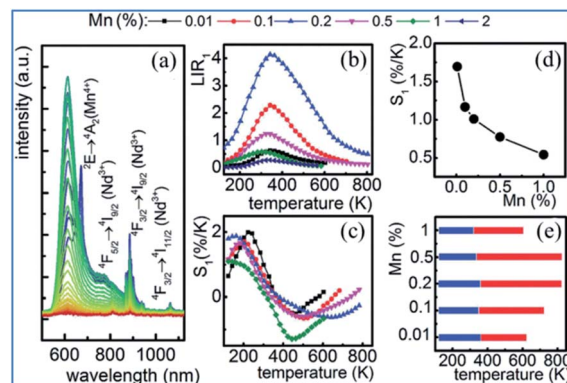


Fig. 24 (a) Thermal evolution of 20 nm  $\text{Y}_3\text{Al}_5\text{O}_{12}:0.1\% \text{Mn}, 1\% \text{Nd}^{3+}$  nanocrystal emission spectra. (b) Impact of temperature on LIR for different Mn concentrations of  $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Mn}^{3+}$ ,  $\text{Mn}^{4+}$ ,  $\text{Nd}^{3+}$  nanocrystals. (c) Thermal evolution of  $S_1$  for thermometers with different Mn concentrations. (d) Dependence of sensitivity on manganese concentration at  $T = 273 \text{ K}$ . (e) UTR of thermometers with different Mn concentrations. Reprinted with permission from ref. 31, Copyright 2018, Pergamon Press Ltd.

indicates that the emission intensity of both the  $^2E_g \rightarrow ^4A_{2g}$  emission band of  $\text{Mn}^{4+}$  and the  $^4F_{3/2} \rightarrow ^4I_{9/2}$  band of  $\text{Nd}^{3+}$  decreases with an increase in temperature. In contrast, the  $^5T_2 \rightarrow ^5E''$  emission of  $\text{Mn}^{3+}$  exhibits different behavior. The upper lying  $^5T_2$  state of  $\text{Mn}^{3+}$  can be populated *via* phonon-assisted energy transfer with the phonon absorption. The probability of this process increases with temperature according to the Miyakawa–Dexter theory.<sup>31,141,142</sup> On the other hand, Kuck *et al.* explained the increase in the  $\text{Mn}^{3+}$  emission at elevated temperatures in terms of the thermal population from the  $^3T_1$  state.<sup>143</sup>

The thermal evolution of  $\text{LIR}_1$  for the series of 20 nm nanocrystals with different manganese concentrations is presented in Fig. 24b. In the low temperature range,  $\text{LIR}_1$  increases with temperature, reaching the maximum at  $T = 400 \text{ K}$ . A further increase in temperature causes a reduction in the value of  $\text{LIR}_1$ . In the low temperature range (below 350 K), the  $\text{LIR}_2$  value is thermally independent, which is related to the high thermal stability of the  $\text{Mn}^{4+}$  luminescence at low temperatures. This shows that the emission intensity of the  $^5T_2$  state of  $\text{Mn}^{3+}$  increases at low temperatures, while that of the  $^2E_g$  state of  $\text{Mn}^{4+}$  becomes stable.

The thermoluminescence glow curves of the all the  $\text{Mn}^{4+}$  and rare earth ion ( $\text{La}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Dy}^{3+}$ , and  $\text{Ho}^{3+}$ ) codoped  $\text{MgAl}_2\text{Si}_2\text{O}_8$  host phosphors recorded after  $\beta$ - and  $\alpha$ -irradiation are shown in Fig. 25.<sup>39</sup> All the phosphors exhibit one main peak at about  $261 \pm 3^\circ \text{C}$  for  $\beta$ -irradiation and many satellite peaks in the low temperature range up to  $200^\circ \text{C}$ . Furthermore, the  $\alpha$ -irradiated phosphors had one main peak at about  $245\text{--}252^\circ \text{C}$  and the same satellite peaks. The addition of  $\text{La}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Dy}^{3+}$ , and  $\text{Ho}^{3+}$  dopants in the  $\text{MgAl}_2\text{Si}_2\text{O}_8:\text{Mn}^{4+}$  phosphor did not cause any new TL peaks, but the peak intensities changed. In addition, the  $\text{Dy}^{3+}$  and  $\text{Gd}^{3+}$  co-doped phosphors had relatively high peak intensities compared with the other phosphors. The main peaks were shifted towards the lower temperature region when the



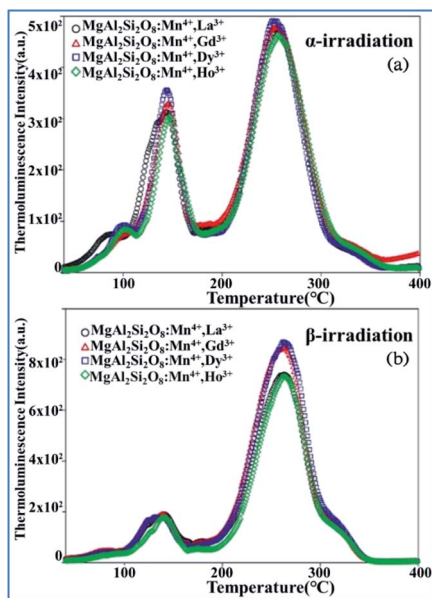


Fig. 25 TL glow curves of all the phosphors recorded after 1 h of (a)  $\alpha$ -irradiation and (b) 37.5 Gy  $\beta$ -irradiation. Reprinted with permission from ref. 39, Copyright 2018, John Wiley & Sons Inc.

phosphors were exposed to  $\alpha$ -irradiation.<sup>144–147</sup> The TL curves of the  $\beta$ - and  $\alpha$ -irradiated phosphors exhibited substantial changes, which can be associated with the type of radiation. Therefore, the TL peak positions of  $\text{MgAl}_2\text{Si}_2\text{O}_8:\text{Mn}^{4+}$  with codoping  $\text{La}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Dy}^{3+}$ , and  $\text{Ho}^{3+}$  activators did not change for  $\alpha$ - and  $\beta$ -irradiation.

The upconversion (UC) luminescence of  $\text{Mn}^{4+}$  can be realized by energy transfer from  $\text{Yb}^{3+}$  to  $\text{Er}^{3+}$ :  $^2\text{H}_{11/2}/^4\text{S}_{3/2}$ ,  $^4\text{F}_{9/2}$ ,  $\text{Ho}^{3+}$ :  $^5\text{S}_2/^5\text{F}_4$ ,  $^5\text{F}_5$  and  $\text{Tm}^{3+}$ :  $^1\text{G}_4$ , and further to  $\text{Mn}^{4+}$ :  $^2\text{T}_{2g}$  and  $^2\text{E}_g$  excited states in  $\text{Mn}^{4+}$ ,  $\text{Yb}^{3+}$ , and  $\text{Er}^{3+}/\text{Ho}^{3+}/\text{Tm}^{3+}$  codoped  $\text{YAlO}_3$ .<sup>32</sup> The different influence of temperature on the emission spectra and decay behaviors of  $\text{Mn}^{4+}$  and rare earth ions exhibits their possible application in optical thermometry. Fig. 26a shows down the converted PL and PLE spectra for  $\text{Mn}^{4+}$  single doped and  $\text{Yb}^{3+}/\text{Ln}^{3+}$  ( $\text{Ln} = \text{Er}, \text{Ho}, \text{Tm}$ ) codoped  $\text{YAlO}_3$ . The PL spectrum of  $\text{Mn}^{4+}$  exhibits two emission bands centered at 694 and 714 nm, which are assigned to the spin-forbidden transition  $^2\text{E}_g \rightarrow ^4\text{A}_{2g}$  of  $\text{Mn}^{4+}$ . The PLE spectrum monitored at 714 nm consists of two strong excitation peaks centered at 340 and 484 nm, which are attributed to the spin-allowed  $^4\text{A}_{2g} \rightarrow ^4\text{T}_{1g}$  and  $^4\text{A}_{2g} \rightarrow ^4\text{T}_{2g}$  transitions of  $\text{Mn}^{4+}$ , respectively.<sup>148–152</sup>

The obvious spectral overlap between the  $\text{Ln}^{3+}$  emission band and  $\text{Mn}^{4+}$  excitation band indicates the possible resonant energy transfer from  $\text{Ln}^{3+}$  to  $\text{Mn}^{4+}$ . As evidenced in Fig. 26b, an extra NIR emission band at around 714 nm assigned to the  $^2\text{E}_g \rightarrow ^4\text{A}_{2g}$  transition of  $\text{Mn}^{4+}$  is observed for all these  $\text{Yb}^{3+}/\text{Ln}^{3+}/\text{Mn}^{4+}$  tri-doped samples, confirming the existence of  $\text{Ln}^{3+} \rightarrow \text{Mn}^{4+}$  ( $\text{Ln} = \text{Er}, \text{Ho}, \text{Tm}$ ) energy transfer.

Similar behavior was observed in the  $\text{Mn}^{4+}$  and  $\text{Tb}^{3+}$  codoped  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$  nanocrystalline phosphor. The intense red emission associated with the  $^2\text{E} \rightarrow ^4\text{A}_2$  electronic transition of  $\text{Mn}^{4+}$  ions was drastically quenched, while the  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  emission of  $\text{Tb}^{3+}$  remained almost thermally independent above 100 °C. The

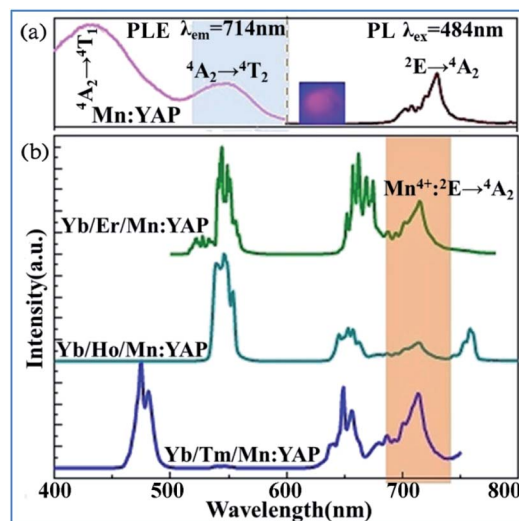


Fig. 26 (a) PL ( $\lambda_{\text{ex}} = 484$  nm) and PLE ( $\lambda_{\text{em}} = 714$  nm) spectra of single  $\text{Mn}^{4+}$ -doped  $\text{YAlO}_3$  and (b) UC emission spectra of  $\text{Yb}^{3+}/\text{Ln}^{3+}/\text{Mn}^{4+}$  codoped  $\text{YAlO}_3$  ( $\text{Ln} = \text{Er}, \text{Ho}, \text{Tm}$ ) under 980 nm laser excitation. Reprinted with permission from ref. 32 and <sup>148</sup>, Copyright 2017, Elsevier BV.

combination of the thermally quenched luminescence from the  $\text{Mn}^{4+}$  ions to the almost temperature-independent emission from  $\text{Tb}^{3+}$  provided a sensitive luminescent thermometer ( $\text{SR} = 2.8\%/^{\circ}\text{C}$  at 150 °C) with strong emission color variability. Thus, the developed thermochromic luminescent nanomaterials based on codoped  $\text{Mn}^{4+}$  and  $\text{Tb}^{3+}$  possess the high application potential for thermal sensing and mapping.<sup>153</sup>

## 7. Challenges and perspectives

$\text{Mn}^{4+}$  and multiple ion-codoped complex oxide phosphors have high stability, abundant starting materials, simple synthetic technology (solid state sintering), and tunable luminescence spectra covering the full visible light region from blue to red, and extending to the NIR region. The challenges and perspectives of the future work focusing on  $\text{Mn}^{4+}$  and multiple ion-codoped materials are proposed as follows:

- (1) Applying the developed  $\text{Mn}^{4+}$  and multiple ion-codoped phosphors for the fabrication of WLED devices, solar energy cells, etc.
- (2) Enhancement of the luminescence efficiency of  $\text{Mn}^{4+}$  by optimizing the synthetic parameters including codoping some content of multiple ions.
- (3) Discovery of novel host lattice materials with multiple crystals sites to accommodate various dopants and luminescence centers in a single host lattice.
- (4) Improvement of the efficiency of energy transfer between  $\text{Mn}^{4+}$  and multiple ion-codoped phosphors to obtain tunable luminescence spectra.

## 8. Conclusions

This review summarized the recent research progress of  $\text{Mn}^{4+}$  and multiple ion such as  $\text{Bi}^{3+}$  and rare earth ions  $\text{Dy}^{3+}/\text{Nd}^{3+}/$



$\text{Yb}^{3+}/\text{Er}^{3+}/\text{Ho}^{3+}/\text{Tm}^{3+}$  codoped phosphors in the complex oxide host lattice, including their structural-dependent optical properties, energy transfer mechanism, and potential optical applications. Thus, these  $\text{Mn}^{4+}$ - and multiple ion-codoped phosphors are potential candidates for application in the fields of solar energy cells, WLEDs, indoor plant cultivation, and temperature sensors. This review provides extensive insight for developing novel  $\text{Mn}^{4+}$ -doped phosphors with desirable functional properties from an application point of view and helps to reveal the underlying energy transfer mechanism between  $\text{Mn}^{4+}$  and multiple ions.

## Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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