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Luminescence properties of single-phase color-tunable $TbZn_{1-x}(B_5O_{10})$:xMn^{2+} phosphor

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ABSTRACT

A series of emission-tunable $TbZn_{1-x}(B_5O_{10})$:xMn^{2+} phosphor were prepared by the conventional high temperature solid-state method. The lattice structure, and particularly the luminescence properties upon ultraviolet light excitation were studied. It is revealed that Mn^{2+} ions only occupy Zn^{2+} sites. And the characteristic $^5D_4$-^7F_J emissions of Tb^{3+} were also studied in $TbZn_{1-x}(B_5O_{10})$:xMn^{2+} under the excitation of 365 nm. By doping Mn^{2+} in the $TbZn(B_5O_{10})$ host, red light at 625 nm was observed due to the transition of $^4T_{1g}(G)\rightarrow{}^6A_{1g}(S)$. The energy transfer mechanism between Tb^{3+} and Mn^{2+} was verified by the fluorescence spectra and decay curves. And the energy transfer efficiencies were discussed. Moreover, color-tunable range from green to red can be realized in $TbZn_{1-x}(B_5O_{10})$:$xMn^{2+}$$(0 < x < 0.01)$ by adjusting the concentration of Mn^{2+} ions. The above investigations indicate that $TbZn_{1-x}(B_5O_{10})$:xMn^{2+} have great potential in luminescent devices.

1. Introduction

Rare earth single doped or co-doped color-tunable phosphors with ultraviolet (UV) excitations have attracted more attention for solid state lighting recently [1–10]. Phosphor materials, like oxynitride, phosphates, silicates, aluminates and borates, which based on lanthanides converting ultraviolet (UV) or near-ultraviolet (n-UV) radiation to visible light, have been extensively studied [1–5]. Moreover, sensitization is a traditional method used for enhancing the luminescence efficiency of a phosphor at excitation in the energy range where absorption by active ions is insignificant [6]. This phenomenon has been known for decades and a classic example of application is color-tunable phosphors [6], for which sensitization of Tb^{3+} emission by Ce^{3+} [7], sensitization of Eu^{3+} emission by Gd^{3+} [8], sensitization of Mn^{2+} emission by Tb^{3+} [9]and so on. However, concentration quenching commonly exists in these materials, which normally leads to a weak luminescence [10]. For instance, in the crystal structure of $Ca_3La_6(SiO_4)_6$:Tb^{3+}, Mn^{2+}, the $^5D_3$-^7F_J transitions are easy to quench at a high Tb^{3+} concentration due to the cross relaxation process [9]. $SrAl_2B_2O_7$:Ce^{3+}, Tb^{3+} has an optimal Ce^{3+} doping concentration of 0.02 [11] and the maximum intensity of Gd^{3+} is at 20 mol% in $(Y_{1-x}Gd_x)BO_3$:$0.01Eu^{3+}$ [12]. To solve this problem, quite a few previous work have proposed methods [4,6,10,13–16]. Specifically, rare-earth-based self-activated materials were synthesized with rare-earth constituting the crystalline lattice. These materials can suffer from high photon flux and exhibit excellent luminescence properties without luminescence quenching [10]. And several rare-earth-based self-activated borates have been studied, such as $Ca_3La_6(SiO_4)_6$:Tb^{3+}, Mn^{2+} [9], $LnMgB_5O_{10}$ (Ln = Tb, Gd) [6], $KBaTbB_2O_6$ [13], $K_3EuB_6O_{12}$ [10] and so on. In addition, solid state method is one of the most commonly used method in synthesis of phosphors under the environment of high temperature.

Nevertheless, different phosphor substrates can be synthesized in a quite difference sintering temperature due to the different melting points. Rare-earth-based borate phosphors can be synthesized in a lower temperature differ from other materials, such as $Ca_8MgLu(PO_4)_7$:Ce^{3+},Tb^{3+},Mn^{2+} [4], $Ca_3La_6(SiO_4)_6$:Tb^{3+}, Mn^{2+} [9], $LaMgAl_{11}O_{19}$:Tb, Mn [17] were respectively synthesized at 1200 °C for 4 h, 1300 °C for 6 h and 1500 °C for 2 h under a specific reducing atmosphere, while rare-earth-based borate $KBaTbB_2O_6$ and $KBaTb_{1-x}Eu_xB_2O_6$ [13] were sintered under CO reducing atmosphere at 935 °C for 8 h, $LnMgB_5O_{10}$ (Ln = Tb, Gd) [6] were synthesized in 1000 °C for 6 h, $K_3EuB_6O_{12}$ [10] were synthesized at 750 °C in the open air for 24 h and so on. Most importantly, synthesizing of borates can skip the complicated procedure of co-solvents. Those merits make borates as an ideal candidate in practical applications, e.g. industrial and residential lighting, LED (light-emitting diode) based cathode ray tubes, field emission displays and PDPs (Plasma Display Panel) [14,18–20].

In this paper, a novel Tb^{3+}-based borate phosphor $TbZn_{1-x}(B_5O_{10})$:xMn^{2+} has been synthesized by solid state method.

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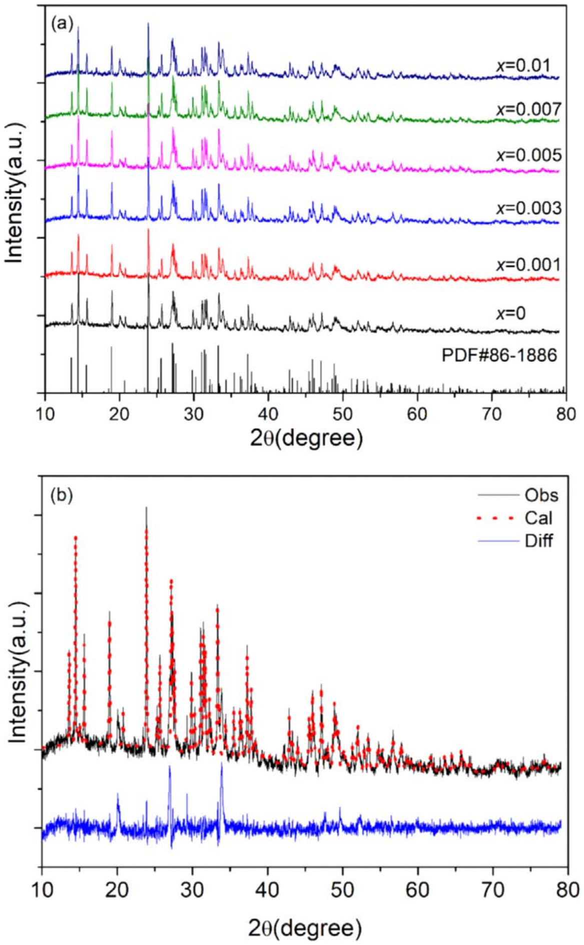

Fig. 1. (a) XRD patterns of $TbZn_{1-x}(B_5O_{10}):xMn^{2+}$ ($0 \le x \le 0.01$) samples and the standard data of JCPDS#86-1886($TbZn(B_5O_{10})$), **(b)** Rietveld refinement XRD patterns of $TbZn_{1-x}(B_5O_{10}):xMn^{2+}$ ($x = 0.007$) by TOPAS package. (Experiment-black line, Refinement-red dot and difference-blue line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

And the structure and elements were determined by Rietveld refinement, powder X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), and energy-dispersive spectrometer (EDS). The energy transfer mechanism was systematically explained by the emission, excitation, diffuse reflection and fluorescence decay spectra. Intense blue light emission can be obtained by UV excitation and color hue can be tuned from green to red by controlling the concentration of Mn^{2+}.

2. Experimental

Powder samples of $TbZn_{1-x}(B_5O_{10}):xMn^{2+}$ ($0 \le x \le 0.01$) were synthesized by a conventional solid state reaction method. The starting materials included Tb_4O_7 (analytical reagent A.R.), ZnO (A.R.), H_3BO_3 (A.R.) and $MnCO_3$ (Chemically Pure C.P.). Stoichiometric amounts of the starting reagents were thoroughly mixed and grinded in crucible and fired in a tube furnace. The mixed homogeneous powders were sintered at 950 °C for 2 h under a reducing atmosphere (5%H_2/95%N_2). The heating rate was controlled at 7 °C/min. The obtained phosphors were cooled down to room temperature and ground into power for further measurements.

Table 1
The refinement data and fractional atomic coordinates of $TbZn_{1-x}(B_5O_{10}):xMn^{2+}$($x = 0.007$).

Space group: $P121/n1$ (14)(monoclinic)					
Cell parameter			**Reliability Factors**		
Crystal density (g/cm^3) = 15.164			Rexp (%) = 4.45		
Z = 4			Rwp (%) = 7.59		
a = 8.5736626 Å			Rp (%) = 5.23		
b = 7.6049338 Å			GOF = 1.71		
c = 9.3861853 Å					
B = 93.50627°					
V = 610.85374 $Å^3$					
Atom	**x**	**y**	**z**	**Occupancy**	**Beq**
Zn1/Mn1	0.60710	0.39615	0.12482	2.182	0.1674
Tb1	0.18691	0.18522	0.23753	2.380	1.5
B1	0.93801	0.62274	0.25559	7.534	19.99
B2	0.49379	0.40062	0.33699	8.178	17.31
B3	0.65568	0.68885	0.56785	6.929	15.95
B4	0.92817	0.64253	− 0.03558	6.009	6.125
B5	1.02296	0.13365	0.44569	7.409	5.725
O1	0.05167	0.67170	0.24000	1.709	− 1.888
O2	0.82290	0.50553	0.10448	2.688	4.649
O3	0.98561	0.42453	0.32246	5.023	7.695
O4	0.79978	0.63464	0.37076	2.451	− 0.9689
O5	0.64704	0.50175	0.34401	4.802	19.55
O6	0.33602	0.46328	0.44982	1.444	− 3.415
O7	0.60515	0.26264	0.51863	1.443	− 2.902
O8	0.82803	0.39519	0.46075	3.274	3.489
O9	0.65388	0.60569	0.03279	2.690	16.59
O10	0.25486	0.47561	0.13208	4.715	11.24

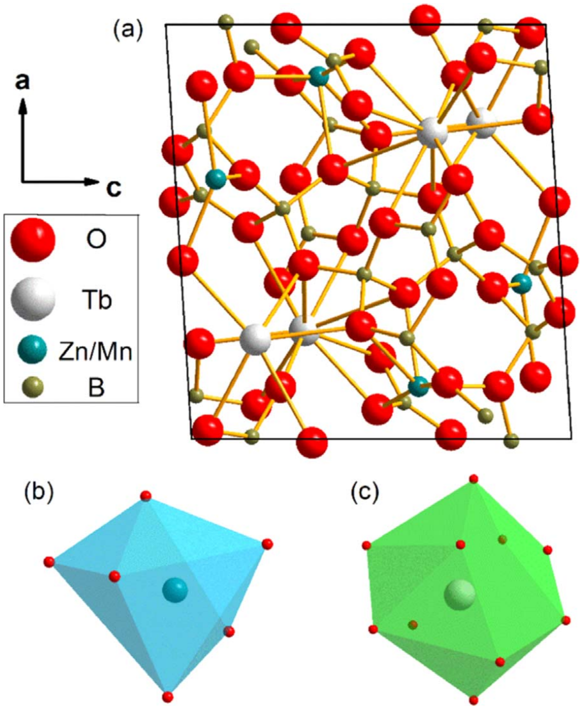

Fig. 2. Schematic structure of $TbZn_{1-x}(B_5O_{10}):xMn^{2+}$ (black solid lines denote the unit cell), (b) and (c) were the coordination environment of Zn/Mn and Tb sites in $TbZn_{1-x}(BO_2)_5:xMn^{2+}$, respectively.

The phase purity was determined by using powder X-ray diffraction (XRD) (Bruker Axs D2 PHASER diffractometer, Cu kα = 0.15406 nm) with 2θ ranging from 10° to 80°, operating at 30 kV and 10 mA. The energy-dispersive spectrometer (EDS) was measured using a field-emission scanning electron microscope (FE-SEM, S-4800, Hitachi, Japan) and the interplanar crystal spacing was examined by a HitachiH-9500 transmission electron microscope (TEM). The excitation and emission spectra of the phosphors were measured by a PL3-211-P spectrometer (HORIBA JOBIN YVON, America) equipped with a 450 W xenon lamp as the exciting source. The fluorescence decay curve was performed employing this equipment with a pulsed spectral LED