

Utilization of Rice Husk to Synthesize High-Performance Phosphors

Liangming XIONG^{1*}, Kazuya SAITO¹, Shigetaka WADA² and Edson H. SEKIYA¹

¹*Frontier Materials Lab, Research Center for Advanced Photon Technology,
Toyota Technological Institute, Nagoya, 468-8511, Japan.*

²*Department of Materials Science, Chulalongkorn University,
Bangkok, 10330, Thailand.*

Abstract

Rice husk (RH) has high C and Si contents, so it can be used not only as a fuel candidate, but also as a low-cost Si source for synthesizing high-performance products. In the present work, we proposed a low-cost route to synthesize high-performance silicate phosphors with RH. RH was burned either as received or as pretreated by HCl washing. The resulting ashes were, respectively, utilized to react with other raw materials at high temperatures to form silicate phosphors. The high-temperature solid-state reaction process was optimized by varying either the temperature or the holding time. The crystallographic and fluorescent properties of the silicate phosphors were investigated by XRD and PL spectroscopy. The Zn₂SiO₄ : Mn phosphors, obtained with both groups of ashes, exhibit a strong green emission, at ~523 nm, the lifetime of which is about 9 ms. The green emission mechanism was explained. The luminescent properties, including the emission spectra and decays, of the phosphors, using non-treated or treated RHs, were studied by comparison. This work opens up the possibility of utilizing RH to synthesize high-performance silicate phosphors.

Key words: Rice husk, Silicate phosphors, Green emission, Low cost.

Introduction

Rice husk (RH) is an abundantly available waste material in many countries. RH has high C and Si contents, so it can be used not only as a fuel candidate, but also as a low-cost Si source. After combustion, some solid products are left, which are rice husk ash (RHA) and the predominant component is silica. Thus RHA can be used as a Si source or a SiO₂ starting material to fabricate a variety of high value-added products. Recently, many attempts have been made to efficiently utilize RH or RHAs in chemical synthesis.^(2,3) However, until now no work has been reported on the utilization of RH or RHA as raw material to prepare light emitting materials.

On the other hand, a lot of commercially available silicate phosphors have been widely used in industry. Among them, the Mn²⁺-doped zinc orthosilicate is one of the most widely used green phosphors.⁽⁸⁾ It has been widely used in cathode ray tubes, fluorescent lamps, and plasma display panels, owing to its high luminescent efficiency and chemical stability. This phosphor also presents the advantage

of highly saturated color.^(5,1) For silicate phosphors, the conventional fabrication method is the high temperature solid state reaction (SSR), which is very straight-forward to operate. Currently, the more and more complete application markets demand that phosphors take the advantage of either excellent properties such as morphology and photoluminescence or the low costs, or the advantages of both. Thus, increasing attention has been paid to the modification of the conventional fabrication processes and the development of new fabrication techniques. To decrease fabrication costs, one of the options is to use cheaper raw materials. If the abundantly available RHs could be used in the fabrication as raw materials, the prices of the silicate phosphors may be decreased vastly. Furthermore, RH combustion can work for power, which may be available for the high temperature SSR process. Thus, the efficient utilization of RHs in high temperature fabrication of silicates phosphors, if possible, may also be an energy-saving process. This would be of particular interest, but also be of challenge.

In the present work, we proposed a novel route to synthesize silicate phosphors by utilization

of RHs as the Si source. The crystallographic and fluorescent properties of the complete-reaction products using either the raw RHs or the acid-washed RHs were investigated. The product which makes use of the acid-washed RHs exhibits even more exceptional luminescent properties than the one that makes use of the raw RHs. Both exhibit a high performance in crystallization and light emitting. To our best knowledge, this work is the first attempt to fabricate phosphors by utilization of RHs.

Materials and Experimental Procedures

Experimental Section

The raw rice husks (RRHs) were received from a local rice milling plant. Some RRHs were first washed with tap water. After drying, the husks were further treated with HCl acid, and then filtered and washed repeatedly with deionized water. Finally, they were dried at 110°C and labeled as WRHs. Both RRHs and WRHs were combusted at 600°C for 1 hour in the same way. The obtained ashes, labeled as RRHAs and WRHAs, respectively, were collected for use.

Both ash powders were, respectively, thoroughly mixed with other raw materials like ZnO and manganese salt. The mixtures were then calcinated at above 1000°C for a few hours to react. After complete reaction, Mn-doped zinc silicates ($Zn_2SiO_4:Mn$) were formed. According to the Si sources, the final product powders are designated as RZSM and WZSM, respectively.

The wide-angle powder X-ray diffraction (XRD) patterns of the ashes were taken on a Rigaku RINT-2500 X-ray diffractometer with $Mo-K_{\alpha}$ ($\lambda = 0.7093 \text{ \AA}$) radiation. The luminescent properties of the silicate powders were examined on a Hitachi FL-7000 fluorescence spectrophotometer using Xe-lamp.

Results and Discussion

Both R-ZSM and W-ZSM products took on the same white color after SSR, and the black C particles, which existed in RRHA before SSR, were completely removed. However, the R-ZSM particles were found being sintered together, which must be related to the high K and P contents in RRHA.

Figure 1 shows the XRD patterns of the mixtures of RHA, ZnO, and manganese salt before

and after SSR. Obtained by combustion at 600°C, the silica in either RRHA or WRHA is amorphous solid, according to our recent work.⁽⁷⁾ Thus, no crystalline SiO_2 diffraction was collected apart from the crystalline ZnO diffractions in the pattern of those raw mixtures that made use of either RRHA or WRHA. In this pattern, the strongest peak is the (101) plane diffraction of ZnO. After the high temperature SSR, the products, both R-ZSM and W-ZSM, exhibit many crystal diffraction peaks, but the strongest ZnO (101) plane diffraction did not occur any more. This disappearance suggests that ZnO should have been reacted out to form zinc silicates. The diffraction positions in both patterns are highly similar each other, implying R-ZSM and W-ZSM belong to the same crystal family. These peak positions match well with those of the standard pattern reported by the JCPDS Card No 83-2270, specifically for Zn_2SiO_4 in a rhomb-centered willemite structure. Thus the obtained SSR products are crystalline Zn_2SiO_4 with willemite structure. According to the standard pattern, the 3 strong lines at 15.4, 14.3, and 11.7° in our patterns correspond to the (410), $(11\bar{3})$, and (220) planes of Zn_2SiO_4 , respectively. Based on the XRD results, it is true that whether RRHA or WRHA has been used, the SSR was processed completely at above 1000 °C, and crystalline Zn_2SiO_4 was produced. When the manganese salt is added, during SSR the Mn^{2+} ion ($\sim 0.67 \text{ \AA}$) would occupy the site of the Zn^{2+} ion ($\sim 0.74 \text{ \AA}$) in the lattice. Thus, Mn ions were doped into the Zn_2SiO_4 lattice.

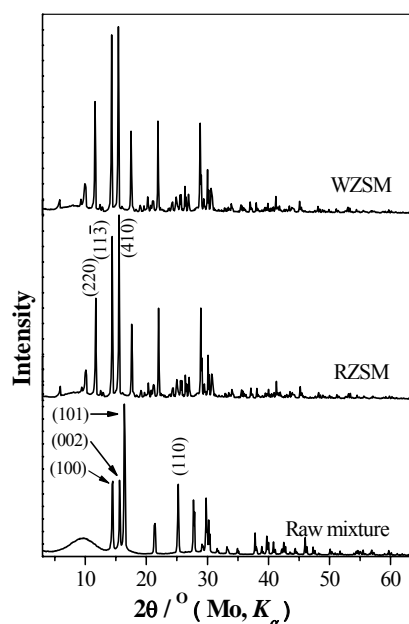


Figure 1. XRD patterns of the mixtures before and after SSR.

Utilization of Rice Husk to Synthesize High-Performance Phosphors

Under UV irradiation both R-ZSM and W-ZSM exhibit green lights. It is generally recognized that the excitation and emission wavelengths of $\text{Zn}_2\text{SiO}_4:\text{Mn}$ phosphors shift slightly depending on the nature of the host and the doping level and uniformity. Figure 2 shows the emission versus excitation relationships of R-ZSM (a) and W-ZSM (b). Obviously, both samples exhibit a similar emission versus excitation relationship: one emission band in the range of 480 – 590 nm and many excitation bands. In Figure (a), a strong emission of R-ZSM can be excited by short-wavelength UV lights in 240 – 280 nm, and the same emission can also be excited by near UV and purple lights in 350 – 390 nm or by blue lights in 420 – 450 nm. The strongest emission occurred at around the point (261 nm, 541 nm), which was proven to be inexact by wavelength scanning below. In Figure 2(b), besides the similar excitation and emission bands, W-ZSM was found to exhibit the strongest emission at around the point (268 nm, 523 nm). The excitation and emission peaks shift slightly between R-ZSM and W-ZSM.

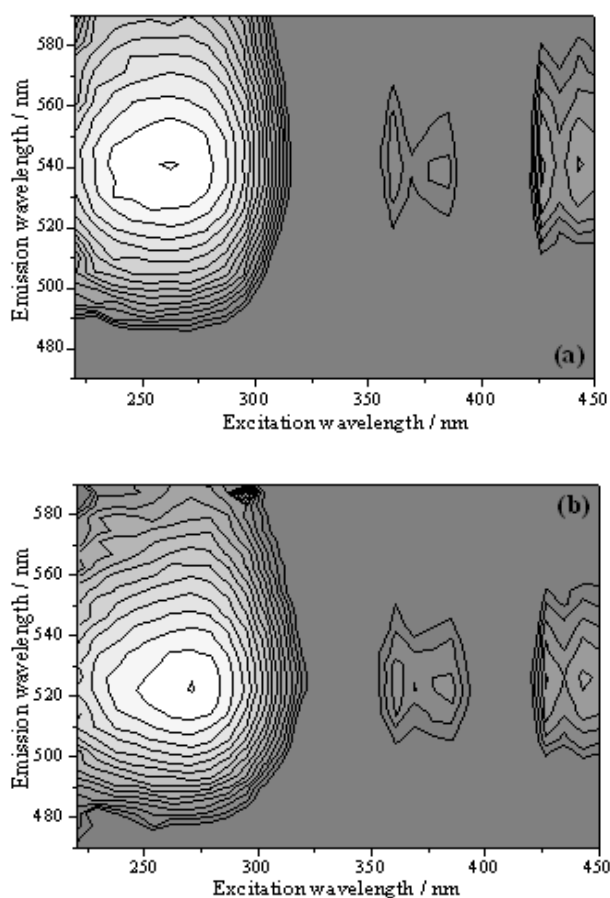


Figure 2. Emission vs excitation of R-ZSM (a) and W-ZSM (b).

Figure 3 shows the excitation and emission spectra of R-ZSM. In the excitation spectrum, the broad and strong excitation band at around 261 nm was ascribed to the strong dipolar $e \rightarrow t_2$ transition of Mn^{2+} ion in willemite.⁽⁸⁾ This band is mainly assigned to excite the green emission at around 525 nm. Thus, for R-ZSM, the optimal excitation and emission occur at around 261 nm and 525 nm, respectively. Both the excitation and emission peak positions shift to a slight longer wavelength, compared with the above result in Figure 2(a). Other various bands at around 357, 379, 422, 434, and 443 nm can also excite the same emission, as shown in the Insets (a). These excitation bands correspond to the electronic transition from the ^6S ground state to the splitting levels of the ^4D and ^4G states of the Mn^{2+} ion.⁽⁴⁾ In the emission spectrum, a broad and strong 525 nm emission was excited by the 261 nm band. This emission is ascribed to the electronic transition from the ^4G excited state to the ^6S ground state associated with the Mn^{2+} ions in willemite. The emissions excited by the 357, 379, 422, 434, or 443 nm bands are much weaker than the strong emission excited by the 261 nm band. They are about 1/30 – 1/10 of the latter in intensity, as shown in the Inset (b). The broad excitation band at 261 nm and the broad emission band at 525 nm in profile may be due to the fact that the Mn^{2+} ^6S state can be further split into several levels.

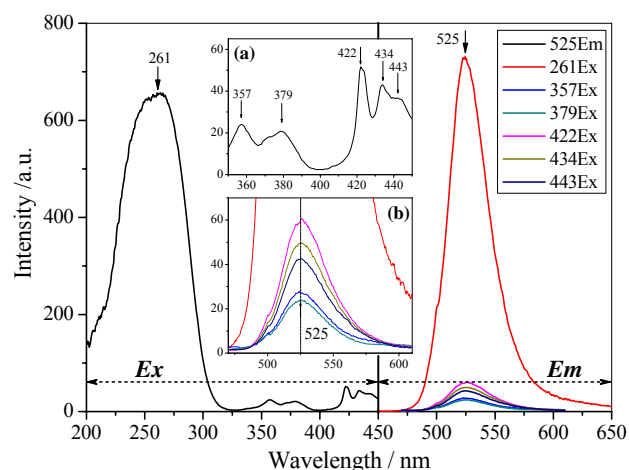


Figure 3. Excitation and emission spectra of R-ZSM. Insets: the enlarged excitation (a) and emission (b) spectra.

Figure 4 shows the excitation and emission spectra of W-ZSM. It exhibits a similar excitation bands and emission band to those of R-ZSM. This means excitation and emission mechanisms of both products are the same: after absorption of the photon energy of the 268 nm UV light, the electron

in the 6S ground state of Mn^{2+} is pumped to the conduction band, then relaxes without radiation to the $Mn^{2+} {}^4G$ excited state, and finally transfers back to the 6S ground state with the 523 nm emission.⁽⁸⁾ The broad and strong excitation band peaks at around 268 nm, by 7 nm higher than that of R-ZSM, and its shape a little differs from that of R-ZSM; the emission peaks at around 523 nm, by 2 nm shorter than that of R-ZSM. In general, in the same phosphor system, a higher doping level can lead to a little longer emission wavelength. Thus the doping level of R-ZSM may be a little higher than that of W-ZSM. More interestingly, both excitation and emission of W-ZSM are much higher than those of R-ZSM, respectively, about twice of the latter. Furthermore, the intensity ratios of the emissions excited at 358, 380, 422, 434, and 443 nm to the emission excited at 261 nm are lower than those of R-ZSM, respectively. Based on the emission results, both products exhibit a strong green emission, but W-ZSM possesses higher luminescent properties than R-ZSM.

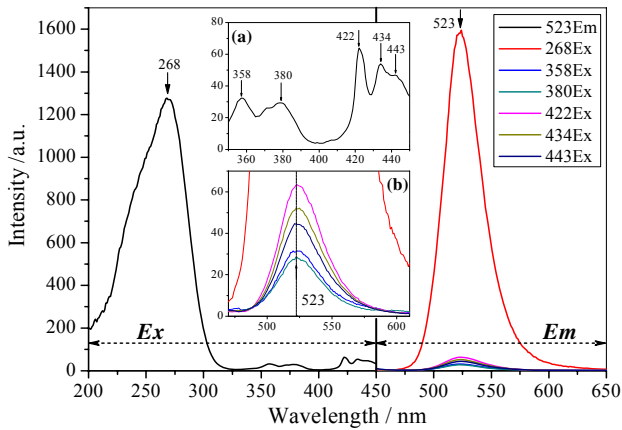


Figure 4. Excitation and emission spectra of W-ZSM. Insets: the enlarged excitation (a) and emission (b) spectra.

Figure 5 shows the green emission decay curves of R-ZSM and W-ZSM. From the curves, it is clear that the emission intensity of W-ZSM is initially much higher than that of R-ZSM, further confirming the high luminescent properties of W-ZSM. Both emissions decay exponentially. When fitted with a single exponential, the green emission lifetime of R-ZSM is about 8.6 ms and the one of W-ZSM is about 9.2 ms. In general, an increase of the doping level can shorten the emission lifetime⁽⁸⁾ Thus, the emission decay result also confirms that the doping level of R-ZSM is slightly higher than that of WR-ZSM.

According to our recent work Xiong, Saito, *et al.* (2009), the silica contents in RRHA and WRHA were different, ~ 92.66 wt% and 93.6 wt%, respectively. The silica content difference resulted in the different amounts of the formed Zn_2SiO_4 in R-ZSM and W-ZSM. Thus, when the same amount of manganese salt was used, the mole ratios of Mn to Zn_2SiO_4 in R-ZSM and W-ZSM were different. The slightly smaller silica content of RRHA means a higher Mn doping level in R-ZSM. As a result, the emission wavelength of R-ZSM is longer and the decay lifetime is shorter in comparison with W-ZSM.

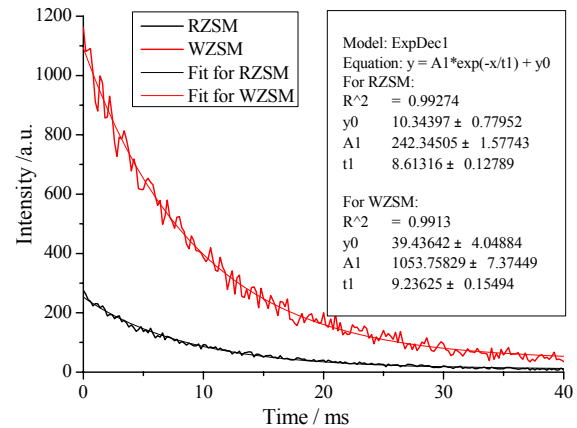


Figure 5. Emission decay curves of R-ZSM (black) and W-ZSM (red).

Conclusions

In summary, we have successfully fabricated Mn-doped zinc silicate phosphors utilizing RH as Si source for the first time. The obtained silicate phosphors both exhibit a strong green emission at around 523 – 525 nm under excitation by the UV lights of 250 – 270 nm. The main excitation by the short-wavelength UV lights is ascribed to the strong dipolar $e \rightarrow t_2$ transition of Mn^{2+} ion, and the strong green emission is ascribed to the electronic transition from the $Mn^{2+} {}^4G$ excited state to the 6S ground state. The phosphor W-ZSM exhibits higher fluorescent properties than R-ZSM. The emission decays were examined to be ~ 8.6 ms for R-ZSM and ~ 9.2 ms for W-ZSM. Although the high impurity in RRHA slightly changed the emission wavelength and lifetime of R-ZSM, both phosphors may find important applications in the optical field. This work, indeed, is of particular practical interest for rice-growing countries to fabricate high-performance silicate phosphors by efficient utilization of the waste rice husks at low costs.

Acknowledgements

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