ZnS: Mn\textsuperscript{2\textsuperscript{+}} Particles Preparation by Spray Pyrolysis

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INTRODUCTION

Mn\textsuperscript{2\textsuperscript{+}}-doped ZnS (ZnS:Mn\textsuperscript{2\textsuperscript{+}}) is conventionally produced by a solid-state process at high temperatures (900–1200°C) as bulk materials. A number of gas and liquid routes have been employed in the synthesis of ZnS:Mn\textsuperscript{2\textsuperscript{+}}. Spray pyrolysis (i.e., aerosol decomposition) has been widely used in the synthesis of a variety of materials. 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\textsuperscript{2\textsuperscript{+}} 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\textsuperscript{2\textsuperscript{+}} and Mn\textsuperscript{2\textsuperscript{+}}, were used as cationic sources. The same anionic sources, e.g. Zn(NO\textsubscript{3})\textsubscript{2} and Mn(NO\textsubscript{3})\textsubscript{2}, were used to produce a ZnS:Mn\textsuperscript{2\textsuperscript{+}} 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\textsubscript{2}S, is not necessary for the synthesis. The experimental apparatus used in this work was the same that described in a previous report.

RESULTS AND DISCUSSION

Below 800°C, ZnS:Mn\textsuperscript{2\textsuperscript{+}} particles derived from nitrate precursor have smooth surfaces and did not show any notable changes in morphology. Above 900°C, particle surfaces became rough. This arises from the rapid crystal growth at 800–1000°C. 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 crystalline sizes are very small. Increasing the Tu concentration in the range 0.4 – 1.0 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\textsubscript{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\textsuperscript{2\textsuperscript{+}} particles were synthesized, for the first time, by spray pyrolysis of nitrate, chloride and acetate precursors and Tu, in the temperature range 400–1000°C. The results show that spray pyrolysis leads to the formation of spherical and dense ZnS:Mn\textsuperscript{2\textsuperscript{+}} with submicron sizes, homogeneous morphologies and non-agglomeration.

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REFERENCES