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## Large enhancement of red upconversion luminescence in beta $\text{Ba}_2\text{Sc}_{0.67}\text{Yb}_{0.3}\text{Er}_{0.03}\text{AlO}_5$ phosphor via $\text{Mn}^{2+}$ ions doping for thermometry

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Here, this study reports single-band red upconversion emission in  $\beta\text{-Ba}_2\text{ScAlO}_5\text{:Yb}^{3+}/\text{Er}^{3+}$  phosphor by doping  $\text{Mn}^{2+}$ . The optimum concentration of  $\text{Mn}^{2+}$  ions in  $\beta\text{-Ba}_2\text{ScAlO}_5\text{:Yb}^{3+}/\text{Er}^{3+}$  phosphor was 0.20. The intensity of red and green emissions is increased by 27.4 and 19.3 times, respectively. Compared with the samples without  $\text{Mn}^{2+}$  ions, the red-green integral strength ratio of  $\beta\text{-Ba}_2\text{ScAlO}_5\text{:Yb}^{3+}/\text{Er}^{3+}/\text{Mn}^{2+}$  sample was significantly increased by 28.4 times, reaching 110.9. The UCL mechanism was explored by analyzing the down-conversion luminescence spectra, absorption spectra, UCL spectra, and upconversion fluorescence lifetime decay curves of  $\text{Yb}^{3+}/\text{Er}^{3+}/\text{Mn}^{2+}$  co-doped  $\beta\text{-Ba}_2\text{ScAlO}_5$ . The enhancement of upconversion red light is achieved through energy transfer between defect bands and  $\text{Er}^{3+}$  ions, as well as energy transfer between  $\text{Mn}^{2+}$  ions and  $\text{Er}^{3+}$  ions. In addition, the  $\text{Mn}^{2+}$  doped  $\beta\text{-Ba}_2\text{ScAlO}_5\text{:Yb}^{3+}/\text{Er}^{3+}$  red UCL phosphors have great potential for ambient temperature sensing in the 298–523 K temperature range. The maximum sensitivity of  $\beta\text{-Ba}_2\text{ScAlO}_5\text{:Yb}^{3+}/\text{Er}^{3+}/\text{Mn}^{2+}$  phosphor as a temperature sensor at 523 K is  $0.0247\text{ K}^{-1}$ .

**Keywords** Upconversion luminescence,  $\text{Mn}^{2+}$  doping, Single red emission, Optical thermometry

In recent years, rare-earth-doped upconversion luminescence (UCL) materials have been widely used in optical anticounterfeiting, optical temperature measurement, and illumination display due to their stable physicochemical properties, low toxicity, and long fluorescence lifetime<sup>1–6</sup>. At present, the UCL efficiency is still one of the focuses of research, but the single-color UCL has gradually become one of the focuses of research at this stage, especially to achieve the single UCL of red and near-infrared light<sup>7,8</sup>. In the UCL process, rare-earth  $\text{Yb}^{3+}$  ions are widely used as sensitizers due to their strong absorption cross section near 980 nm. Meanwhile,  $\text{Er}^{3+}$  ions have abundant step energy states that can be coupled with sensitizers and become commonly used as activators<sup>9,10</sup>. Upconversion materials co-doped with  $\text{Yb}^{3+}$  and  $\text{Er}^{3+}$  ions tend to emit strong green light and relatively weak red light<sup>11</sup>. Unfortunately, the poor penetration of green luminescence into biological tissues limits the biomedical applications of this class of materials, whereas light located in the red to near-infrared wavelength band (650–1350 nm) has a strong biological tissue penetration capability<sup>12,13</sup>. Therefore, red UCL materials are very interesting for optical temperature measurement, bio-imaging, and medical diagnostics<sup>14–16</sup>. Optical temperature measurement technology, due to its non-contact measurement, fast response and high sensitivity, has shown great application potential in daily life, medical treatment, scientific research and other fields<sup>17,18</sup>. Optical temperature sensing is a technology to obtain temperature information by measuring the change of optical properties of objects, including fluorescence intensity, fluorescence ratio and decay lifetime<sup>19,20</sup>. The single emission temperature measurement is based on the change of the relationship between a certain luminous intensity and temperature in the luminous center of the material. The application of upconversion green emission luminescence technology in optical temperature measurement has been studied, but the penetration of green light in complex environments and biological tissues is poor<sup>21,22</sup>. Therefore, it is urgent to develop upconversion red light emission materials for optical temperature measurement.

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Various techniques have been employed to modulate the UCL performance and single-colour UCL, such as substrate selection, rare-earth ion doping type, concentration, crystal field modulation, surface plasmon, and doping of transition metals<sup>23–27</sup>. Wang et al. synthesized a novel  $K_3(Y_{0.88}Yb_{0.10}Er_{0.02})Si_2O_7$  phosphor, which enhanced the UCL intensity and thus increased the absolute and relative sensitivity<sup>28</sup>. Lin and colleagues designed a novel spindle probe with an adjustable aspect ratio for mitochondrial imaging and coated gold nanoparticles (SPS@Au) layer by layer on the surface of the probe, which has the property of enhancing the red UCL and can be used for synergistic immune-photodynamic anticancer therapy<sup>29</sup>. Bai et al. gave the  $CeO_2: Yb/Er$  samples stronger UCL by doping transition metal  $Fe^{3+}$  ions, which enhanced the photoelectric conversion efficiency<sup>30</sup>. In addition, Bi et al. achieved single-band red light emission and improved the red to green ratio (R/G) by adjusting the  $Mn^{2+}$  content in  $NaLnF_4: Er/Mn^{3+}$ . Recently, we found that a new  $\beta-Ba_2ScAlO_5: 0.3Yb^{3+}/0.03Er^{3+}$  (BSAO: Y/E) phosphor could achieve red upconversion emission<sup>32</sup>. However, the upconversion red emission intensity of BSAO: Y/E phosphors is still low and cannot satisfy the optical temperature measurement. Therefore, we need to further increase the intensity of red light emission to meet current needs.

This study achieved an intense single-band red UCL by doping  $Mn^{2+}$  in BSAO: Y/E samples. The study results show that the red emission was enhanced in the optimum sample of 0.20  $Mn^{2+}$ , and the red to green integral intensity ratio reaches a high value of 110.9. The UCL mechanism was explored by analyzing the down-conversion luminescence spectra, absorption spectra, UCL spectra, and upconversion fluorescence lifetime decay curves of  $\beta-Ba_2ScAlO_5: Yb^{3+}/Er^{3+}/Mn^{2+}$  (BSAO: Y/E/M) phosphors. The enhancement of upconversion red light is achieved through energy transfer between defect bands and  $Er^{3+}$  ions, as well as energy transfer between  $Mn^{2+}$  ions and  $Er^{3+}$  ions. The BSAO: Y/E/M phosphors have a wide range of applications in optical temperature measurement.

## Experimental Materials

BSAO: Y/E/M phosphors were synthesized using a solid-phase method at high temperatures<sup>32</sup>. Primary raw materials, including high-purity  $BaCO_3$ ,  $Sc_2O_3$ ,  $Al(OH)_3$ ,  $Mn_2O_3$ ,  $Yb_2O_3$ , and  $Er_2O_3$ , were directly purchased from Aladdin Corporation without additional refinement.

## Synthesis

Unprocessed materials ( $BaCO_3$ ,  $Sc_2O_3$ ,  $Al(OH)_3$ ,  $Mn_2O_3$ ,  $Yb_2O_3$ , and  $Er_2O_3$ ) were weighed in a beaker according to stoichiometry. The mixture was then placed in a blender with anhydrous ethanol and stirred for 1 h to create a well-mixed suspension. After standing at ambient temperature for 2 h and incubating at 70 °C for 24 h, the dried raw materials were ground in an agate bowl and pressed into tablets. The samples were subjected to a high-temperature reaction furnace: temperature was raised to 900 °C for 30 min, then to 1700 °C for 1.5 h<sup>33,34</sup>. Finally, the temperature was lowered to ambient temperature. The samples were ground in an agate bowl to obtain BSAO: Y/E/M phosphors.

## Instruments

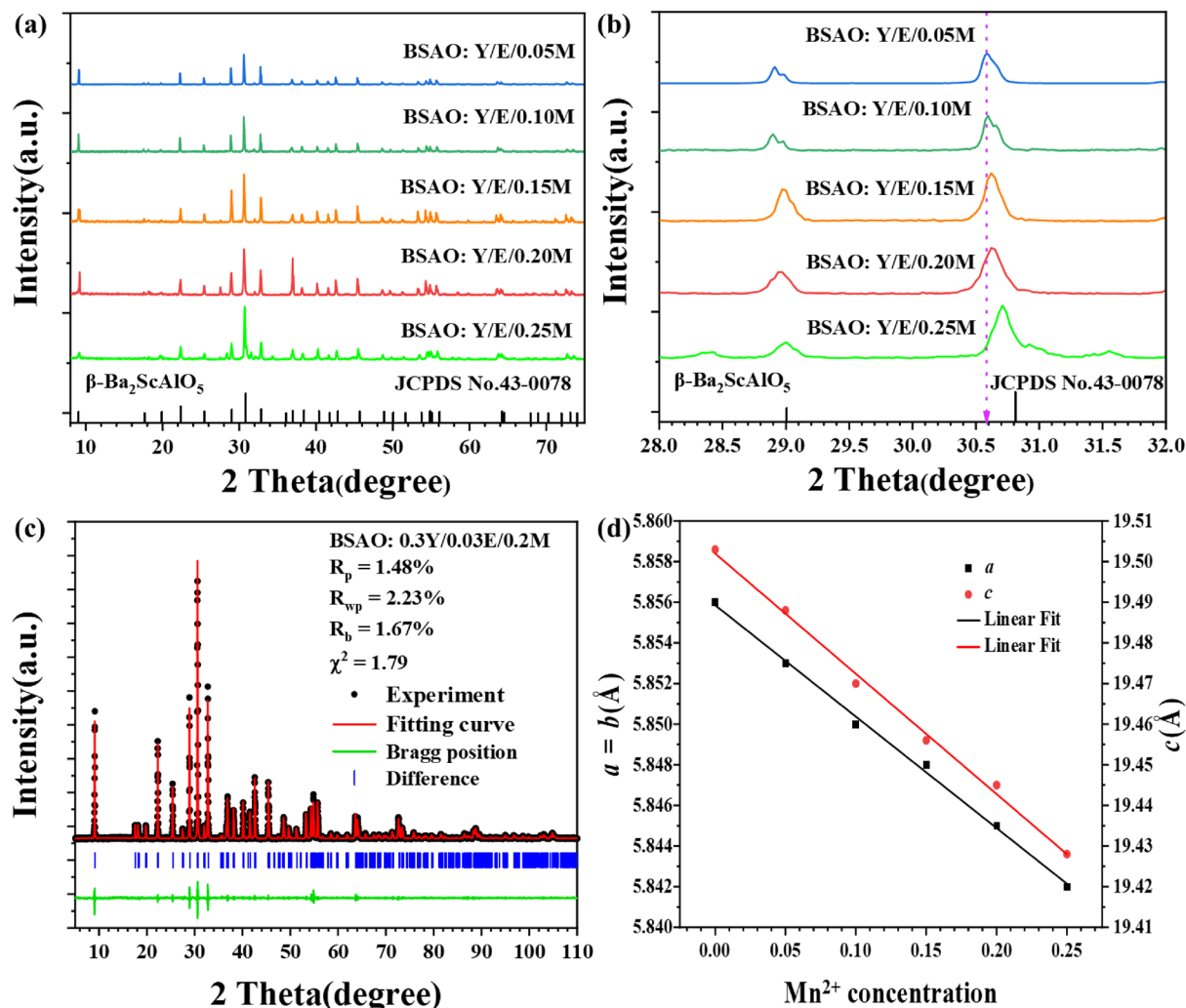
X-ray diffractograms of prepared compounds were obtained using a diffractometer (BRUKER D8 ADVANCED, MA, Germany, Cu target  $K\alpha$  radiation,  $\lambda = 1.54184 \text{ \AA}$ ) in the  $2\theta$  range of 8° to 75° at steps of 0.02°. Shape and size of prepared materials were examined using a Japan JEOL JSM6701F field emission scanning electron microscope (FESEM). Elemental composition was analyzed using a JEOL JED-2300 energy dispersive spectrometer (EDS) attached to a FESEM. A fluorescence spectrophotometer (Acton Spectra Pro 2300i) with a 980 nm near-infrared laser emitter was used to test the 300–800 nm spectral range by Princeton Instruments, USA. The absorption spectrum was characterized using the Lambda 750 absorption spectrometer by Perkin Elmer, USA<sup>35,36</sup>.

## Results and discussion

Figure 1a shows the XRD diffraction spectra of BSAO: Y/E phosphor doped with different concentrations of  $xMn^{2+}$  ( $x = 0.05, 0.10, 0.15, 0.20$  and  $0.25$ ) and  $\beta-Ba_2ScAlO_5$  standard card (JCPDS No. 43-0078). The diffraction peaks of all samples agree with the diffraction pattern of pure phase  $\beta-Ba_2ScAlO_5$  of JCPDS No. 43-0078 [space group  $P6_3/mmc$  (194)]<sup>37</sup>. This result confirms the effective doping of  $Mn^{2+}$ ,  $Yb^{3+}$  and  $Er^{3+}$  ions in  $\beta-Ba_2ScAlO_5$  phosphor. All the diffraction peaks of the XRD of the samples were shifted to a high angle with increasing  $Mn^{2+}$  ion doping concentration (see Fig. 1b). Rietica program was used to perform Rietveld refinement calculations on cell parameters of BSAO: Y/E/M, and the results are shown in Fig. 1c,d. The unit parameters and atomic coordinates after refinement are shown in Table 1. The results show that the ionic radius of  $Mn^{2+}$  (0.67 Å, CN = 4) is smaller than that of  $Ba^{2+}$  (1.34 Å, CN = 4), and the parameters  $a$  and  $c$  decrease with the increase of  $Mn^{2+}$  content. The refinement of atomic coordinates and position occupation reveal the changes of internal structure of  $Mn^{2+}$  doped crystals: (1)  $Mn^{2+}$  ions occupy  $Ba^{2+}$  2a, 4f. and  $Al^{3+}$  4e sites simultaneously; (2) The oxygen vacancy content of the doped  $Mn^{2+}$  sample was 6.2%, which was significantly higher than that of the undoped  $Mn^{2+}$  sample (1.3%). Structural changes usually result in the optical properties of the material<sup>33,34</sup>.

The morphology and elemental composition of the BSAO: Y/E/0.2 M sample were characterized using FESEM and EDS. The mass fractions of Ba, Mn, Sc, Al, O, Yb and Er elements are very close to the theoretical values of 58.38%, 5.06%, 6.94%, 6.17%, 18.37%, 11.92%, and 1.16%, respectively, in Fig. 2a. The EDS spectra show that they are uniformly distributed in the phosphor in Fig. 2b–i. The results show that  $Yb^{3+}$ ,  $Er^{3+}$  and  $Mn^{2+}$  ions were successfully doped into the  $\beta-Ba_2ScAlO_5$  lattice, reducing concentration quenching and improving UCL efficiency.

Figure 3 shows the UCL spectra of the BSAO: Y/E/ $xMn^{2+}$  ( $x = 0–0.25$ ) phosphor under 980 nm laser excitation. Weak green and strong red emission peaks appeared at 530 nm, 566 nm and 664 nm, respectively. The green (530 nm and 566 nm) and red (664 nm) upconversion emission of BSAO: Y/E/M samples corresponds



**Figure 1.** (a,b) XRD patterns and partial enlargement of different concentrations of BSAO: Y/E/M, (c) the refined XRD patterns of BSAO: Y/E/0.2 M and (d) cell parameters of different concentrations of BSAO: Y/E/M.

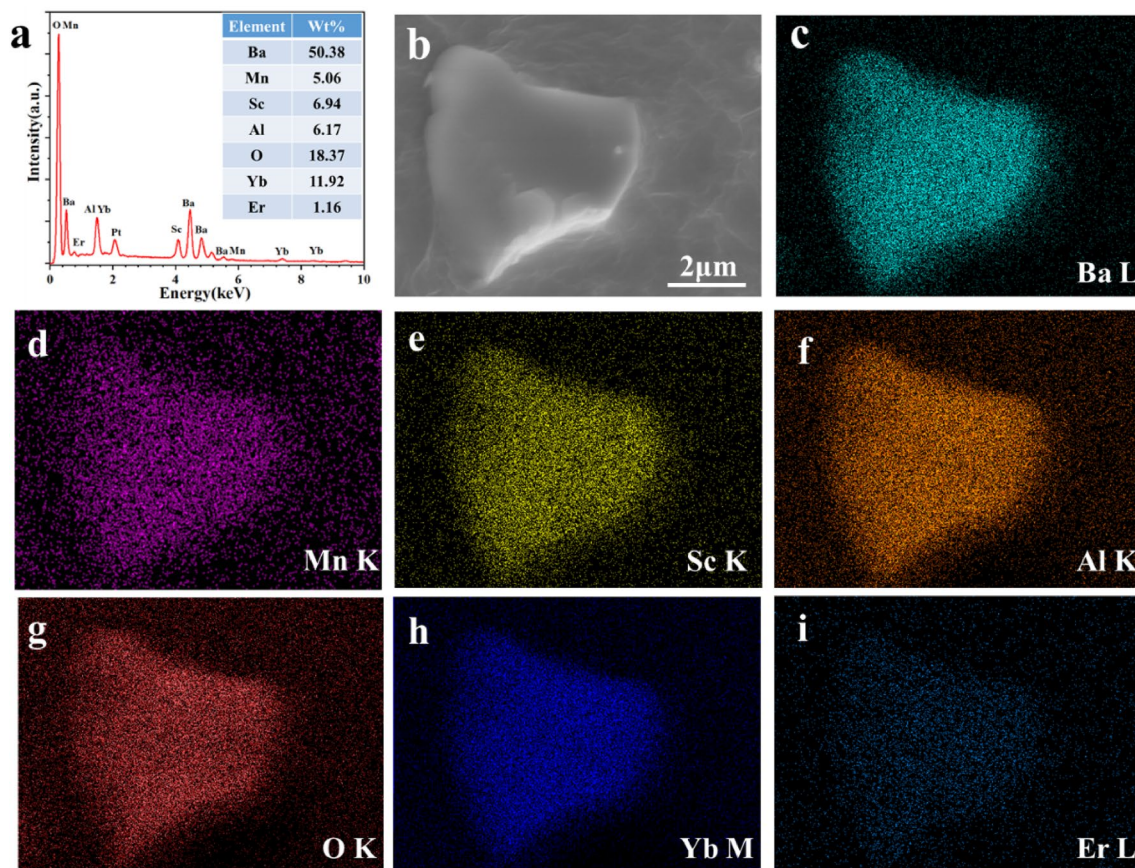
to the radiative transitions of the  $Er^{3+}$  energy levels  ${}^2H_{11/2} \rightarrow {}^4I_{15/2}$ ,  ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$  and  ${}^4F_{9/2} \rightarrow {}^4I_{15/2}$ , respectively. The increase of  $Mn^{2+}$  concentration enhances the upconversion red emission intensity of the sample. With the increase of  $Mn^{2+}$  concentration, the luminous intensity of the upconversion red emission was first enhanced and then weakened. When the  $Mn^{2+}$  concentration was 0.20, the red emission reached the strongest. The intensity of red and green emissions is increased by 27.4 and 19.3 times, respectively. At a doping concentration of 0.20, the ratio reaches 110.9, an increase of 28.4 compared to the undoped  $Mn^{2+}$  sample, which has a ratio of 82.5<sup>32</sup>. A single red upconversion emission was achieved for BSAO: Y/E/0.20 M.

In order to explore the luminescence mechanism of BSAO: Y/E/xM ( $x=0-0.25$ ) phosphor, the power dependence of BSAO: Y/E/0.2 M under 980 nm laser excitation was investigated. In Fig. 4a, the upconversion red-green luminescence intensity of BSAO: Y/E/0.2 M phosphor is enhanced with increased excitation power. Meanwhile, the mathematical relationship between the UCL intensity ( $I$ ) and the pump power ( $P$ ) is given by<sup>38</sup>:  $I \propto P^n$ . The exponent  $n$  denotes the number of photons required for the upconversion process. The double logarithmic coordinate plots from the above equation are shown in Fig. 4b, and the slopes of the fitted curves indicate that the quantum numbers  $n$  required for UCL at 664 nm and 566 nm are 1.52 and 1.71, respectively. The  $n$  values are close to 2, which suggests that the  ${}^4S_{3/2}$  and  ${}^4F_{9/2}$  energy levels of the  $Er^{3+}$  ion are involved in the two-photon process. The numerical coefficients  $n$  associated with the red and green UCL of BSAO: Y/E are 1.46 and 1.57, respectively<sup>32</sup>. Doping of the  $Mn^{2+}$  ion increases the number of photons emitted by red light from 1.46 to 1.52 and that emitted by green light from 1.57 to 1.71. Interestingly, although the number of photons increases in both cases, the number of photons for the green light is significantly larger than that for the red light, suggesting that the doping of  $Mn^{2+}$  ions may have changed the UCL mechanism<sup>39,40</sup>.

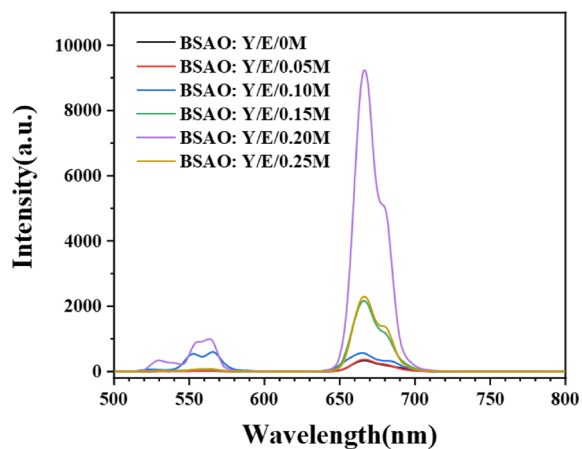
In order to investigate the upconversion red luminescence enhancement mechanism of BSAO: Y/E/M phosphor, its absorption spectra were characterized as shown in Fig. 5. Figure 5a shows the absorption spectra of BSAO: Y/E/xM ( $x=0, 0.2$ ). The two samples have six identical absorption bands at the same location: one broad band (main peak at 300 nm) and five peaks (380, 488, 530, 664, and 980 nm). The absorption band near 300 nm is the intrinsic absorption of the  $Ba_2ScAlO_5$  main matrix. The absorption peaks at 488, 530 and 664 nm are the

Parameter	Sample									
	$x=0$		$x=0.2$							
Space group	$P6_3/mmc$									
Cell constant ( $\text{\AA}$ )	$a=b=5.856, c=19.503$		$a=b=5.845, c=19.445$							
Overall thermal displacement ( $\text{\AA}^2$ )	0.793		1.113							
Atom	Site	$x$	$y$	$z$	$n$	$x$	$y$	$z$	$n$	
Sc	4f	0.33333	0.66667	0.56476	0.11891	0.33333	0.66667	0.56371	0.11543	
Ba	2a	0.00000	0.00000	0.00000	0.08333	0.00000	0.00000	0.00000	0.06101	
Ba	2d	0.33333	0.66667	0.75000	0.07741	0.33333	0.66667	0.75000	0.08333	
Ba	4f	0.33333	0.66667	0.38956	0.16667	0.33333	0.66667	0.38951	0.15266	
Al	4e	0.00000	0.00000	0.16417	0.16667	0.00000	0.00000	0.17139	0.15002	
O	12k	0.16600	0.33200	0.63406	0.50000	0.16600	0.32755	0.62816	0.42051	
O	2b	0.00000	0.00000	0.25000	0.05938	0.00000	0.00000	0.25000	0.08333	
O	6g	0.50000	0.00000	0.00000	0.21517	0.50000	0.00000	0.00000	0.20332	
Yb	4f	0.33333	0.66667	0.56476	0.04776	0.33333	0.66667	0.56371	0.05124	
Mn	2a	–	–	–	–	0.00000	0.00000	0.00000	0.02232	
Mn	4f	–	–	–	–	0.33333	0.66667	0.38951	0.01401	
Mn	4e	–	–	–	–	0.00000	0.00000	0.17139	0.01665	
Oxygen vacancy	~1.3%		~6.2%							

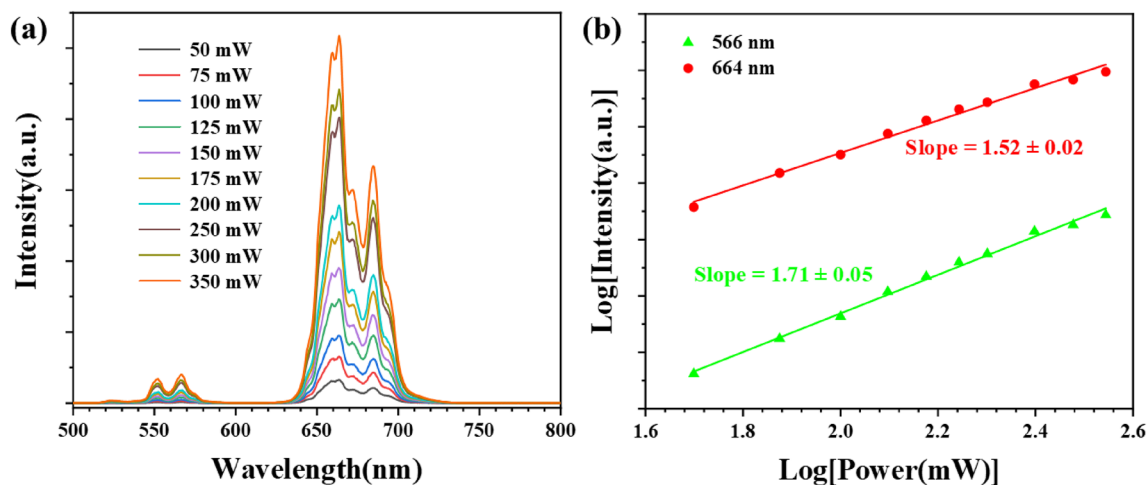
**Table 1.** Refined results of the  $(\text{Ba}_{1-x}\text{Mn}_x)_2(\text{Sc}_{0.67}\text{Yb}_{0.3}\text{Er}_{0.03})\text{AlO}_5$  samples with  $x=0$  and 0.2. The concentration of rare earth  $\text{Er}^{3+}$  in the compounds is so low (3 at% of the  $\text{Sc}^{3+}$  site) that it is not included in the refinement.



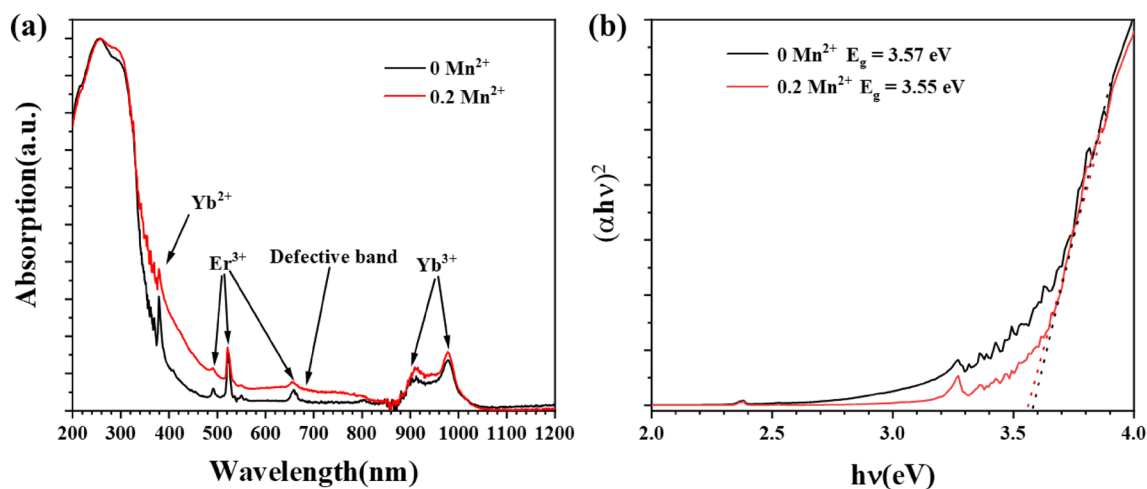
**Figure 2.** (a) and (b) show the EDS and FESEM images of BSAO: Y/E/0.2 M phosphor, respectively. The EDS mapping depicted in (c–i) provides a detailed profile of the chemical composition of BSAO: Y/E/0.2 M phosphor.



**Figure 3.** The UCL spectra of BSAO: Y/E/ $x$ M ( $x=0-0.25$ ) excited by a 980 nm laser with a power of 300 mW.



**Figure 4.** (a) The UCL spectrum of BSAO: Y/E/0.2 M under 980 nm laser excitation versus pump power; (b) Pump power dependence of the green and red luminescence intensity of BSAO: Y/E/0.2 M.



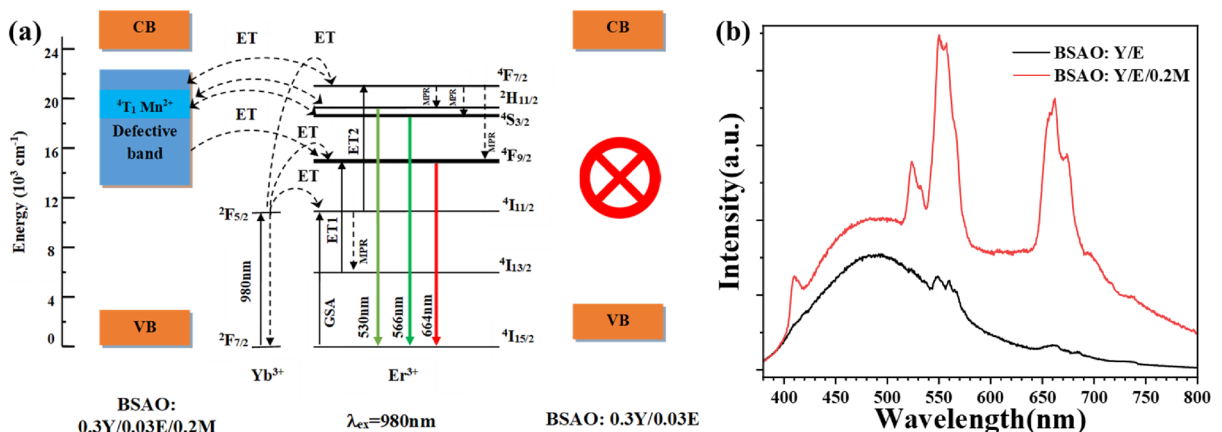
**Figure 5.** (a) Absorption spectra and (b) graph of  $(\alpha hv)^2$  versus  $hv$  correspondence of BSAO: Y/E/ $x$ M ( $x=0, 0.2$ ).

characteristic absorption of the rare-earth  $\text{Er}^{3+}$  ions. The absorption peak at 980 nm is from the rare-earth  $\text{Yb}^{3+}$  ion. The absorption peak at 380 nm is from the  $\text{Yb}^{2+}$  ion. The change in the valence state of the Yb ion from +3 to +2 results in a decrease in the number of positive charges in the crystal<sup>41</sup>. Therefore, the increase in oxygen vacancies is necessary to maintain the electroneutrality of the material<sup>42</sup>. Furthermore, a broad absorption band from 470 to 820 nm is observed in BSAO: Y/E/M doped with 0.2  $\text{Mn}^{2+}$  ions compared to the undoped  $\text{Mn}^{2+}$  sample. The center wavelength is about 640 nm. The broad absorption band ranging from 470 to 820 nm is due to oxygen vacancy defects caused by doping with 0.2  $\text{Mn}^{2+}$ . Figure 5b shows the correspondence between  $(\lambda h\nu)^2$  and  $h\nu$  for BSAO: Y/E/ $x\text{M}$  ( $x=0, 0.2$ ) samples. The calculated results show that the band gap of  $\text{Mn}^{2+}$  doped is 3.55 eV, and that of undoped  $\text{Mn}^{2+}$  is 3.57 eV<sup>43–45</sup>. Therefore, the band gap can be reduced by doping  $\text{Mn}^{2+}$  ions, which confirms the above conclusion.

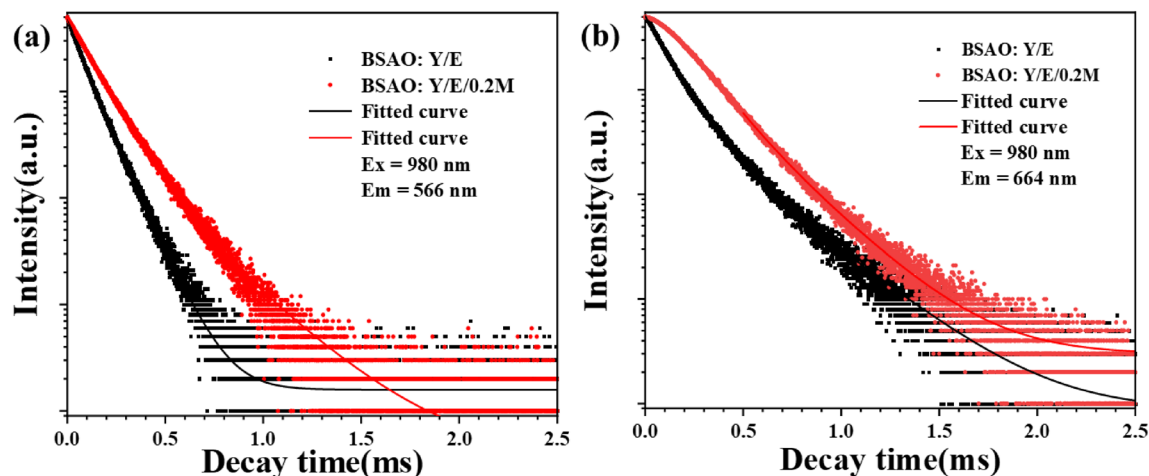
The upconversion excitation processes mainly include multiphonon relaxation (MPR), ground state absorption (GSA), and energy transfer (ET) processes<sup>46</sup>. Figure 6a shows the conversion mechanism of BSAO: Y/E/M phosphor, demonstrating its energy transfer paths. Based on a previous report, we demonstrated that the main excitation pathway for the red upconversion emission is GSA + MPR + ET1<sup>32</sup>. In the BSAO: Y/E/0.2 M phosphor, the broad absorption band from 470 to 820 nm is due to oxygen vacancy defects. As shown in Fig. 6a, the defect bands coincide precisely with the emission levels in red ( ${}^4\text{F}_{9/2}$ ) and green ( ${}^2\text{H}_{11/2}$  and  ${}^4\text{S}_{3/2}$ ), which leads to the energy transfer process between the defect bands and the corresponding energy levels of  $\text{Er}^{3+}$  ions ( ${}^4\text{F}_{7/2}$ ,  ${}^4\text{F}_{9/2}$ ,  ${}^2\text{H}_{11/2}$  and  ${}^4\text{S}_{3/2}$ ). The first energy transfer pathway for enhanced UCL: the energy of the  ${}^4\text{F}_{7/2}$  energy level of  $\text{Er}^{3+}$  is transferred to the defect band through energy transfer, and then the defect band is transferred to the  ${}^2\text{H}_{11/2}$ ,  ${}^4\text{S}_{3/2}$ , and  ${}^4\text{F}_{9/2}$  energy levels through energy transfer to emit the corresponding green (530 and 566 nm) and red (664 nm) light. Since the  ${}^4\text{F}_{9/2}$  energy level is located at the edge of the absorption band, the defect band transfers more energy to the  ${}^4\text{F}_{9/2}$  energy level<sup>47</sup>. This finding is consistent with the significant enhancement of red light in the UCL spectrum (Fig. 3). The second energy transfer pathway for enhanced UCL: the non-radiative energy transfer of  $\text{Er}^{3+}$  to  $\text{Mn}^{2+}$  ( ${}^2\text{H}_{11/2}/{}^4\text{S}_{3/2} \rightarrow {}^4\text{T}_1$ ), followed by the back energy transfer to  $\text{Er}^{3+}$  ( ${}^4\text{T}_1 \rightarrow {}^4\text{F}_{9/2}$ )<sup>48</sup>. As the content of  $\text{Mn}^{2+}$  increases, the weak green radiation of  $\text{Er}^{3+}$  hardly changes, while the red radiation is greatly enhanced, indicating that the energy transfer between  $\text{Er}^{3+}$  and  $\text{Mn}^{2+}$  is very efficient. As a result, higher R/G ratios can be achieved.

Figure 6b shows the down-conversion luminescence spectra of BSAO: Y/E and BSAO: Y/E/0.2 M. A broad emission band centered at 485 nm is observed for both samples beside the characteristic emission peaks of rare earth  $\text{Yb}^{3+}$  and  $\text{Er}^{3+}$ . This emission band corresponds to the conduction band to the valence band leap of the two samples. As can be seen from the black line in Fig. 6b, the BSAO: Y/E phosphor exhibits a strong green emission under 365 nm excitation with a green–red ratio of 2.97. After  $\text{Mn}^{2+}$  doping, BSAO: Y/E/0.2 M has a green emission peak and a red emission peak [red line in Fig. 6b] with a green–red ratio of 0.95. Under 365 nm laser excitation, BSAO: Y/E/0.2 M directly leaps the energy of  $\text{Er}^{3+}$  in the  ${}^4\text{F}_{7/2}$  energy level to the  ${}^2\text{H}_{11/2}$ ,  ${}^4\text{S}_{3/2}$ , and  ${}^4\text{F}_{9/2}$  excited states via MPR. The emission of red light indicates that more photons relax to the  ${}^4\text{F}_{9/2}$  excited state, while very few photons go to the  ${}^2\text{H}_{11/2}$  and  ${}^4\text{S}_{3/2}$  energy levels, so the red light is stronger and the green light is weaker. The BSAO: Y/E shows red light under 980 nm excitation with a red–green ratio of about 82.5<sup>32</sup>. For the BSAO: Y/E/0.2 M sample, red emissions were enhanced under 980 nm laser excitation, and a high R/G ratio of 110.9 was observed. This shows that the upconversion emission excitation path of BSAO: Y/E/0.2 M does not change compared with BSAO: Y/E, only two energy transfer paths are added to increase the number of electrons at the luminous level, thus enhancing the upconversion emission (Fig. 6a).

To further understand the effect of  $\text{Mn}^{2+}$  doping on the upconversion of BSAO: Y/E, Fig. 7a,b shows the upconversion green (566 nm) and red (664 nm) decay curves of BSAO: Y/E/ $x\text{M}$  ( $x=0, 0.2$ ) fluorescent material. BSAO: Y/E/ $x\text{M}$  ( $x=0, 0.2$ ) decay curves for both red ( ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$ ) and green ( ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$ ) light show biexponential decay curves, which are in good agreement with the second-order exponential decay mode. Since the curves exhibit double-exponential decay characteristics, the average fluorescence decay lifetime can be determined by the following equation<sup>49</sup>:  $\tau = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$ .  $A_1$  and  $A_2$  are constants,  $\tau$  represents the



**Figure 6.** (a) The energy leap mechanism of BSAO: Y/E/0.2 M. (b) The photoluminescence spectra of BSAO: Y/E/0.2 M under 365 nm laser excitation.



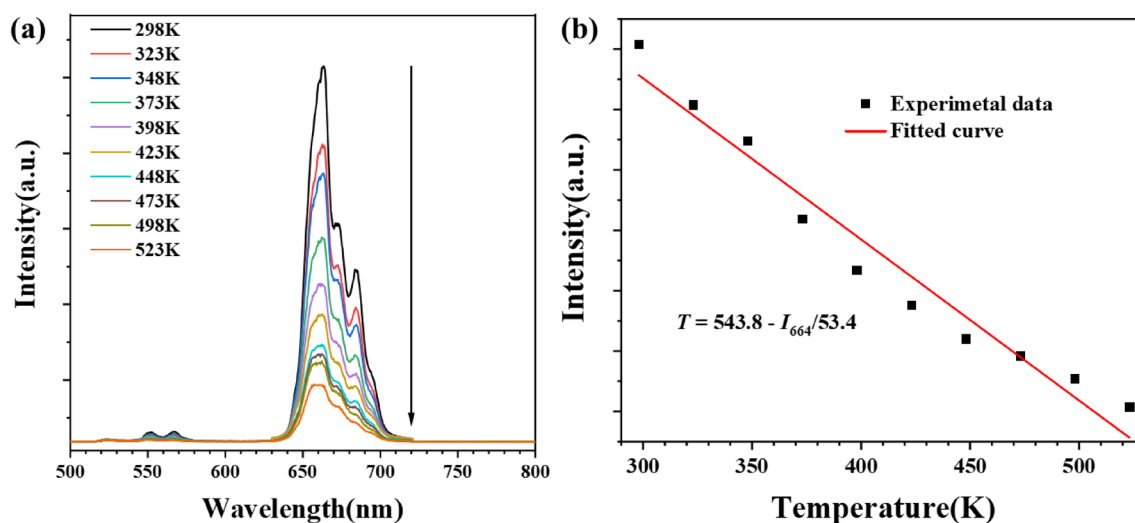
**Figure 7.** Fluorescence decay lifetime of BSAO: Y/E and BSAO: Y/E/0.2 M.

decay time, and  $\tau_1$  and  $\tau_2$  represent the fast and slow exponential components. As can be seen from Fig. 7a,b, the fluorescence decay lifetime of 0.2Mn<sup>2+</sup> ions doped with BSAO: Y/E is longer than that of BSAO: Y/E. The results show that the doping of Mn<sup>2+</sup> increases the population number of Er<sup>3+</sup> excited states. It is confirmed that the energy of the oxygen-vacancy induced defect band in the BSAO: Y/E/M phosphor is transferred to the excited state of the Er<sup>3+</sup> ion<sup>50,51</sup>. Thus, the number of electrons in Er<sup>3+</sup> ion transition from excited state to ground state is increased, and the UCL is enhanced.

BSAO: Y/E/0.2 M phosphor has a strong red UCL, making it an ideal candidate for single-parameter temperature sensors. In order to investigate the temperature sensitivity of BSAO: Y/E/0.2 M samples, the temperature dependence of the red UCL of the samples under 980 nm laser irradiation in the temperature range of 298–523 K is measured in Fig. 8a. The intensity of the red UCL decreases with increasing temperature. Figure 8b shows the temperature dependence of the red UCL integral intensity for BSAO: Y/E/0.2 M, where  $T$  and  $I_{664}$  are the absolute temperature and red integral intensity of the BSAO: Y/E/0.2 M samples, respectively, which can be fitted with  $T = 543.8 - I_{664}/53.4$ . The sensitivity ( $S$ ) of the material is generally defined as  $S = (\partial I_{664}/\partial T)/I_{664}$ <sup>52</sup>. The maximum sensitivity of BSAO: Y/E/0.2 M phosphor as a temperature sensor at 523 K is 0.0247 K<sup>-1</sup>. The Mn<sup>2+</sup> doped BSAO: Y/E red UCL phosphor has excellent potential for temperature sensing and can be used for practical non-contact sensing applications in harsh environments.

## Conclusion

This study successfully employed the solid-phase reaction strategy to synthesize a triple-doped BSAO: Y/E/M phosphor. Optimally doped with 0.20 Mn<sup>2+</sup> ions, the sample showed a single upconversion red emission with a red-to-green integrated intensity ratio of 110.9, a 28.4-fold enhancement over the undoped BSAO: Y/E phosphor with Mn<sup>2+</sup> ions. The intensity of red and green emissions is increased by 27.4 and 19.3 times, respectively. There are two pathways for red light enhancement. The first enhancement pathway: the energy of the <sup>4</sup>F<sub>7/2</sub> energy level



**Figure 8.** (a) The UCL spectra of BSAO: Y/E/0.2 M sample for different temperatures from 298 to 523 K. (b) The red integrated intensity as a function of the temperature.

of  $\text{Er}^{3+}$  is transferred to the defect band through energy transfer, and then the defect band is transferred to the  ${}^2\text{H}_{11/2}$ ,  ${}^4\text{S}_{3/2}$ , and  ${}^4\text{F}_{9/2}$  energy levels through energy transfer to emit the corresponding green (530 and 566 nm) and red (664 nm) light. The second enhancement pathway: the non-radiative energy transfer of  $\text{Er}^{3+}$  to  $\text{Mn}^{2+}$  ( ${}^2\text{H}_{11/2}/{}^4\text{S}_{3/2} \rightarrow {}^4\text{T}_1$ ), followed by the back energy transfer to  $\text{Er}^{3+}$  ( ${}^4\text{T}_1 \rightarrow {}^4\text{F}_{9/2}$ ). The maximum sensitivity of BSAO: Y/E/0.2 M phosphor as a temperature sensor at 523 K is  $0.0247 \text{ K}^{-1}$ . The BSAO: Y/E/M phosphor has a wide range of applications in optical thermometry.

## Data availability

All data generated or analysed during this study are included in this published article.

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## Author contributions

Y.L. is involved in conceptualization, methodology, validation, characterization, formal analysis, investigation, writing – original draft, visualization. B.D. is involved in conceptualization, methodology, characterization, formal analysis, data curation, writing-review and editing. L.Z. is involved in investigation, methodology. Y.W. is involved in investigation, methodology. F.W. is involved in writing – review & editing. C.D. is involved in writing – review & editing, funding acquisition. J.H. is involved in writing – review & editing, conceptualization, methodology, project administration, funding acquisition. All authors read and approved the final manuscript.

## Competing interests

The authors declare no competing interests.

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