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RESEARCH ARTICLE

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Preparation and properties of luminous materials of $CaSiO_3:Pb$, Mn by sol-gel method

Abstract The luminous materials of $CaSiO_3:Pb$, Mn were synthesized by sol-gel method and ultrasound technology. The properties of the phosphors were characterized by luminescence spectrum, differential thermal analysis and thermal gravimetry analysis (DTA-TG), X-ray diffraction (XRD), Fourier transform infrared spectrometer (FT-IR) and transmission electron microscopy (TEM). The effects of factors such as the synthetic material compositions, ultrasound time and annealed temperature on phosphorescent brightness of sample were studied and the optimum synthetic conditions were determined. The results show that, compared with the sample made by the high temperature solid-state reaction, the luminescent intensity of the $CaSiO_3:Pb$, Mn sample increased by about 200% and the mean diameter of particles of the sample decreased by about 300 nm.

Keywords sol-gel method; ultrasound; luminescent materials; $CaSiO_3:Pb$, Mn

1 Introduction

$CaSiO_3$ phosphor has excellent chemical stability and thermal stability, and it is one of the promising host luminescent materials [1,2]. $CaSiO_3:Pb$, Mn is just one kind of photoluminescence and cathode-ray luminescence phosphors. Because the price of raw material is low, and the capability of production is stable, it has been widely used [3,4]. At present, the sample is often made by the high temperature solid-state reaction, by which the diameter of particles is bigger and the luminescence intensity is not high.

Sol-gel is a soft chemical synthesis method. The reaction begins from solution, in which the proportion of components can be easily controlled, the synthesis temperature is low, and the impurity introduction is avoided, so the purity of the sample can be guaranteed, and the uniformity can reach to molecule and atom size. It is effective for the synthesis of nano-functional material [5–7]. Ultrasound technology as an assistant method for material preparation has been gradually regarded [8,9]. Using the ultrasonic cavitation role, i.e. the physical and chemical effect produced from the vibration, growth, shrinkage and breakdown of the micro air bubble in the solution under the acoustic field, which can accelerate the material transfer and heat conduction, and the reunite of nano-particles can be removed, the capability of material can also be improved.

There are so many advantages in the above two methods, so the $CaSiO_3:Pb$, Mn phosphors were synthesized by sol-gel method combined with ultrasound technology. Through research on the relationship between the synthesis conditions and luminescence properties, the optimum conditions are obtained. The particles prepared are small with the relatively strong luminescent intensity compared with the sample made by the high temperature solid-state reaction.

2 Experimental

Sol-gel preparation: the raw materials of $Ca(NO_3)_2$ (A.R), $Pb(NO_3)_2$ (A.R) and $Mn(NO_3)_2$ (A.R) were exactly weighed according to a certain stoichiometric ration, and the proper nitric acid and deionized water was added. Stirring makes these materials dissolved and its solution was poured into sol which is prepared by 380 SiO_2 aerosol and ethanol. Then, it was placed in an ultrasonic instrument (the power is 45 W) with a water temperature of 45°C, and ultrasonic reaction after different time lengths. The phosphor precursor was obtained after the gel had been dried at 110°C for about 4 h, and put into corundum crucible, then annealed it under CO reducing atmosphere with different temperatures. At last, the sample was cooled, grinded and put into desiccator for future use.

For comparison, the sample was also made by the high temperature solid-state reaction: the raw materials of $Ca(NO_3)_2$

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(A.R), $Pb(NO_3)_2$ (A.R) and $Mn(NO_3)_2$ (A.R) were exactly weighed according to a certain stoichiometric ration. These materials were annealed at 900°C under CO reducing atmosphere, and then annealed again at 1,200°C for about 4 h. At last, the sample was cooled, grinded and put into desiccator for future use.

The phase and crystal structure of the prepared particles were examined by X-ray diffraction (XRD) measurement performed on a Rigaku-D/MAXIIIB diffractometer with monochromatic Cu-Kα radiation (wavelength $\lambda = 1.540\ 56$ Å). The crystallization behavior was also monitored by using a SHIMADZU DTG-60H differential thermal analysis and thermogravimetric analysis (DTA-TG) instrument. The photoluminescence properties of the particles were measured by a Varian Cary-Eclipse 500 spectrofluorimeter equipped with a 60 W xenon lamp as the excitation source (slit = 5 nm). The Fourier transform infrared spectrometer (FT-IR) absorption spectrum of a sample dispersed in a KBr disk was measured by a Nicolet Avatar 370 DTGS spectrometer. The morphology and particle size of the samples were investigated by using a JEOL JEM-100CXII transmission electron microscopy (TEM).

3 Results and discussion

3.1 Optimal materials ration

The emission spectra of $CaSiO_3:Pb$, Mn phosphors excited at 254 nm is shown in Fig. 1. It contains two main emission peaks corresponding to the characteristic emission of Pb^{2+} at 350 nm and the characteristic emission of Mn^{2+} ($^4T_1$-$^6A_1$ transitions) at 650 nm. Because the excitation transition is parity forbidden but spin allowed, and Mn^{2+} can not absorb energy effectively, but it can be excited by the energy which is released by the dipole allowed transition of Pb^{2+} [10]. The different materials ration has big influence on the luminescent intensity, so the ultrasonic time of sol-gel preparation and calcined condition (first calcined at 900°C for about 2 h, then calcined again at 1,200°C for about 4 h) was fixed, and the influence of the different materials ration on the emission intensity of visible region (650 nm) was investigated in Table 1. With the increase in the mol concentration of Pb^{2+}, the red emission intensity of Mn^{2+} was increased, and as the mol concentration of Pb^{2+} reached 0.025, the emission intensity was the strongest. However, as the mol concentration of Pb^{2+} was further increased, the emission intensity was decreasing. Therefore, the optimal mol concentration of Pb^{2+} is 0.025.

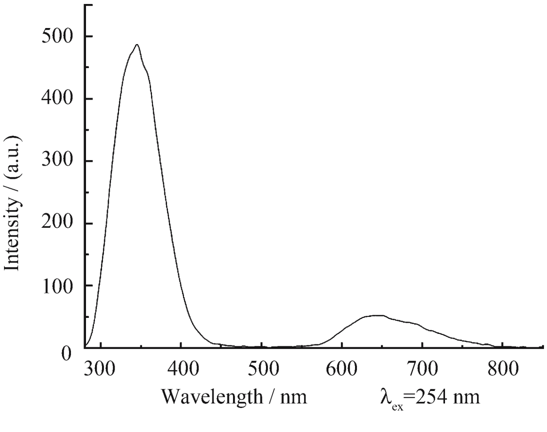

Fig. 1 Emission spectrum of $CaSiO_3:Pb$, Mn

Table 1 Influences of Pb^{2+} concentration on the emission intensities of $CaSiO_3(0.7):Pb(x)$, Mn(0.033)

x	0.015	0.025	0.035	0.045
Relative emission intensity at 650 nm /%	19	100	96	94

The $CaSiO_3:Pb$, Mn phosphors with host material of β-$CaSiO_3$ have stronger emission intensity than that of α-$CaSiO_3$ [1], which is approved by our experiment. In addition, as the raw material of SiO_2 is properly superfluous by changing the proportion of $Ca^{2+}:Si^{4+}$, the emission intensity of the phosphors can be increased. When the mol ration of $Ca^{2+}:Si^{4+}$ was 0.7 : 1.3, the emission intensity was the strongest, but as the proportion was further increased, the emission intensity was reduced, which is shown in Table 2. The reason may be that the properly superfluous SiO_2 can advance the formation and stabilization of the structure of β-$CaSiO_3$ [11], so the emission intensity of the sample was increased. However, once the proportion of SiO_2 was overabundant, the concentration of the emission center ion was diluted, and the excitation of Pb^{2+} by absorbing ultraviolet radiation was also influenced, so the emission intensity was reduced.

Table 2 Effects of $n(Ca^{2+}):n(Si^{4+})$ on fluorescent intensity

$n(Ca^{2+}):n(Si^{4+})$	0.7 : 0.7	0.7 : 1.0	0.7 : 1.3	0.7 : 1.6
Relative emission intensity at 650 nm /%	28	66	100	96

Accordingly, the results of experiments showed that the optimal mol ration of $Ca(NO_3)_2$, SiO_2, $Pb(NO_3)_2$ and $Mn(NO_3)_2$ is 0.7 : 1.3 : 0.025 : 0.033.

3.2 Optimal ultrasound time

When the sample is prepared by sol-gel method combined with ultrasound technology, the process of polycondensation, nucleation and crystal growth can be promoted or changed. If the ultrasonic time is short, the ultrasound cavitation effect can not be played. If the ultrasonic time is long, the particle may be reunited afresh because of the exquisite physical chemistry effect. Therefore, the formation of sol-gel and the uniform distribution of Pb^{2+}, Mn^{2+} in gel are all influenced, and the emission intensity of the sample is weak. Table 3 shows that the samples with the ultrasound time of 2 or 3 h

Table 3 Influences of ultrasound time on emission intensity

	Ultrasound reaction				No ultrasound stir 2 h
t/h	1	2	3	4	
Relative emission intensity at 650 nm/%	4	98	100	7	65

had the strongest emission intensity in the visible region (at 650 nm), and the difference of that was very small, so the optimal ultrasound time is 2 h. Meanwhile, the sample with ultrasonic vibrating for 2 h has obviously stronger emission intensity than that of no ultrasound, which shows the superiority of the ultrasound technology.

3.3 Optimal calcination temperature

Figure 2 shows the DTA-TG curves of the precursor. The DTA endothermic peak at 101°C can be attributed to the evaporation of residual water and ethanol. The TG curve shows about 5.2% weight loss from room temperatur 36°C to 200°C corresponding to the endothermic DTA peaks. The big endothermic peak at 513°C on DTA curve, and the associated about 39.9% weight loss between 208°C and 843°C on TG curve is supposedly due to the decomposition of nitrate and the formation of unformed $CaSiO_3$. When the temperature is over 843°C, there is almost no weight loss, and a wide exothermic peak at 893°C is related to the crystallization from amorphism to β-$CaSiO_3$. Exothermic peak appeared after 1,200°C is attributed to the crystalline transformation from β-$CaSiO_3$ to α-$CaSiO_3$.

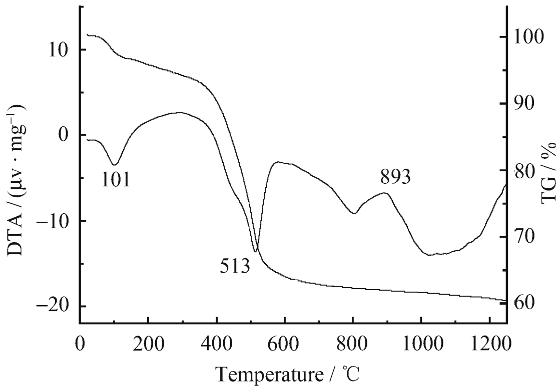

Fig. 2 DTA-TG curves of the precursor

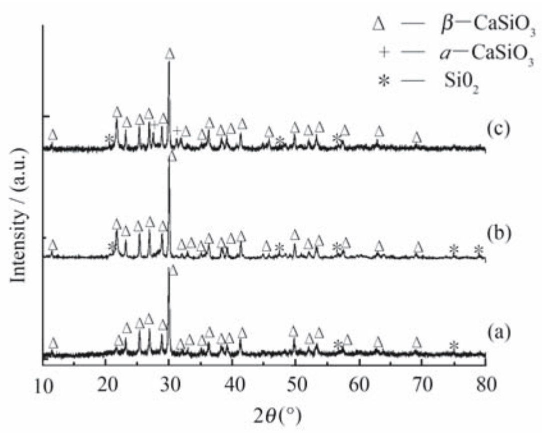

Fig. 3 XRD patterns of $CaSiO_3$: Pb, Mn calcined at different temperature
(a) 900°C, 2 h; (b) 900°C, 2 h + 1,200°C, 4 h; (c) 900°C, 2 h + 1,300°C, 4 h

Figure 3 presents the XRD patterns of $CaSiO_3$: Pb, Mn calcined at 900°C, 1,200°C and 1,300°C respectively. When the sample was calcined at 900°C, the crystalline phase of β-$CaSiO_3$ was observed, and the stronger diffraction peak appeared after calcining at 1,200°C. Further calcination at 1,300°C leads to the weaker diffraction peak and a little crystalline transformation from β-$CaSiO_3$ to α-$CaSiO_3$, which was consistent with the DTA-TG curves. Therefore, the calcination temperature between 900°C and 1,200°C is relatively proper.

Consequently, the sample was prepared with the optimal materials ration and 2 h under ultrasound, and first it was calcined at 900°C for 2 h, then was calcined again at different temperature for 4 h. Figure 4 shows the influence of the second calcination temperature on the emission intensity. With the increase in the second calcination temperature, the emission intensity increased and it reached the strongest as calcined at 1,200°C. However, as further calcined at 1,300°C, the emission intensity rapidly reduced. Because the color of the sample calcined at 1,300°C was turned from white to coffee, which indicated Mn^{2+} in the sample was partially oxidated. The XRD patterns and DTA-TG curves also show that there was a little quantity of β-$CaSiO_3$ turned to α-$CaSiO_3$, which made the emission intensity of the sample calcined at 1,300°C reduced.

Table 4 Influences of second annealed temperature on fluorescent intensity

T /°C	900	1,000	1,100	1,200	1,300
Relative emission intensity at 650 nm /%	29	73	85	100	11

3.4 IR spectra of the $CaSiO_3$: Pb, Mn

The IR spectrum presented in Fig. 4 shows the precursor (Fig. 4(a)) and the product calcined at 1,200°C (Fig. 4(b)) respectively. As shown in Fig. 4(a), a strong absorption band at 1,640 cm^{-1} shows the bending libration of −OH, and two weak absorption bands at 1,380 and 825 cm^{-1} can be attributed to the characteristic of NO_3^- in the IR spectra. Furthermore, the strong absorption bands at 1,090 and 470 cm^{-1} show the stretches and bending modes of Si−O−Si

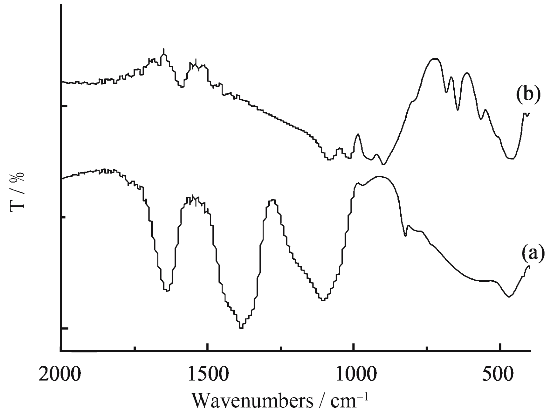

Fig. 4 IR spectra of the $CaSiO_3:Pb$, Mn
a) Precursor; b) Heat treated sample

bonds [12]. After being calcined at 1,200°C, as shown in Fig. 4(b), the characteristic absorption of OH and NO_3^- almost disappears, which indicates that the residual H_2O, ethanol and NO_3^- have all volatilized or burnt. The characteristic absorption around 1,080, 1,013, 942, 890, 689, 645, 567 and 463 cm^{-1} is attributed to the β-$CaSiO_3$ [13], which indicates that the host material of $CaSiO_3:Pb$, Mn is β-$CaSiO_3$ and that is consistent with XRD curves.

3.5 Comparing the sample made by sol-gel method with high temperature solid-state reaction

The emission intensity of the $CaSiO_3:Pb$, Mn phosphors made by the optimal sol-gel method is about two times stronger than that made by the high temperature solid-state reaction, which is shown in Fig. 5, and the size of the two particles is shown in Fig. 6. The mean diameter of the particles made by sol-gel method is about 200 nm, and it has better dispersant. The sample made by high temperature solid-state reaction is almost congregative, and the mean diameter is about 500 nm.

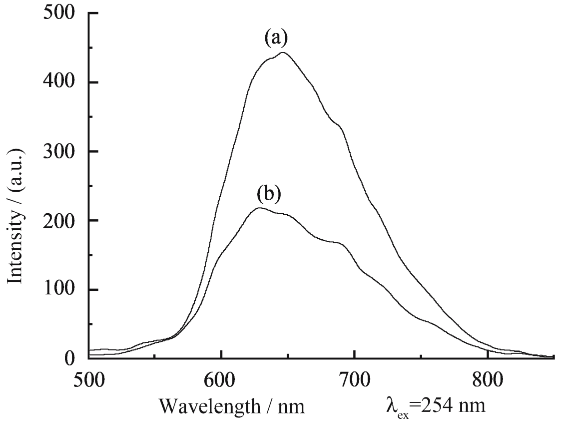

Fig. 5 Emission spectra of the $CaSiO_3:Pb$,Mn
(a) Sol-gel method; (b) solid state reaction method

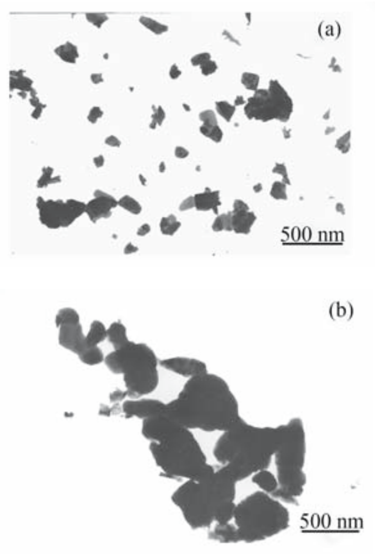

Fig. 6 TEM images of the $CaSiO_3:Pb$, Mn
(a) Sol-gel method; (b) solid state reaction method

4 Conclusions

In sum, the luminous materials of $CaSiO_3:Pb$, Mn are synthesized by sol-gel method and ultrasound technology. The mol ration of optimal raw materials is $Ca(NO_3)_2:SiO_2:Pb(NO_3)_2:Mn(NO_3)_2 = 0.7:1.3:0.025:0.033$, and the optimal ultrasound time is 2 h, then the precursor is calcined at 900°C for 2 h, and further calcined at 1,200°C for 4 h. The emission intensity of the sample prepared is about two times stronger than that made by solid state reaction method, and the mean diameter of particles decreased by about 300 nm.

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References

1. Liu Xingren, Zhang Xiao, Lu Shuhua, Zhang Yinglan. Luminescence preperties of Ce^{3+} in calcium metasilicate. Chinese Journal of Luminescence, 1989, 10(3): 177–185
2. Yu Lixin, Cao Lin, Li Dianchao. The luminescence preperties of Dy in calcium metasilicate. Jounal of the Chinese Ceramic Society, 2002, 25(5): 16, 63
3. Qiu J R, Sugimoto N, lwabuehi Y, Hirao K. Photostimulated luminescence in Ce^{3+}-doped silicate glasses. J Non-Crystalline Solids, 1997, 209: 200–203
4. Glynn T J, Kuleshov N V, Mikhailov V P, Scherbitsky V G, Minkov B I, Sherlock R. Luminescence study of Cr^{4+}-doped silicates. Optical Mater, 1995, 4: 507–513
5. Lin J, Sanger D U, Mennig M, Barner K. Sol-gel deposition and characterization of Mn^{2+}-doped silicate phosphor films. Thin Solid Films, 2000, 360(1–2): 39–45
6. Lin Jun, Yu Min, Pang Maolin. State of the art: Luminescent films prepared by sol-gel process. Chin J Lumin, 2001, 22(4): 373–283 (in Chinese)

7. Yu Min, Liu Jun, Zhou Yonghui, Feng Maolin, Han Xiumei, Wang Shubin. Synthesis and properties of Sr_2CeO_4 powder phosphor by sol-gel method. Chin J Lumin, 2003, 24(1): 91−94 (in Chinese)
8. Schmid C, Sbaizero O. Ultrasonic homogenization of equivolumetric Al_2O_3/ZrO_2 suspensions. J Mater Sci, 2000, 35: 1,213−1,217
9. Wang G Z, Chen W, Liang C H, Wang Y W, Meng G W, Zhang L D. Preparation and characterization of CdS nanoparticles by ultrasonic irradiation. Inorg Chem Commun, 2001, 4: 208−210
10. Sun Jiayue, Du Haiyan, Hu wenxiang. Solid Luminescence Materials. Beijing: Chemical Industry Press, 2003, 343−344
11. Zhang Xiao, Liu Xingren. The luminescence properties and energy transfer characteristics of Ce^{3+} and Mn^{2+} in calcium metasilicate. Jounal of the Chinese Ceramic Society, 1989, 17(2): 140−145
12. Farmer V C, Ying Yupu. The IR Spectra of Minerals. Beijing: Chemical Industry Press, 1982, 289
13. Yuan Ximing, Shi Lan, He Yinglv, Tang Yuanjun. Syntheses of $CaSiO_3:Eu^{3+}$, $CaSiO_3:Gd^{3+}$, $CaSiO_3:Mn^{2+}+Pb^{2+}$. Earth Science —The Journal of China Geology University, 1994, 19(1): 60−64