$ZnS:Mn^{2+}$ Particles Preparation by Spray Pyrolysis

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INTRODUCTION

Mn^{2+}-doped ZnS ($ZnS:Mn^{2+}$) is conventionally produced by a solid-state process at high temperatures (900~1200^{o}C) as bulk materials. A number of gas and liquid routes have been employed in the synthesis of $ZnS:Mn^{2+}$.[1] Spray pyrolysis (i.e., aerosol decomposition) has been widely used in the synthesis of a variety of materials.[2] A precursor solution is atomized into aerosol droplets and then carried by a gas into a hot reactor. After the droplets have been dried, the precursor is precipitated and thermally decomposed to form the desired product. In this study, $ZnS:Mn^{2+}$ particles were synthesized via spray pyrolysis route, in a rapid (~ seconds) and continuous process.

EXPERIMENTAL

Three types of precursors, nitrates, chlorides and acetates of Zn^{2+} and Mn^{2+}, were used as cationic sources. The same anionic sources , e.g. $Zn(NO_3)_2$ and $Mn(NO_3)_2$, were used to produce a $ZnS:Mn^{2+}$ sample. Thiourea (Tu) was employed as a sulphur source. Tu prevents the metal sulfide from being oxidized in the reactor, and therefore, an external protective gas, e.g. H_2S, is not necessary for the synthesis. The experimental apparatus used in this work was the same that described in a previous report.[2,3]

RESULTS AND DISCUSSION

Below 800^{o}C, $ZnS:Mn^{2+}$ particles derived from nitrate precursor have smooth surfaces and did not show any notable changes in morphology. Above 900^{o}C, particle surfaces became rough. This arises from the rapid crystal growth at 800~1000℃. Typical TEM images show that the particles have dense microstructures. Non-agglomerated particles were formed from nitrate and acetate precursors. From XRD patterns, it is obvious that the crystals grow rapidly at temperatures above 800^{o}C, while below 700^{o}C the crystalline sizes are very small.

Particles at various Mn^{2+} doping levels (from 0 to 8.0 %) showed similar morphologies. Larger particles were produced with increasing $Zn(NO_3)_2$ concentration. All products have spherical shapes and dense structures (confirmed by TEM) with mean sizes of around 0.5 μm. From FE-SEM images, the chloride product shows the largest crystalline size among the precursors. This is also evident in their XRD spectra.

Solid-state made $ZnS:Mn^{2+}$ fired below 1000^{o}C is a cubic phase (zinc blende), and a hexagonal (wurtzite) is produced at above 1000^{o}C.For our nitrate products, the 400 and 600 ^{o}C samples show cubic phases, and hexagonal phase predominates when the temperature reaches 800 ^{o}C. The chloride products show the presence of hexagonal phase even at 600 ^{o}C. Increasing the Tu concentration in the solution slightly enhances the crystallinity of the products in all cases.

In the excitation spectra (emission wavelength λ = 580 nm), the 400~700^{o}C nitrate samples do not show any significant PL (doping level was 1.0 at.% for all samples). This indicates that Mn^{2+} is not activated in these products. The 800 ^{o}C products have significant PL (excitation 359 nm), which is a characteristic emission of $ZnS:Mn^{2+}$ and can be attributed to a $^4T_1 \rightarrow {}^6A_1$ transition of Mn^{2+} ion in T_d symmetry.[1] The band then becomes blue shifted and the intensity increases from 800 to 900^{o}C. The band does not continue to shift and the intensity increases only marginally from 900 to 1000^{o}C. The emission bands are centered at 580 nm. From the PL and XRD spectra, it is clear that the hexagonal phase is luminescence active. The $ZnS:Mn^{2+}$ nanocrystals formed had mean sizes from < 3 nm to > 70 nm. The results show that the higher the crystallinity of the hexagonal phase the higher the photo-emitting efficiency, which is different from the quantum size effect.

For nitrate precursors at 800^{o}C, with increasing [Tu] concentration in the range 0.4 ~ 1.0 mol/L, the intensities of the excitation/emission bands increased and the excitation bands shifted to blue (from 375 to 359 nm). With increasing Zn concentration from 0.2 to 0.6 mol/L, the excitation bands become red shifted and the emission intensities decreased. When the Zn concentration decreased to 0.1 mol/L, the PL intensity dropped significantly. The excitation bands are blue shifted in the sequence of nitrate, chloride and acetate products, while the band strengths decrease in the same order. The nitrate product has the strongest PL.

In a spray pyrolysis, ligands are precipitated with the cations during droplet drying/pyrolysis, and can then either reside in products as impurities or form gaseous products that can be removed. For nitrate precursors, since they usually decompose to NO_x gases at relatively low temperatures, the products are ligand contaminant-free and show a high degree of luminescence. For the acetate and chloride precursors, carbon or chlorine may be left in the particles, especially when a sufficiently high temperature is used.

CONCLUSION

$ZnS:Mn^{2+}$ particles were synthesized, for the first time, by spray pyrolysis of nitrate, chloride and acetate precursors and Tu, in the temperature range 400~1000^{o}C. The results show that spray pyrolysis leads to the formation of spherical and dense $ZnS:Mn^{2+}$ with submicron sizes, homogeneous morphologies and non-agglomeration.

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