Y₂O₂S:Eu³⁺赤色微粒子蛍光体の合成

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あらまし 硫化剤としてチオ硫酸ナトリウムを用いて、サブミクロンサイズの Eu 添加YOHCO₃前躯体から Y₂O₂S:Eu³⁺微粒子赤色蛍光体を合成した。合成した蛍光体はX線回折、紫外線励起発光 (PL) 測定及び走査型電子顕微鏡観察（SEM）により評価した。蛍光体粉末の組成、形状及び粒径は硫化剤の割合及び焼成温度に依存した。600℃での焼成においても Y₂O₃相を含まない Y₂O₂S が形成され、900℃焼成で1乃至2μmの結晶性の良好な蛍光体が形成された。この蛍光体のPLは市販のものに匹敵し得る強度を示した。

キーワード Y₂O₂S:Eu、蛍光体、微粒子、PL、CL、FED

Synthesis of fine particle Y₂O₂S:Eu³⁺ red phosphor

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Abstract Homogeneously europium doped yttrium oxysulfide (Y₂O₂S:Eu³⁺) red phosphor with fine grains has been synthesized from a mono dispersed sub micron size yttrium-europium hydroxy carbonate precursor, using sodium thio-sulphate as sulfiding flux. The materials synthesized have been characterized by powder x-ray diffraction, photoluminescence emission spectroscopy and scanning electron microscopy. Phase purity, morphology, and grain sizes of phosphor powders depend on the flux composition and the calcination temperature. The result indicates that grain size distribution of the phosphor materials is retaining the grain size of starting material at low temperature and increase at high temperature.

key words Y₂O₂S:Eu³⁺, phosphor, fine particle, PL, CL, FED
1. INTRODUCTION

Low voltage high resolution display devices such as field emission displays and plasma displays require phosphor with fine grains (1 - 3 microns) and narrow particle size distribution. Phosphor prepared by normal solid state reaction yield products in the range of 5-10 microns size without regular shape and requires high temperature, to yield better efficiency. Moreover, the sizes of large particles are reduced to smaller by milling, which leads to decrease the luminous efficiency and no control over the particle morphology. Hence, attempts has been taken to synthesis fine grain phosphor employing hydrothermal, sol-gel, combustion techniques [1-3].

Trivalent europium activated yttrium oxysulfide, is an extensively applied red primary in color television screens, because of its high luminous efficiency and color purity under cathode ray excitation. Among all the synthesis methods flux sulfiding technique is well established in commercial scale production because of its factory reclaimability and good control over particle morphology [4-5]. For uniform doping of europium, mixed oxide is prepared from oxalate co-precipitation and employed with sulfiding flux to get the respective oxysulfides. While the fine grained YOS particles with narrow particle size distribution is considered the particle size of yttrium(europium) oxalate starting material should be controlled during the precipitation. Direct addition of a precipitating agent to a solution results in temporary heterogeneous condition in which the concentration of the ions in solution may vary over a wide range in the vicinity where the precipitation reaction has been introduced. This leads to a concentration gradient in solution and particles obtained in the heterogeneous precipitation, yields various sizes. This in turn can be controlled by adjusting the pH of the solution, concentration of the reactant, temperature of the reaction, rate of addition etc. For this reason it is imperative that the preparation methods for suitable precursor to be established for the synthesis of phosphor with fine grains and improved performance.

Preparation of monodispersed particles from homogeneous precipitation techniques, using urea, under hydrothermal conditions is an ideal technique [6] as it provides a slow precipitation process which allows near equilibrium between the surface of the precipitate and the solution. The fundamental requirement for the preparation of monodispersed particles under such conditions is to control the generation of the precipitating agent so as to obtain narrow particle size distribution. In this process only one burst of nuclei is formed which then grow to the desirable size. More over homogeneous precipitation provides an excellent method for co-precipitation of more than one ion available in trace quantity.

In this paper we have discussed some of the results on the formation of fine grain Y₂O₂S:Eu³⁺ red phosphor from a monodispersed sub micron sized yttrium (europium) hydroxy carbonate precursor using sodium thiosulphate as the sulfiding agent.

2. Experimental

Homogeneously europium doped YOHCO₃ precursor was prepared from the mixed nitrates of yttrium and europium with urea under hydrothermal conditions. Yttrium oxide with 4 mole % of europium oxide dissolved in hot dil.HNO₃ and the excess nitric acid was boiled off to bring the pH of the solution in the range of 5.5 - 6.0. Then urea (AR grade) was added to the solution in the mol. of 3-12 for 2 mole of Y₂Eu(NO₃)₃. The
resultant solution in a beaker was kept in an autoclave for 3 hours at the pressure of 12 psi. After the completion of reaction, a fine, white mass was obtained. The material obtained was filtered, washed thoroughly with deionized water and dried in an oven at 80°C and mixed with sodium thiosulphate in a ball mill and prefired at 250°C for 1 hr. The resultant mixture was transferred to alumina crucible and kept inside a silica crucible with activated carbon, and fired at various temperature for 2-3 hours. These products were washed and characterized by XRD, PL emission spectroscopy and scanning electron microscopy.

3. Results and discussion

Fine grains Y₂O₃S:Eu red phosphor, in the range of 1-3 microns, can be prepared from a monodispersed submicron size yttrium-europium hydroxy carbonate. Here we adopted flux technique using sodium thiosulphate as the sulfiding agent instead of sodium carbonate-sulfur, because of the advantage of getting sodium polysulfide at 350°C and yield phase pure oxysulfide at 600°C [7].

The FT-IR spectrum of the precursor obtained from the urea hydrolysis under hydrothermal condition is given in Fig.1.

![Fig.1. Infrared spectrum of YOHCO₃](image)

It can be seen from the figure that the material has characteristic peaks at 3421, 1404 and 1512 cm⁻¹. The peak at 3421 cm⁻¹ arises due to OH functional group and the remaining peaks due to CO₃²⁻ functional group. The broadening of the -OH group shows that along with the lattice OH some hydrated water is also present. The formation of hydroxy carbonate further confirmed by thermo gravimetric analysis with expected weight loss of 32%.

**Growth of Y₂O₃S:Eu from YOHCO₃:Eu**

It is well known that yttrium oxysulfide particles are grown on the yttria nuclei through the action of sulfurization process by molten sodium sulfide flux obtained from sodium carbonate-sulfur mixture [8]. In order to study the formation of oxysulfide and fluxing action of Na₂S₂O₃, the preparative temperature is varied from 400 to 800°C for 4 hr in an inert atmosphere. The XRD pattern of the materials prepared at various temperatures are given in Fig.2.

![Fig.2. X-ray powder diffraction pattern of YOHCO₃ - thiosulphate heated at (a) precursor only (b) 400°C (c) 600°C and (d) 800°C](image)
It indicates that the precursor obtained is amorphous in nature (Fig.2 a). However, the material obtained at 400°C shows newer lines indicating the growth of new phase which cannot be assigned due to the growth of oxide and oxysulfide (Fig.2 b). At 600°C the material shows the formation of oxysulfide phase with the crystallite size of 18 nm (Fig.2 c). The line broadening shows that the YOS crystallite size formed is very fine, because of the decomposition of raw material YOHCO$_3$ with the simultaneous growth of YOS at low temperature. From these observations it could be concluded that the formation of phase pure oxysulfide is achieved only at 600°C. Above 600°C (Fig. 2 d), the XRD pattern shows peak sharpening with high crystallite size. It is worthy to point out from the XRD pattern that at any time, oxide phase was not detected. This suggest that the oxide phase generated *in situ*, during the decomposition of hydroxy carbonate, was consumed instantaneously by sodium polysulfide generated at 350°C from sodium thiosulphate.

More over, when YOHCO$_3$ is considered as the source for Y$_2$O$_2$S, firing temperature and thiosulphate concentration are important factors, which have a drastic effect on the final phase content of the material. The relative phase contents were estimated using X-ray powder diffraction from the relative intensity of the major lines of Y$_2$O$_3$ and Y$_2$O$_2$S and are given in Table 1.

The X-ray powder pattern of these samples were compared with the JCPDS files (No:12-51200, 24-1424 for Y$_2$O$_3$ and Y$_2$O$_2$S). From the table it is observed that when temperature increases, the oxysulfide phase content decreases. At the same time using of separated oxide has lead to the growth of only Y$_2$O$_2$S [7] when temperature increases. This can be explained as follows. It is well known that when YOHCO$_3$ is heat treated it decompose to yttrium oxide with the evolution CO$_2$ and H$_2$O. The evolution of carbon dioxide has the advantage for the preparation YOS as it creates an inert atmosphere to avoid the oxidation of YOS. At the same time, the evolution of water has the disadvantage as it is known to play a major role with metal sulfide compounds, in making sulfur deficiency by removal of sulfide as free sulfur, sulfite, sulfate, sulfur dioxide and hydrogen sulfide [9]. Generation of H$_2$O leads to the expulsion of sulfides from the reaction mixture, making a sulfide deficient flux. Further more, it is well established that fine particles of YOS will be oxidized more efficiently to the oxide phase at high temperature [10]. In order to overcome the formation of unwanted oxide phase and to improve the optimum emission efficiency, it is mandatory to use excess of thiosulphate to ensure complete formation of YOS. Hence, higher mole ratio of thiosulphate was used i.e., three mole of thiosulphate with two mole of Y(Eu)OHCO$_3$.

The PL emission spectra of the materials prepared at different temperatures are given in Fig.3. The PL emission spectra of the precursor (Fig.3a) is found to be the characteristics line emission of Eu$^{3+}$ with broadening. When it is exposed to UV at 260 nm, the material shows feeble uniform red emission without any non- luminescent phase. It indicates the uniform doping of europium in yttrium hydroxy carbonate. The material prepared at 400°C shows the emission

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Y$_2$O$_2$S (%)</th>
<th>Y$_2$O$_3$ (%)</th>
</tr>
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<tbody>
<tr>
<td>900</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>1000</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>1100</td>
<td>60</td>
<td>40</td>
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characteristics of oxysulfide as well as that of the precursor (Fig.3.b). It is interesting to mention at this juncture that the XRD pattern did not reveal lines that correspond to oxysulfide phase. When the firing temperature is 600° C (Fig.3.c) the PL emission spectrum shows only the emission characteristics of oxysulphide phase.

Fig.3. PL emission spectra of precursor
(a) Y(OH)CO₃:Eu³⁺ and with thiosulphate heated at (b) 400° and (c) 600° C.

The particle morphology of the Y(OH)CO₃ and Y₂O₃ derived from Y(OH)CO₃ at different temperature is given in Fig.4. The figure shows that the precursor obtained from hydrothermal reaction yields a mono dispersed sub micron sized spheres (Fig.4.a). When it is heated in the presence of thio sulfate at various temperature, the particle morphology obtained shows various sizes with uniform distribution, depending on the temperature. When the temperature is low, the growth shows fine grained spherical and oval shaped phosphor crystal with defined size in the range of 1 - 2 microns (Fig.4.b). When the temperature increases, the smaller particles get dissolved into larger particles in the range of 2 - 3 microns with well defined shapes (Fig.4c).

Fig.4. Morphological appearance of (a) Y(Eu)OHCO₃ as formed and Y₂O₂S:Eu obtained with thiosulphate at (b) 900° (c) 1100° C.
4. Conclusion

It has been demonstrated that trivalent europium activated yttrium oxysulfide red phosphor with fine grains can be prepared from the monodisperded submicron size homogeneously europium doped yttrium hydroxy carbonate by using sodium thiosulphate as the sulphiding agent. The $Y_2O_2S$ growth even though observed at 400° C but complete growth is achieved at 600° C. The phosphor consists of a well crystallized fine particle in the range of 1 - 2 microns. The grain size distribution is a function of the firing temperature. The product has matching emission intensity when compared to the standard commercial red phosphor.

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