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Effect of Some Mineralizers and Organic Acids on the Structural and Luminescence Properties of Zn_2SiO_4 : Mn Phosphor Synthesized at Low Temperature by Impregnation – Coprecipitation Method

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Abstract. Suitable mineralizers promote the formation of the desired phases upon sintering, and organic acids have reducing properties that make the Mn^{2+} ions more stable during synthesis. The purpose of this work is to study the effect of some mineralizers and organic acids as well as sintering temperature on the structural and luminescence properties of manganese-doped zinc orthosilicate phosphor, synthesized at low temperature by impregnation-coprecipitation method. Photoluminescence spectroscopy, XRD, SEM and EDS were used to investigate the samples. The results show that the most suitable mole ratio of the constituents in the precursor is: 1.97 Zn : 0.03 Mn : 1.0 SiO_2 : 0.03 H_3BO_3 : 0.03 CH_3COOH. During 45 minutes, the sample calcined at 700 °C is a bi-phase mixture of β-Zn_2SiO_4 and α-Zn_2SiO_4, emitting yellow light at 575 nm wavelength when excited by 254 nm UV radiation. Boric acid is the mineralizer for α-Zn_2SiO_4. At 800 °C, there is a phase transition from the orthorhombic β-Zn_2SiO_4 to the rhombo H. axes α-Zn_2SiO_4. The sample calcined at 900 °C is a single-phase zinc manganese borosilicate solid solution with rhombo H. axes structure of α-Zn_2SiO_4, consisting of fairly uniform spherical particles with size from 0.3-0.5 µm and emitting 525 nm green light with a luminescence intensity of 46% higher than that of the control sample. The resulting luminescent pigment has the potential for security applications.

Keywords: Coprecipitation, Organic Acids, Mineralizers, Phosphor, Zn_2SiO_4:Mn

INTRODUCTION

The manganese-doped zinc orthosilicate is widely used as a green phosphor in plasma display panels (PDPs), cathode ray tubes (CRT), tri-color lamps, color television, and other optoelectronic devices (Cavourasa *et al.*, 2000; Cich *et al.*, 1998, Morell *et al.*, 1993; Parmar *et al.*, 2009; Takesue *et al.*, 2009; Yen *et al.*, 2006) backlights for LCD (Wang *et al.*, 2020). Although it has been mentioned for a long time, this phosphor is still of research interest because of its high chemical and thermal stability and high luminescence efficiency (Takesue *et al.*, 2009). Manganese-doped zinc orthosilicate phosphors are usually synthesized using the solid phase reaction method. However, this method

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consumes a lot of energy because it requires grinding and then heating the post-crushed materials at high temperatures from 1100 °C to 1400 °C and for a long time, from 2 to 4 hours (Takesue *et al.*, 2009; Vien *et al.*, 2019). The obtained products after calcination are often agglomerated and not uniform, and to produce single-phase products, in many cases, grinding and reheating are required (Kim *et al.*, 2010; Krasnenko *et al.*, 2020a, 2020b; Parmar *et al.*, 2009). In addition, to protect Mn(II) ions from oxidation by atmospheric oxygen during calcination, it is necessary to sinter the milled raw materials in nitrogen or nitrogen/hydrogen atmosphere (Kim *et al.*, 2010; Sohn *et al.*, 1999, 2000). Therefore, the study of reducing the sintering temperature and increasing the stability of Mn(II) ions when synthesizing single-phase Zn_2SiO_4:Mn luminescent materials is of great significance.

Complex metal oxides have applications in many fields, such as ceramics, pigments, catalysts, and magnetic or luminescent materials. When preparing complex oxides by coprecipitation, the cations are kept adjacent, and the precipitated precursors are often nanoscale, thus easily interacting with each other during calcination to produce the desired product. However, there are currently only a few studies on synthesizing Zn_2SiO_4:Mn luminescent pigments by homogeneous precipitation method (Yoshizawa *et al.*, 2012), coprecipitation (Rivera-Enríquez *et al.*, 2016) or related to precipitation method (Cho *et al.*, 2003; Bertail *et al.*, 2011), probably because, according to the coprecipitation method, many of the necessary components cannot be incorporated into the composition of the precipitating precursor because they are soluble. This disadvantage is overcome when using the impregnation-coprecipitation method. According to our results mentioned in the document (Thanh *et al.*, 2021), the Zn_2SiO_4:Mn phosphor synthesized by impregnation - coprecipitation method has higher luminescence efficiency than that of the control sample prepared by the coprecipitation method.

Fluxes and mineralizers are defined as materials that promote the formation of melt and of intended phases, respectively, already at lower burning temperatures during sintering, thereby allowing a reduction of sinter temperature or an increased conversion at the same temperature (Haha *et al.*, 2015). According to Eppler *et al.* (2005), mineralizers are included in most pigment preparations to increase the reaction rate and make the mixture more uniform. However, studies on the influence of fluxes on the luminescence efficiency of Zn_2SiO_4:Mn are quite few (Sivakumar *et al.*, 2012, 2014). The results mentioned by these papers are contradictory as the influence of boric acid and the effect on the concentration change of boric acid has not been mentioned yet (Sivakumar *et al.*, 2014). Almost no works mention the influence of organic acids on the luminescence efficiency of Zn_2SiO_4:Mn. When synthesized by impregnation–coprecipitation method, these acids can act as reducing agents, increasing the stability of Mn^{2+} ions when impregnated or calcined.

From the above mentioned, this work studies the influence of some mineralizers and organic acids as well as sintering temperature on the structural and luminescence properties of manganese-doped zinc orthosilicates, synthesized at low temperature by impregnation-coprecipitation method and initial testing on water-based fluorescent ink from the obtained product for security applications. The samples were characterized by X-ray diffraction, photoluminescence spectroscopy (PL), scanning electron microscopy, and energy-dispersive X-ray spectroscopy (EDS).

MATERIALS AND METHODS

Synthesis of Phosphors

The $Zn_{2-x}Mn_xSiO_4$ phosphors were synthesized by the impregnation-coprecipitation method with the following raw materials: high pure $Zn(CH_3COO)_2.2H_2O$ (≥ 99.0%; Xilong, China), $Na_2SiO_3.9H_2O$ (the ratio between Na_2O and SiO_2: 1.03 ± 0.03, Xilong, China), $MnSO_4.H_2O$ (≥ 99%, Xilong, China) and H_3BO_3 (≥ 99.5%, Xilong, China}, NaCl (≥ 99.5%, Xilong, China), Na_2SO_4 (≥ 99,0%, Guangdong Guanghua Sci-Tech Co., China} and Na_2CO_3 (≥ 99.8%; Guangdong Guanghua SciTech Co., China) as mineralizers, CH_3COOH (≥ 99.5% ; Xilong, China), $H_2C_2O_4.2H_2O$ (≥ 99.5%; Xilong, China), citric acid monohydrate $C_6H_8O_7.H_2O$ (≥ 99,5%; Guangdong Guanghua Sci-Tech Co., China) and ascorbic acid (≥ 99.7%; Xilong; China) as organic acids. Consistent with the results mentioned in the documents (Bertail *et al.*, 2011; Cho *et al.*, 2003; Rivera-Enríquez *et al.*, 2016; Thanh *et al.*, 2021), the manganese content was kept constant at 3 mol% per mol of the phosphor or 1.5 mol% per mol of metal ions. To synthesize $Zn_{1,97}Mn_{0,03}SiO_4$ phosphor, a solution of precipitating agent consisting of 10 ml of 1M Na_2SiO_3 and 9.7 ml of 1M Na_2CO_3 was added with stirring at 500 rpm into a beaker containing 19.7 ml of $Zn(CH_3COO)_2$ solution. Stirring for 20 minutes to ripen the precipitate (Thanh *et al.*, 2021). Filter and wash the precipitate with distilled water until no soluble salts remain. Impregnate the precipitate with 1.2 ml of 0.25M $MnSO_4$ solution and grind for 6-8 min (marked as sample 1.1). Dry the precipitate with mixing at 80 °C, then sinter the precursor at 900 °C at a heating rate of 10 °C/min for 45 min. Precursors when adding a required amount of mineralizers / organic acids when impregnating were carried out similarly (see Figure 1).

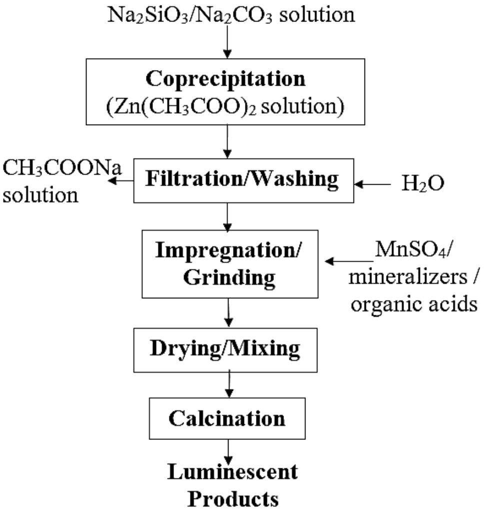


Fig. 1: Flow scheme for the synthesis of phosphors by impregnation - coprecipitation method.

Based on the molar ratio between the components when preparing sample 1.1, the reactions that occur with Zn^{2+} ions at the coprecipitation stage are as follows (for simplicity, ignore the hydrolysis of the SiO_3^{2-} ions):

$$CO_3^{2-}(aq) + H_2O(l) \rightleftarrows OH^-(aq) + HCO_3^-(aq) \quad (1)$$

$$aZn^{2+}(aq) + aCO_3^{2-}(aq) \rightarrow aZnCO_3(s) \quad (2)$$

$$bZn^{2+}(aq) + 2bOH^-(aq) \rightarrow bZn(OH)_2(s) \quad (3)$$

$$(1.97–a–b)Zn^{2+}(aq) + SiO_3^{2-}(aq) \rightarrow ZnSiO_3(s) \quad (4)$$

with $1.97 – a – b = 1$.

According to the above reactions, $ZnSiO_3$ and basic zinc carbonate were in the precursor composition, so they easily interact to form Zn_2SiO_4 products when calcined.

The reaction that occurs when sintering the precursor after impregnating and drying is as follows:

$ZnSiO_3(s) + a\ ZnCO_3(s) + b\ Zn(OH)_2(s) + 0.03\ MnSO_4(s) \rightarrow Zn_{1.97}Mn_{0.03}SiO_4(s) + a\ CO_2(g) + b\ H_2O(g) + 0.03\ SO_3(g)$ (5)

Initial Testing on Water-Based Fluorescent Ink

Water-based fluorescent ink is prepared as follows: polyvinyl alcohol (QualiChem's, India), after dissolving in distilled water at 70 °C was put into an agate mortar, add the luminescent pigment product, Gum Arabic (Acros Organics, UK), and ethanol (99.8%, Fisher Chemical, Loughborough, UK), and ground to disperse for 30 minutes. The mass ratio of the components in printing ink was polyvinyl alcohol 5 : luminescent pigment 20 : Gum Arabic 1 : ethanol 18 : distilled water 56.

Characterization Techniques

The photoluminescent properties of samples were measured by a PL spectrophotometer (Nanolog, Horiba Jobin Yvon) at 254 nm excitation wavelength. The crystalline phase was characterized by X-ray powder diffractometry using a Bruker D8 Advance equipped with CuKα radiation. From XRD data, crystallite sizes (G, nm) were estimated by using Scherrer's equation (Ghoul *et al.* 2020, Mir *et al.* 2015): $G = 0.9\ \lambda/B\ \cos\theta_B$, where λ was the X-ray wavelength (0.15406 nm), θ_B is the maximum of the Bragg diffraction peak, and B was the linewidth at half maximum (in radians). The sample morphology was evaluated by scanning electron microscopy with an S4800-NIHE at an accelerating voltage of 10 kV. The composition of the highest luminescent sample was checked by the EDS method using the HORIBA instrument, model 7593-H, integrated with the FESEM HITACHI S-4800 system.

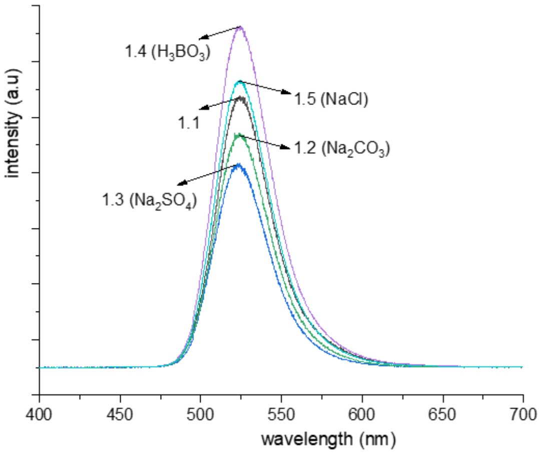
RESULTS AND DISCUSSION

Effect of Some Mineralizers on Luminescence

Boric acid is one of the well-known flux materials (Sivakumar *et al.*, 2014) and is the mineralizing agent for the synthesis of spinel pigment (Eppler, 2005). When heated, it will lose water to form B_2O_3. Vitreous B_2O_3 softens between 325 °C and 450 °C, and α-B_2O_3 melts at 450 °C (Smith 2005). Na_2CO_3 is an important flux in silicate industries (Thieme, 2005), NaCl and Na_2SO_4 are the substances that control crystal growth in the production of lithopone pigments (Völz *et al.*, 2006), and according to the literature (Viswanathan *et al.*, 1983), the halides and sulfates are important mineralizers in the formation of di/tricalcium silicate minerals.

Precursors were prepared by impregnation - coprecipitation method with a Mn content of 3.0 mol%, without and with the addition of the mineralizer Na_2CO_3, Na_2SO_4, H_3BO_3 or NaCl with a content of 3.0 mol% (mol% per mol of the phosphor). The samples are denoted as 1.1 to 1.5, respectively. It was then heated at 900 °C for 45 min. The powder samples after calcination were white, indicating that all doped - manganese (II) ions had been incorporated into the Zn_2SiO_4 crystal lattice (Sivakumar *et al.*, 2012, 2014; Sohn *et al.*, 1999). The effect of mineralizers on the luminescence of the samples after calcination is shown in Figure 2 and Table 1.

According to Figure 2, under 254 nm excitation (Ghoul *et al.* 2020, Mir *et al.* 2015, Parmar *et al.* 2009, Sivakumar *et al.* 2014 or Rakova *et al.* 2024), the calcined samples have similar photoluminescence spectra and emit green light at a maximum wavelength of 525 nm. Consistent with the results indicated in the literature (Sivakumar *et al.* 2014), sample 1.4 supplemented with 3.0 mol% H_3BO_3 after calcination enhanced the maximum PL emission, which was 23% greater than the control sample 1.1 (Table 1). This is because boric acid, when impregnated, can interact with alkaline compounds in precipitating precursors such as zinc hydroxide to form zinc borate.



(1.1 – control sample)

Fig. 2: Effect of some mineralizers on luminescence

Table 1. Relative PL efficiency of samples 1.1 – 1.5, sintered at 900 °C for 45 minutes with various mineralizers (3.0 mol%).

Sample	Mineralizer	Relative PL efficiency	Melting point (°C)
1.1	---	1.00	---
1.2	Na_2CO_3	0.87	851 (Thieme, 2005)
1.3	Na_2SO_4	0.77	884 (Plessen *et al.* 2005)
1.4	H_3BO_3	1.23	170.9* (Robert 2005)
1.5	NaCl	1.05	801 (Westphal *et al.* 2005)

**heated in a closed space*

In addition, due to having the lowest melting point and similarity in properties between B^{3+} and Si^{4+} ions (diagonal similarity in the periodic table), boric acid has the best effect of promoting the reaction between the components to produce the desired luminescent product. Unlike the sample with added NaCl, the samples with Na_2CO_3 and Na_2SO_4 had lower luminescence than the control sample. This result is because the CO_3^{2-} and SO_4^{2-} ions are incompatible with the zinc orthosilicate network, so they function as impurities that strongly reduce luminescence performance (Table 1).

Effect of H_3BO_3 3.0 mol% and Some Organic Acids on Luminescence

From the results shown in previous section, precursors were prepared by impregnation - coprecipitation method with the Mn content of 3.0 mol%, H_3BO_3 of 3.0 mol%, without and with the addition of acetic, oxalic, citric or ascorbic acid with a content of 3.0 mol% (mol% per mol of the phosphor). Samples are denoted as 2.1 to 2.5, respectively (sample 2.1 is also sample 1.4). The precursor samples were then heated at 900 °C for 45 min. The effect of H_3BO_3 (3.0 mol%) and organic acids on the luminescence efficiency of the samples after calcination is shown in Figure 3.

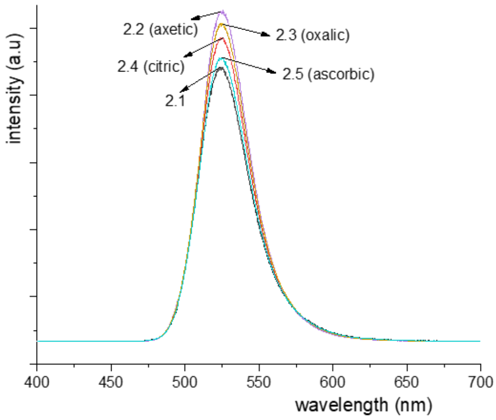


Fig. 3: Effect of H_3BO_3 (3.0 mol%) and some organic acids on luminescence (2.1 – control sample)

Organic acids can interact with alkaline compounds, such as zinc hydroxide in the precipitated precursor, and form the corresponding salts. According to Figure 3, all organic acids-impregnated samples after calcination have higher luminescence than the control sample 2.1. This result is because when heated, organic acid salts decompose and release gases that reduce and limit air oxygen diffusion to the sample's surface, making it more difficult for Mn^{2+} ions to be oxidized. Among the surveyed acids, sample 2.2, impregnated with 3.0 mol% H_3BO_3 and 3.0 mol% acetic acid, had the highest luminescence compared to the remaining acids and was 19% higher than that of the control sample 2.1 or 1.4 (impregnated with 3.0 mol% H_3BO_3). The reason is probably stronger and more soluble, so the impregnation effect is better.

Effect of H_3BO_3 3.0 mol% and Acetic Acid Content on Luminescence

From the results shown in previous sections, precursors samples were prepared by impregnation - coprecipitation method with the Mn content of 3.0 mol%, H_3BO_3 of 3.0 mol%, adding acetic acid with the content from 0, 1.0, 2.0, 3.0, 4.0 and 5.0 mol%. Samples are denoted as 3.1 to 3.6, respectively (sample 3.4 is also sample 2.2). The precursor samples were then heated at 900 °C for 45 min. The effect of H_3BO_3 (3.0 mol%) and acetic acid content on the luminescence efficiency of the samples after calcination is shown in Figure 4.

As mentioned before, acetic acid interacts with zinc hydroxide present in the precursor to form zinc acetate. The acetate ions can act as reducing agents during sintering as they can react with atmospheric oxygen and thus potentially increase the stability of the Mn^{2+} ion during synthesis (Equation 6). However, the formation of soluble zinc acetate reduces the degree of aging of the precipitated precursor and thus reduces the crystallinity or luminescence efficiency of the sample after calcination. From Figure 4, luminescence increases when the acetic acid content increases from 0 to 3.0 mol% due to reduced acetate anions' increased content. The decrease in luminescence when the acetic acid content increases from 3.0 to 5.0 mol% is due to a decrease in the aging degree of the precipitated precursor. Sample 3.4 or sample 2.2, impregnated with 3.0 mol% H_3BO_3 and 3.0 mol% acetic acid, showed the highest luminescence.

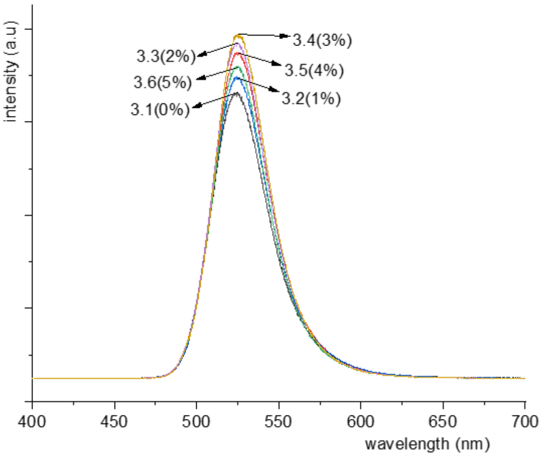


Fig. 4: Effect of H_3BO_3 (3.0 mol%) and acetic acid content on luminescence (3.1 – control sample)

$$Zn(CH_3COO)_2(s) + 4\ O_2(air) \rightarrow ZnO(s) + 4\ CO_2(k) + 3\ H_2O(k) \qquad (6)$$

Effect of Acetic Acid (3.0 mol%) and Boric Acid Content on Luminescence

From the results shown in previous sections, precursor samples were then prepared by impregnation - coprecipitation method with the Mn content of 3.0 mol%, acetic acid of 3.0 mol% and change the content of H_3BO_3 from 0 – 5.0 mol%. Samples are denoted as 4.1 to 4.5, respectively (sample 4.4 is also sample 3.4 or sample 2.2). The precursor samples were then heated at 900 °C for 45 min. From Figure 5, when the content of H_3BO_3, acting as a mineralizer, increases from 0 to 3.0 mol%, the luminescence of the sample increases. However, with content greater than 3.0 mol%, H_3BO_3 acts as an impurity and thus reduces luminescence. Sample 4.4 (3.0%) has a luminescence intensity of 35% higher than control sample 4.1 (0%).

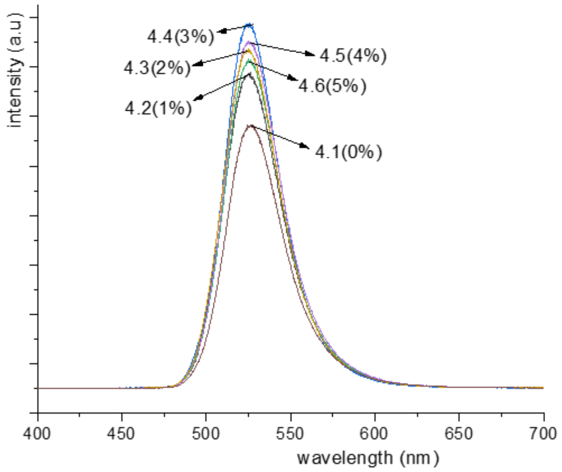


Fig. 5: Effect of acetic acid (3.0 mol%) and H_3BO_3 content on luminescence (4.1 – control sample)

Effect of Calcination Temperature on the Structure and Luminescence

From the results shown in previous sections, precursor samples were prepared by impregnation - coprecipitation method with the content of Mn, acetic acid, and H_3BO_3 being 3.0 mol% per mol of the phosphor (marked as sample 5). The precursor sample were then heated at different temperatures: 700 °C, 800 °C, 850 °C, and 900 °C for 45 minutes, and the samples after firing are denoted as 5(700), 5(800), 5(850), and 5(900) respectively (sample 5(900) is also sample 4.4, sample 3.4 or sample 2.2, sintered at 900 °C for 45 minutes). The X-ray diffraction patterns, crystallite sizes by Scherrer, crystal structure, and PL spectra of the samples after calcination are shown in Figure 6, Table 2, Figure 7, and Figure 8, respectively. For comparison, the relative PL efficiency of samples 1.1, 1.4, and 5(900), sintered at 900 °C for 45 minutes, is mentioned in Table 3.

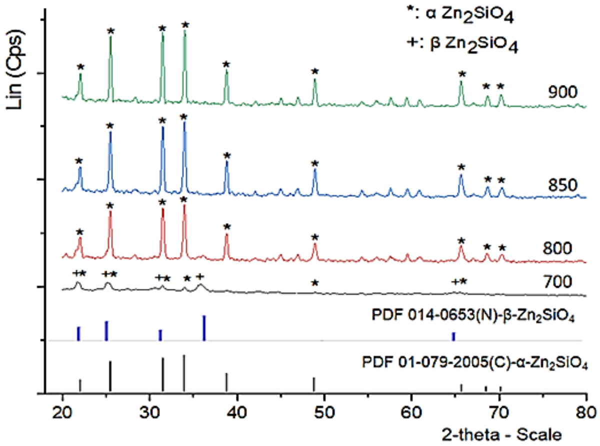


Fig. 6: XRD patterns of samples 5(700) – 5(900).

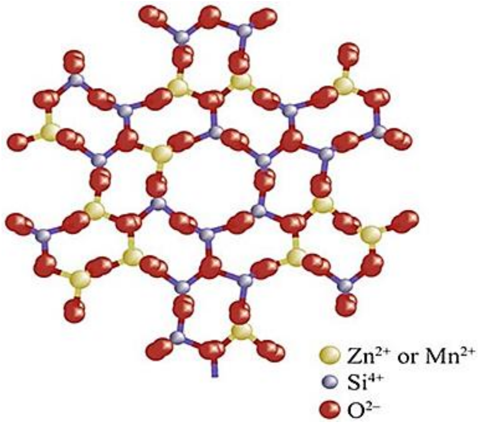


Fig. 7. Crystalline structure of α-Zn_2SiO_4

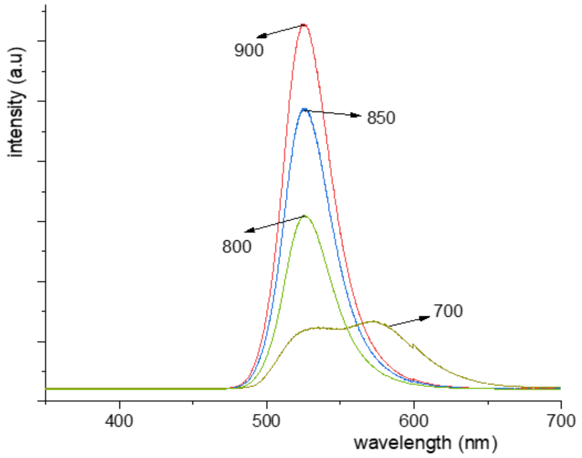


Fig. 8: PL spectra of samples 5(700) – 5(900).

Table 2. Crystallite sizes (G, in nm) of samples 5(700) – 5(900).

Samples	2θ (degree)[(a)]	B (degree)	G (nm)
5(700)	25.13	0.458	17.78
5(800)	33.953	0.317	26.20
5(850)	33.968	0.293	28.35
5(900)	33.996	0.283	29.35

(a) major diffraction peak

Table 3. Relative PL efficiency of samples 1.1, 1.4 and 5(900), sintered at 900 °C for 45 minutes.

Calcined sample	Mineralizer	Organic acids	Relative PL efficiency
1.1	--	--	1.00
1.4	H_3BO_3 (3.0 mol%)	--	1.23
5(900)	H_3BO_3 (3.0 mol%)	CH_3COOH (3.0 mol%)	1.46

Zn_2SiO_4 is polymorphic and may exist in the α, β, and other phases (Takesue *et al.*, 2009). The β-phase is meta-stable and transforms to the α-phase at elevated temperatures (Rivera-Enríquez *et al.*, 2016, Samigullina *et al.*, 2020; Kang *et al.*, 2021). From Figure 6, the sample calcined at 700 °C is a bi-phase mixture of β-Zn_2SiO_4 and α-Zn_2SiO_4. Consistent with the results mentioned by Taylor (1962) and Rivera-Enríquez *et al.* (2016), the obtained β-Zn_2SiO_4 has orthorhombic structure with a = 8.40000, b = 5.10000, c = 32.20000 Å, α = β = γ = 90° - JCPDS 00-014-0653(N). And the samples calcined at 800 °C, 850 °C, and 900 °C contain only one α-Zn_2SiO_4 phase with rhombo H. axes structure, a = b = 13.94800 Å, c = 9.31500 Å, α = β = 90°, γ = 120° - JCPDS 0 01-079-2005(C). No XRD peaks from other phases of Zn_2SiO_4 or impurities were detected, indicating the high purity of obtained crystals (Tripathi *et al.*, 2021). According to Lukic´ *et al.*, 2008 or Takesue *et al.*, 2009, the crystal structure of manganese-doped zinc orthosilicate luminescent material based on α-Zn_2SiO_4 (willemite) is shown in Figure 7, in which Zn and Si are both tetrahedrally coordinated with O, forming ZnO_4 and SiO_4 tetrahedra as the building blocks (Dai *et al.*, 2022) and Mn^{2+} ions with a radius of 0.80 Å (close to the radius of Zn^{2+} 0.74 Å) also occupy tetrahedral sites in the willemite structure and act as activating centers. As mentioned above, boric acid, when impregnated, can interact with zinc hydroxide to form zinc borate. Due to the similarity in properties, B^{3+} ions can enter the zinc silicate network to replace Si^{4+} ions when sintering. According to the document (Völz *et al.*, 2006), in stable lattices, even if some sites in the unit cell are unoccupied, substances with different formulae can form solid solutions (anomalous mixed crystals). From the above statement, the samples calcined at 800 °C to 900 °C are single-phase zinc manganese borosilicate solid solutions with the structure of α-Zn_2SiO_4. Figure 7 allows us to visualize the structure of the obtained material. Based on the molar ratio of the components in the precipitated precursor after impregnating, the composition of the obtained phosphors can be written in oxides as $1.97ZnO.\ 0.03MnO\ .\ 0.015B_2O_3\ .\ SiO_2$. The results show a transition from the β-Zn_2SiO_4 phase to the α-Zn_2SiO_4 phase at 800 °C. According to Taylor (1962), this transformation was caused by a rearrangement of atoms. Compared with the results mentioned by Samigullina *et al.* (2020), where the metastable β-Zn_2SiO_4 phase undergoes a transition to α-Zn_2SiO_4 at 873 °C, boric acid here with a content of 3.0 mol% acts as a mineralizer, promoting the formation of the α-Zn_2SiO_4 phase at lower temperatures.

From Figure 8 and consistent with the

XRD results, the sample calcined at 700 °C emits a yellow band peaking at 575 nm (Mir *et al.*, 2015: Ye *et al.*, 2013), corresponding to orthorhombic β-Zn_2SiO_4 (Ye *et al.*, 2013). The samples calcined at 800 °C to 900 °C, emitting green light at 525 nm, corresponding to rhomboid H.axes α-Zn_2SiO_4. All these emitted lights correspond to the $^4T_1(^4G)$–$^6A_1(^6S)$ transition of the Mn^{2+} ion in different crystal fields (Bertail *et al.*, 2011; Mir *et al.*, 2015; Takesue *et al.*, 2009). Consistent with the increase in crystallite size (Table 2), the luminescence of the samples increased with the calcination temperature. Under the sintering conditions at 900 °C for 45 minutes, sample 5(900) luminescence efficiency was 46% greater than the control sample 1.1 (Table 3). Compared with the results mentioned in the documents (Parmar *et al.*, 2009; Krasnenko *et al.*, 2020a, 2020b; Kim *et al.*, 2010; Vien *et al.*, 2019) or in the documents (Samigullina *et al.*, 2022; Bharti *et al.*, 2023), the single-phase 5(900) product obtained at significantly lower firing temperature and time. For example, according to Samigullina *et al.* 2022, using the solid-state method from ZnO, SiO_2, and Mn_2O_3, the sample after heating at 900°C is a mixture of willemite Zn_2SiO_4 and heterolite and at about 1250 °C, this heterophase mixture forms the final single-phase product - the Zn_2SiO_4:Mn phosphor. According to Bharti *et al.*, 2023, monophase α-Zn_2SiO_4 material was formed by the sol-gel method when the resulting gel was heated at 1000 °C for 6 h. In addition to the high luminescence intensity, the single-phase 5(900) product synthesized at 900°C is easily dispersed in the media when used as a luminescent pigment.

EDS Analysis and SEM Image

The composition of the highest luminescent 5(900) sample was checked according to the EDS method. As shown in Figure 9, EDS analysis did not detect boron (B) in the sample because of the limitation of detector sensitivity (Liao, 2007) or according to the literature (Bengisu, 2001), EDS spectrometers can detect elements with atomic numbers as low as 5 (B) only if windowless detectors and high-quality vacuum systems are used. However, the results in Table 4 also show a good agreement between the calculated sample composition based on the ratio of components when synthesized and tested by the EDS method.

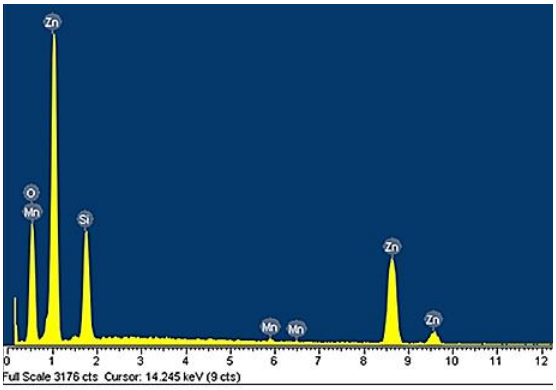


Fig. 9: EDS spectrum of sample 5(900).

Table 4. Composition of sample 5(900) by EDS and by calculations

Element	Weight %	
	By EDS	By calculations
O	29.04	29.05
Si	13.22	12.57
Mn	0.72	0.74
Zn	57.02	57.49
B	----	0.15
Total	100	100

The morphology and particle size of sample 5(900) are shown in Figure 10. Since polycrystalline particles are made up of several crystallites with identical structure but different orientations (Schaffer *et al.*, 1999), the obtained product consists of spheroidal and relatively uniform particles with sizes of about 0.3-0.5 µm (Figure 10), much larger than its crystallite size calculated from X-ray diffraction data (Table 2). Besides phase purity and crystallinity, particle size and morphology affect luminescence efficiency. Morphologically, due to being more favorable in terms of energy, spherical particles tend to form the coating with the highest closed packing factor (74%), for example, in a close-packed hexagonal arrangement: one particle is in contact with six ones in the same plane, three on the upper and three on the under plane (Schaffer *et al.*, 1999). Fine particles with a size of 0.1 to 1.0 µm have very high hiding power, and this hiding capacity decreases as the particle size increases (Buxbaum *et al.* 2005). According to the results shown by Cho *et al.* (2003), the Zn_2SiO_4:Mn phosphor prepared by the solution reaction method at 1200 °C includes spherical particles with a size of about 0.5–1.0 µm, which has a higher luminescence efficiency than the sample prepared by solid phase reaction method at 1400 °C, consisting of rectangular particles with size about 1–2 µm. The product 5(900), with high phase purity and crystallinity, has suitable morphology and particle size for application as a luminescent pigment.

Initial Testing on Water-Based Fluorescent Ink

Luminescent pigments are widely used in the fields of security or anticounterfeiting (Yu *et al.*, 2021; Nguyen *et al.*, 2024). The water-based fluorescent ink was prepared as described in the experimental section with the luminescent pigment used as sample 5(900). The ink is printed on paper under normal conditions, using a screen printing mold covered with diazo adhesive film with a resolution of 160 lines/cm. The results are shown in Figure 11. From Figure 11, under normal light, it is difficult to detect the printed pattern (Figure 11a), and the pattern emits green light when exposed to a 254 nm UV lamp. This result shows that the synthesized luminescent pigment can be applied in the production of fluorescent ink for use in security or anti-counterfeiting.

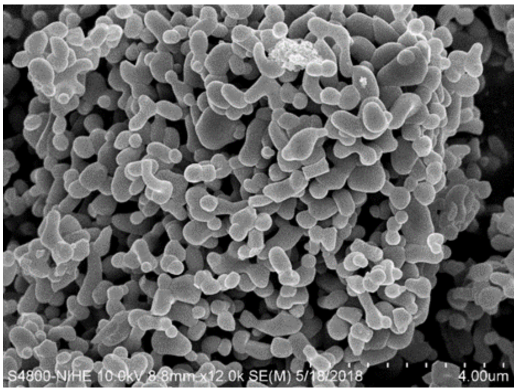
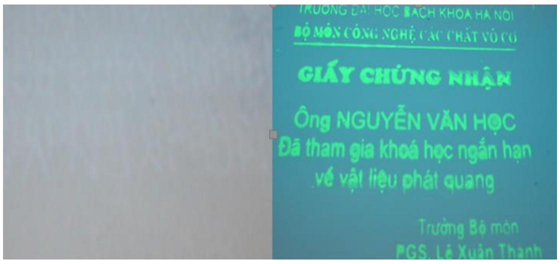


Fig. 10: SEM image of sample 5(900).



TRƯỜNG ĐẠI HỌC BÁCH KHOA HÀ NỘI
BỘ MÔN CÔNG NGHỆ CÁC CHẤT VÔ CƠ

GIẤY CHỨNG NHẬN

Ông NGUYỄN VĂN HỌC
Đã tham gia khoá học ngắn hạn
về vật liệu phát quang

Trưởng Bộ môn
PGS. Lê Xuân Thành

(a) (b)

Fig. 11: Paper sample printed with fluorescent ink: (a) sample observed under daylight, (b) emitting green light when exposed to 254 nm UV lamp.

CONCLUSIONS

By impregnation - coprecipitation method, in the organic acids and mineralizers surveyed, based on the solubility or similarity in properties with Si^{4+} ions, acetic and boric acid with the ratio in the precipitated precursor such as 1.97 Zn : 0.03 Mn : 1.0 SiO_2 : 0.03 H_3BO_3 : 0.03 CH_3COOH (sample 5), has the best effect on increasing the luminescence intensity of the product after calcination compared to that of the control sample. The sample calcined at 700 °C for 45 min, emitting yellow light at 575 nm when excited by 254 nm UV radiation, was a bi-mixture of β-Zn_2SiO_4 and α-Zn_2SiO_4. Boric acid is the mineralizer for α-Zn_2SiO_4. At 800 °C, there is a phase transition from the orthorhombic β-Zn_2SiO_4 to the rhombo H.axes α-Zn_2SiO_4 and samples calcined from 800 °C to 900 °C emitting green light at 525 nm, were single-phase zinc manganese borosilicate solid solution with rhombo H. axes structure of α-Zn_2SiO_4. The sample calcined at 900 °C for 45 minutes has a luminescence efficiency of 46% higher than that of the control sample. It consists of fairly uniform spherical particles with a size of around 0.3-0.5 µm. The obtained luminescent pigment has potential for use in security applications. Compared with the solid-phase reaction method, the single-phase phosphors are synthesized at significantly lower temperatures and time and aremore energy-efficient.

REFERENCES

Bengisu, M. (Ed.), 2001. Engineering Ceramics. Springer-Verlag Berlin Heidelberg GmbH , New York. 395.

Bertail, C., Maron, S., Buissette, V., Mercier, T. L., Gacoin, T., and Boilot, J.-P., 2011. "Structural and photoluminescent properties of Zn_2SiO_4:Mn^{2+} nanoparticles prepared by a protected annealing process." *Chem. Mater. 23*, 2961–2967.

Bharti, D. K., Verma, R., Rani, S., Agarwal, D., Mehra, S., Gangwar, A. K., Gupta, B. K., Singh, N., and Srivastava., A. K., 2023. "Synthesis and characterization of highly crystalline bi-functional Mn-doped Zn_2SiO_4 nanostructures by low-cost sol–gel process." *Nanomater. 13*, 538.

Buxbaum, G. and Pfaff, G., 2005. Industrial Inorganic Pigments. Buxbaum, G. and Pfaff, G., ed., Willey-VCH, Germany, 262.

Cavourasa, D., Kandarakisa, I., Nomicosb, C.D., Panayiotakisc, G.S., Fezoulidisd, I., 2000. "Assessing the information content of phosphor produced medical images: application to Zn_2SiO_4:Mn phosphor." *Appl. Radiat. Isot. 52*, 119–126.

Cho, T.H., Chang, H.J., 2003. "Preparation and characterizations of Zn_2SiO_4:Mn green phosphors." *Ceram. Int. 29*, 611–618.

Cich, M., Kim, K., Choi, H., Hwang, S.T., 1998. "Deposition of $(Zn,Mn)_2SiO_4$ for plasma display panels using charged liquid cluster beam." *Appl. Phys. Lett. 73*, 2116–2118.

Dai, R; Cheng, R; Wang, J; Zhang, C; Li, C; Wang, H; Wang, X; 2022. "Tunnel-structured willemite Zn_2SiO_4: Electronic structure, elastic, and thermal properties Article." *J. Adv. Ceram. 11(8)*, 1249–1262

Eppler, R. A., 2005. Ceramic Colorants, in: Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH, Germany, 10.

Ghoul, J. E., All, N. A., 2020. "Synthesis and characterization of Mn^{+2}-doped zinc silicate as potential green nanophosphor materials." *Indian J. Phys. 94*, 1343–1350.

Haha, M. B., Bullerjahn, F., Schmitt, D., Spencer, N., Tebbe, M., 2015. Patent. AU2014317427B2.

Kang, T., Kang. H., Park, S., Deressa, G., Park, J., Kim, J., 2021. "Critical synthesis parameters of β-phase Zn_2SiO_4:Mn^{2+} phosphor and its metastability." *Mater. Today Commun. 26*, 101798

Kim, Y.-Il, Im, W. B., Ryu, K.-S., Kim, K.-B., Lee, Y.-H., Lee, J. S., 2010. "Combined Rietveld refinement of Zn_2SiO_4:Mn^{2+} using X-ray and neutron powder diffraction data." *NIMPB 268*, 346–351.

Krasnenko, T. I., Zaitseva, N. A., Ivanova, I. V., Baklanova, I. V., Samigullina, R. F., and Rotermel, M. V., 2020a. "The effect of Mg introduction on structural and luminescence properties of Zn_2SiO_4:Mn phosphor." *J. Alloys Compd. 845*, 156296.

Krasnenko, T. I., Enyashin, A. N., Zaitseva, N. A., Samigullina, R. F., Tyutyunnik, A. P., Baklanova, I. V., Rotermel, M. V., Onufrieva, T. A., 2020b. "Structural and chemical mechanism underlying formation of Zn_2SiO_4:Mn crystalline phosphor properties." *J. Alloys Compd. 820*, 153129.

Liao, Y., 2007. Practical Electron Microscopy and Database. GlobalSino, 1381.

Lukic´,S.R., Petrovic´, D.M., Dramic´anin, M.D., Mitric´, M. and Đacˇanin, Lj., 2008 "Optical and structural properties of Zn_2SiO_4:Mn^{2+} green phosphor nanoparticles obtained by a polymer-assisted sol–gel method." *Scr. Mater. 58*, 655–658

Mir, L. E., Omri, K., Ghou, J. E., 2015. "Effect of crystallographic phase on green and yellow emissions in Mn-doped zinc silicate nanoparticles incorporated in silica host matrix." *Superlattices Microstruct. 85*, 180–184.

Morell, A., El Khiati, N., 1993. "Green phosphors for large plasma TV screens." *J. Electrochem. Soc. 140*, 2019–2022.

Nguyen, T. P., Dang, H. P. Nguyen, L. G., Le, C. D., 2024 "Synthesis of ZnO nanoparticles-based fluorescent ink for information encryption and security applications". *Opt. Mater. 157* 116296

Parmar, M. C., Zhuang, W. D., Murthy, K.V.R., Huang, X. W., Hu, Y. S., Natarajan, V., 2009. "Role of SiO_2 in Zn_2SiO_4:Mn^{2+} phosphor used in optoelectronic material." *Indian J. Eng. Maters. 16*, 185-187.

Plessen, H. v., Aktiengesellschaft, H., Frankfurt/Main, 2005. Sodium Sulfates, in: Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH, Germany, 2.

Rakova, N., Matiasa, F., Xingb, Y., Macielb, G. S., 2024. "Mn^{2+}doped Zn_2SiO_4 phosphors: A threefold-mode sensing approach for optical thermometry in the visible region at 525 nm." *Opt. Mater. X 24*, 100359

Rivera-Enríquez, C.E., Fernández-Osorio, A., Chávez-Fernández, J., 2016. "Luminescence properties of α- and β-Zn_2SiO_4:Mn nanoparticles prepared by a co-precipitation method." *J. Alloys Compd. 688* Part B, 775–782.

Samigullina, R. F., Krasnenko, T. I., 2020. "Thermal analysis and mechanism of formation of Zn_2SiO_4:Mn phosphor under heating of synthetic hemimorphite." *Mater Res Bull. 129*, 110890.

Samigullina, R. F., Ivanova, I. V., Zaitseva, N. A., Krasnenko, T. I., 2022. "Solid-state synthesis of the Zn_2SiO_4:Mn phosphor: Sequence of phase formation, localization and charge state of Mn ions in the intermediate and final reaction products." *Opt. Mater.132*,112788.

Schaffer, J. P.,Saxena A., Antolovich, S. D., Sanders, Jr. T. H., Warner, S. E., 1999. The science and design of engineering materials. McGraw–Hill International, Singapore, pp.82-84, 95-96.

Sivakumar, V., Lakshmanan, A., Kalpana, S., Rani, R. S., Kumar, R. S., and Jose, M. T., 2012. "Low-temperature synthesis of Zn_2SiO_4:Mn green photoluminescence phosphor." *J. Lumin. 132*, 1917–1920.

Sivakumar, V., Lakshmanan, A., 2014. "Pyrolysis synthesis of Zn_2SiO_4:Mn^{2+} phosphors - effect of fuel, flux and co-dopants." *J. Lumin. 145*, 420–424.

Smith, R. A., 2005. Boric Oxide, Boric Acid, and Borates, in: Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH, Germany, pp. 3-4.

Sohn, K.-S., Cho, B., Chang, H., and Park, H. D., 1999. "Effect of co-doping on the Photoluminescence Behavior of Zn_2SiO_4:Mn Phosphors." *J. Electrochem. Soc. 146*, 2353–2356.

Sohn, K.-S., Cho, B., Park, H. D., Choi, Y. G., Kim, K. H., 2000. "Effect of heat treatment on photoluminescence behavior of Zn_2SiO_4:Mn phosphors." *J. Eur. Ceram. Soc. 20*, 1043–1051.

Takesue, M., Hayashi, H., Smith Jr., R. L., 2009. "Thermal and chemical methods for producing zinc silicate (willemite): A review." *Prog. Cryst. Growth Charact. Mater. 55*, 98–124.

Taylor, H.F.W., 1962. "The dehydration of hemimorphite." *Am. Mineral. 47*, 932–944.

Thanh, N. T., Ha, P. T., Quang, N. V., Thanh, L. X., 2021. "A novel approach to the preparation of manganese - doped zinc silicate luminescent material according to the precipitation method." *Vietnam J. Catal. Adsorpt. 3*, 40-46.

Thieme, C., 2005. Sodium Carbonates, in: Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH, Germany, p.3,16.

Tripathi N. and Akai T., 2021. "Structural designing of Zn_2SiO_4:Mn nanocrystals by co-doping of alkali metal ions in mesoporous silica channels for enhanced emission efficiency with short decay time. *RSC Adv. 11*, 36348

Vien, L. T. T., Tu, N., Phuong, T. T., Tuan, N. T., Quang, N. V., Bui, H. V., Duong, A.-T., Trung, D. Q., Huy, P. T., 2019. "Facile synthesis of single phase α-Zn_2SiO_4:Mn^{2+} phosphor via high-energy planetary ball milling and post-annealing method." *J. Lumin. 215*, 116612.

Viswanathan, V. N. and Ghosh, S. N., 1983. Mineralizers and Fluxes in Clinkerization, in: Advances in Cement Technology, Ghosh, S. N., ed., Elsevier Ltd, pp.177-202.

Völz, H. G., Kischkewitz, J. *et al.*, 2006. Pigments, Inorganic, in: Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH, Germany, pp.29,38.

Wang, C., Wang J., Jiang J., Xin S., Zhu G., 2020. "Redesign and manually control the commercial plasma green Zn_2SiO_4:Mn^{2+} phosphor with high quantum efficiency for white light emitting diodes." *J. Alloys Compd. 814*, 152340.

Westphal, G., Kristen G., Wegener, W., Ambatiello, P., Geyer, H., Epron, B., Bonal, C., Steinhauser, G., 2005. Sodium Chloride, in: Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH, Germany

Ye, R., Ma, H., Zhang, C., Gao, Y., Hua, Y., Deng, D., Liu, P., Xu, S., 2013. "Luminescence properties and energy transfer mechanism of Ce^{3+}/Mn^{2+} co-doped transparent glass - ceramics containing β-Zn_2SiO_4 nano - crystals for white light emission." *J. Alloys Compd. 566*, 73–77.

Yen, W. M., Shionoya, S., Yamamoto, H., 2006. Practical Applications of Phosphors. Yen, W. M., Shionoya, S., Yamamoto, H., ed., CRC Press, New York, pp.131-133, 257–258.

Yoshizawa, K., Katoa, H. and Kakihana, M., 2012. "Synthesis of Zn_2SiO_4:Mn^{2+} by homogeneous precipitation using propylene glycol-modified silane." *J. Mater. Chem. 22*, 17272–17277.

Yu, X., Zhang, H., Yu, J., 2021. "Luminescence anti-counterfeiting: From elementary to advanced." *Agg. 2,* 20–34.