Synthesis of High-Brightness Sub-micrometer Y_2O_2S Red Phosphor Powders by Complex Homogeneous Precipitation Method

Yoshiyuki Kawahara,[‡] Valery Petrykin,[†] Takahashi Ichihara,[§] Naoto Kijima,[||] and Masato Kakihana*,[†]

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, 980-8577, Japan, Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Yokohama 226-8503, Japan, Kasei Optonix Ltd., Narita 1060, Odawara 250-0862, Japan, and Mitsubishi Chemical Group Science and Technology Research Center Inc., 1000 Kamoshida-sho, Aoba-ku, Yokohama 227-8502, Japan

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High-brightness Y_2O_2S red phosphor powders with sub-micrometer particle size were prepared by complex homogeneous precipitation method employing hydrolysis of urea in water solutions of various diols. Sulfurization was carried out by annealing of the obtained powders at 700−1200 °C in the presence of Na_2CO_3−S mixture. Despite the small particle size, the luminescence intensity for most of the samples was comparable with one of the best available commercial Y_2O_2S phosphors, while Y_2O_2S samples doped with Eu and a small amount of Tb were superior to the commercial reference.

Introduction

The manufacturing of the new generation of display equipment in recent years raised a stringent demand on the fluorescent materials. Particular interest is focused on the high-brightness phosphors having sub-micrometer particle size. Conventional solid-state synthesis of phosphors followed by milling generally results in a dramatic decline of emission intensities for 1−3 μm size particles due to the defects introduced by crushing.[1] Therefore, wet-chemical methods seem to be an attractive alternative to the classical approach. The attempts to prepare fine powders of Y_2O_3:Eu, perhaps the simplest oxide among industrially used phosphors, usually lead to broadening of the emission peaks and overall decrease of the luminescence performance.[2−3] In addition, it is difficult to control particle shape and avoid agglomeration if simple solution methods are applied. Nevertheless, sub-micrometer particles of Y_2O_3:Eu with outstanding brightness can be prepared if one achieves low concentration of defects[4] and extends quenching concentration of Eu.[5]

Yttrium oxosulfide doped with Eu(III) has been used as a red "no mill" phosphor for decades.[6] Its high brightness, excellent color definition, and linear response in the wide range of current density make it promising also for the future generation of display equipment. Many profound studies on the synthesis, control of particle morphology, and tuning luminescence properties have been carried out during the 1970s and 1980s. Although the major impact was made on the 5−30 μm particles, many conclusions are still useful for planning the synthesis strategy for sub-micrometer powders. The most important observations can be summarized as follows. Transformation of Y_2O_3 into Y_2O_2S becomes noticeable above 700 °C and above 1180 °C it becomes extremely rapid.[7] Atmosphere control is absolutely crucial above 1050 °C due to the oxidation of flux and oxidation of oxosulfide into $Y_2O_2SO_4$ byproduct.[8] Synthesis of Y_2O_2S above 900 °C yields particles with high emission intensity,[7] which is attributed to the annealing of extended defects. However, above 1000−1050 °C particle growth is accelerated[7,8] and the particles tend to agglomerate. Flux synthesis does not provide much control over morphology because Y_2O_2S forms in a dissolution−precipitation process.[8] On the other hand, it is possible to obtain Y_2O_2S when sulfur is transported through the gas phase.[6,7,9] In this case, sulfurization is a topochemical process, which does not alter the original morphology. Very small concentration of Tb or Pr (below 50 ppm) increases luminescence intensity.[6,10,11]

In recent years there were several successful attempts to prepare Y_2O_2S:Eu nanopowders,[12−15] and the best samples demonstrated emission intensity close to the powders pre-

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* Corresponding author. Tel./Fax: +81-22-217-5649. E-mail: kakihana@tagen.tohoku.ac.jp.
[†] Tohoku University.
[‡] Tokyo Institute of Technology.
[§] Kasei Optonix Ltd.
[||] Mitsubishi Chemical Group Science and Technology Research Center Inc.

(1) Narita, K. *Phosphor Handbook*; CRC Press LLC: Boca Raton, FL, 1999.
(2) Williams, D. K.; Yuan, H.; Tissue, B. M. *J. Lumin.* **1999**, *83−84*, 297.
(3) Polizzi, S.; Battagliarin, M.; Bettinelli, M.; Speghini, A.; Fagherazzi, G. *J. Mater. Chem.* **2002**, *12*, 742.
(4) Wakefield, G.; Holland, E.; Dobson, P. J.; Hutchison, J. L. *Adv. Mater.* **2001**, *13*, 1557.
(5) Imanaka, N.; Masui, T.; Chiga, T. *Electrochem. Solid State Lett.* **2004**, *7*, D7.
(6) Royce, M. R. U.S. Patent 3418246, 1968.
(7) Kanehisa, O.; Kano, T.; Yamamoto, H. *J. Electrochem. Soc.* **1985**, *132*, 2023.
(8) Ozawa, L. *J. Electrochem. Soc.* **1977**, *124*, 413.
(9) Kottaisamy, M.; Jagannathan, R.; Rao, R. P.; Avudaithai, M.; Srinivasan, L. K.; Sundaram, V. *J. Electrochem. Soc.* **1995**, *142*, 3205.
(10) Yamamoto, H.; Kano, T. *J. Electrochem. Soc.* **1979**, *126*, 305.
(11) Pham-Thi, M.; Morell, A. *J. Electrochem. Soc.* **1991**, *138*, 1100.
(12) da Vila, L. D.; Stucchi, E. B.; Davolos, M. R. *J. Mater. Chem.* **1997**, *7*, 2113.

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pared by the classical flux method starting from metal oxides according to the schematic reaction

$$Y_2O_3 + Eu_2O_3 + \text{flux } (S + Na_2CO_3 + K_3PO_4) \rightarrow Y_2O_2S{:}Eu + \text{flux residue}$$

Unfortunately, such studies often lack the comparison of emission brightness against industrial products and therefore it is difficult to judge real materials' performance. One should keep in mind that commercial products have been optimized for decades under the strong pressure of market competition and usually they are far more superior to the conventional samples prepared in a laboratory according to the simplified procedures described in the literature.

In the present study we have synthesized a series of red emission phosphors Y_2O_2S:Eu by a chemical solution method. We focused on Y_2O_2S:Eu as one of the most promissing compositions. To control particle size and morphology, slow homogeneous precipitation in the presence of various diols as complexing agents has been carried out. The obtained precursor was heat-treated in the sulfur atmosphere over the Na_2CO_3−S mixture. Such Y_2O_2S samples generally have particles of regular shape and narrower size distribution than the powders obtained through a conventional precipitation method from water solution. This method provides a reproducible way to prepare fine Y_2O_2S:Eu powders of the size between 150 and 600 nm that exhibited luminescence brightness of up to ∼110% of that for one of the best commercial samples available, and having similar chromaticity coordinates.

Experimental Section

In the typical experiment 50 mmol of $Y(NO_3)_3 \cdot 6H_2O$ (99.99%, Kanto Chemicals), 2 mmol of $Eu(NO_3)_3 \cdot 6H_2O$ (99.95% Kanto Chemicals), and 500 mmol of urea (reagent grade, Kanto Chemicals) were dissolved in 150 mL of distilled water. Then 2.4 mol of a glycol (ethylene glycol, propylene glycol, or hexamethylene glycol) were added to the solution. Since hexamethylene glycol is a solid at room temperature, it was heated up and mixed with water first, and then the solution was mixed with metal and urea solution. We also carried out synthesis without a glycol for comparison. In this case, the final volume of the solution was adjusted to 300 mL.

After dissolution of reagents, the temperature of the hotplate was set to 100 °C and the sample was kept at this temperature for 5 h with continuous magnetic stirring. The hydrolysis reaction yielded a fine precipitate of yttrium−europium hydroxide that was separated from liquid by centrifugation and decantation. Then the precipitate was washed with distilled water in an ultrasonic bath and separated again in the centrifuge. The procedure was repeated four times. Finally, the powders were dried in an oven at 100 °C for 12 h.

For annealing in a sulfur atmosphere, the dried powder was placed into an alumina crucible, which was placed into another crucible of larger diameter. Then both crucibles were put into a crucible of larger volume filled with the mixture of Na_2CO_3 and sulfur and covered by a lid as shown in Figure 1. The ratio of 1 g of the hydroxide precursor powder to 4 g of Na_2CO_3 and 4 g of sulfur mixture was maintained in most experiments. The samples were placed into the furnace and heat-treated at 600−1100 °C for 2 h (furnace heating rate was 10 °C/min). For synthesis of Tb co-doped samples at higher temperature, we had to carry out slight optimization of Na_2CO_3−S ratio and in addition we compared results with K_2CO_3−S mixture. The best samples were prepared by annealing for 1 h at 1200 °C using a Na_2CO_3/S = 6 g/12 g ratio.

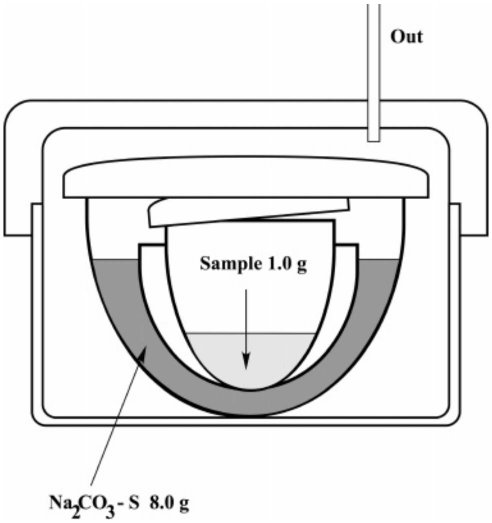

Figure 1. Schematic view of the sample setup for synthesis of Y_2O_2S:Eu in a sulfur atmosphere.

The obtained samples were characterized by powder X-ray diffraction using a MacScience MXP 3VA powder X-ray diffractometer with Cu Kα radiation in the 2θ/θ scanning mode at 4°/min and 0.02° step. SEM analysis was performed on the Pt−Pd coated samples using a Hitachi FE-SEM (Model S-4500) operated at 15 kV and 10 mkA.

For measurements of cathodoluminescence intensity and chromaticity coordinates 0.6 g of phosphor powder was dispersed into potassium silicate based solution "Ohka Seal-A" (Tokyo Ohka Kogyo Co.) to obtain 10 vol % concentration and stirred for 10 min. This solution is referred to as "Solution A". The 0.046% barium acetate aqueous solution was used as "Solution B". Two slide glasses of 25 mm × 30 mm × 1 mm size were immersed in Solution B. After that, Solution A was added to Solution B for sedimentation of phosphor powder onto the slide glass. Both slide glasses had been dried at 80 °C for 30 min. The amount of the phosphor powder on the slide glass was approximately 15 mg/cm^2. For excitation a 20 kV electron beam with the current density of 1 μA/cm^2 was applied. The beam focused into the 0.5 mm diameter spot scanned the sample with a 60 Hz refresh rate and 15734 kHz horizontal synchronization rate. The emission light during 262 scans was analyzed by a color luminescence meter BM-5A (Topcon Co. Ltd.).

The intensities and chromaticity coordinates of the prepared Y_2O_2S samples were compared against the high-performance commercial Y_2O_2S materials produced by Kasei Optonix.

Results and Discussion

The powders obtained from plain water solutions after washing and drying are X-ray amorphous. The XRD patterns of the samples prepared in the glycol solutions also do not contain diffraction from the crystalline phases; however, the diffuse scattering was more pronounced in the 2θ range

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(13) Dhanaraj, J.; Jagannathan, R.; Trivedi, D. C. *J. Mater. Chem.* **2003**, *13*, 1778.

(14) Chou, T. W.; Mylswamy, S.; Liu, R. S.; Chuang, S. Z. *Solid State Commun.* **2005**, *136*, 205.

(15) Kuang, J.; Liu, Y.; Yuan, D. *Electrochem. Solid State Lett.* **2005**, *8*, H72.

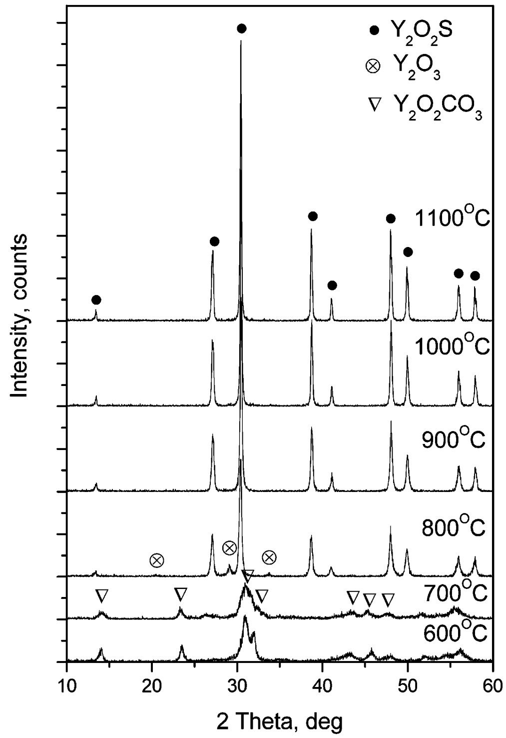

Figure 2. XRD patterns of Y_2O_2S samples prepared by homogeneous precipitation from plain water solution and annealed at 600−1100 °C in a sulfur atmosphere provided by a Na_2CO_3−S mixture.

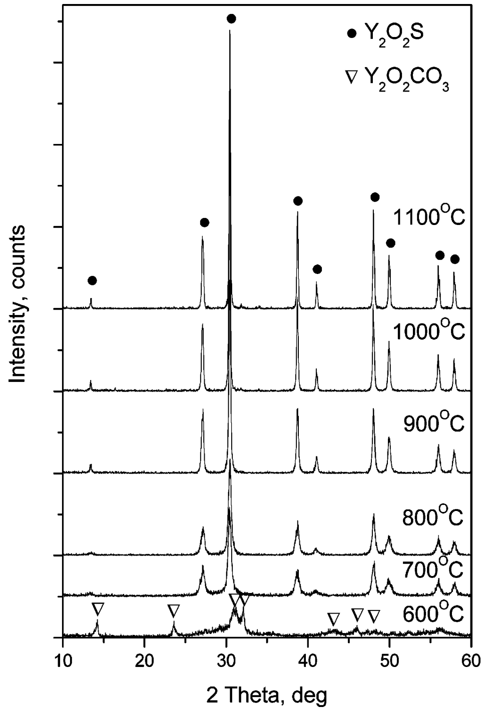

Figure 3. XRD patterns of Y_2O_2S samples prepared by homogeneous precipitation from water−ethylene glycol solution and annealed at 600−1100 °C in a sulfur atmosphere provided by a Na_2CO_3−S mixture.

corresponding to the strong reflection of $Y_2O_2CO_3$. Annealing of these powders at 600−1000 °C results in the formation of single-phase Y_2O_3. Figure 2 and Figure 3 present XRD patterns of the samples prepared from water and water−ethylene glycol solutions respectively after annealing at 600−1100 °C in a sulfur atmosphere. In the closed system with a Na_2CO_3−S mixture when the partial pressure of CO_2 is higher, annealing at 600−700 °C yields $(Y,Eu)_2O_2CO_3$ as the only phase (see Figures 2 and 3). Sulfurization and decomposition of oxocarbonate takes place above 800 °C, giving Y_2O_2S as the main product. Occasionally, Y_2O_3 can be found in the samples annealed at 800 °C, similar to the diffraction pattern in Figure 2, but it is completely absent after annealing at higher temperatures. There seems to be a correlation between particle size and presence of yttrium oxide after annealing at 800 °C, which means probably that sulfurization occurs in two independent processes:

$$2Y_2O_2CO_3 + 3S = 2Y_2O_2S + 2CO_2 + SO_2$$

and

$$Y_2O_2CO_3 = Y_2O_3 + CO_2$$

$$2Y_2O_3 + 3S = 2Y_2O_2S + SO_2$$

In the second process, the reaction between yttrium oxide and sulfur vapor is slower and we observe a residual Y_2O_3 in the samples with larger or agglomerated particles after annealing for 2 h. Annealing at higher temperature allows complete conversion into Y_2O_2S for all samples regardless of particle size and morphology. SEM photographs in Figure 4 presents Y_2O_2S:Eu powders prepared from water−ethylene glycol solution after annealing at 900−1100 °C. The most interesting observation is that, after annealing at 1100 °C, particles maintain their original morphology and crystallites growth or sintering is still insignificant, which is different from the reports on synthesis in a flux when liquid phase is present. This result demonstrates an obvious advantage of the separation of sample and flux in the space and gas transport of sulfur.

The luminescence intensities of the prepared samples were tested under excitation by an electron beam and compared against one of the best commercial samples. The data are summarized in Table 1. One may notice that even though the particles were significantly smaller than they are in the commercial product, the samples demonstrated excellent color definition and high relative intensities despite the fact that the commercial sample was tremendously refined with respect to its functional property. Increase of annealing temperature to 1200 °C leads to almost a 2-fold increase of particle size (Figure 5a) and at the same time it provides ~10% increase of relative brightness. Therefore, we decided to extend our synthesis technique for the samples with additional Tb co-doping since it is known that a small amount of Tb may increase emission intensity of Y_2O_2S:Eu.[6,10,11] The procedures were the same except for the fact that the starting solutions contained a small amount of Tb corresponding to 12.5, 25, and 50 ppm doping. Exact concentration of Tb in the obtained samples presented in Table 1 was determined by ICP-Atomic Emission Spectroscopy. Terbium co-doping and change of Na_2CO_3/S ratio during this set of experiments had very little effect on the powder morphology. SEM images of the corresponding samples are available as Supporting Information. Such Tb co-doped samples demonstrated about 10% higher intensities than one of the best commercial samples, even though Tb co-doped samples had particle size of approximately 600 nm. For 64.5 ppm Tb

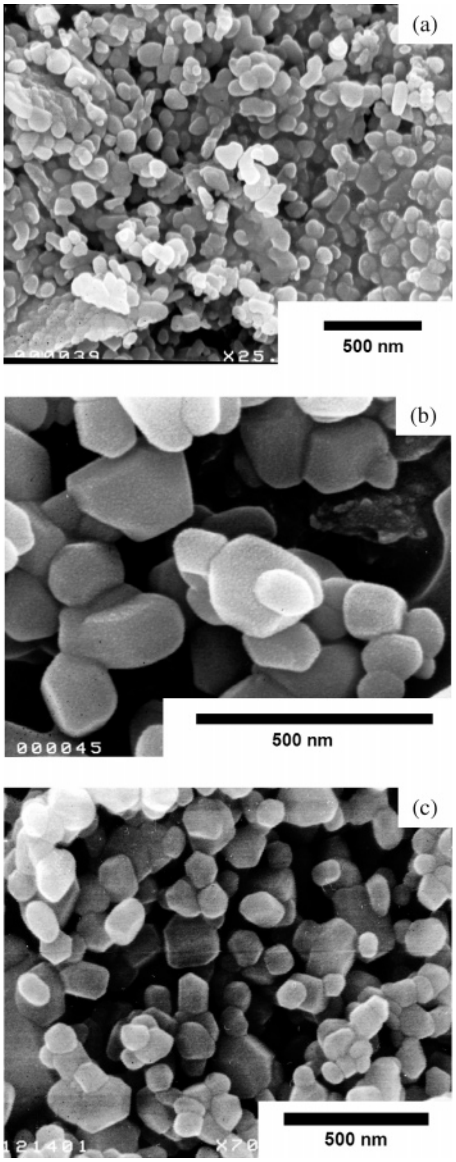

Figure 4. SEM photographs of Y_2O_2S:Eu samples prepared by homogeneous precipitation from water−ethylene glycol solution and annealed at (a) 900 °C, (b) 1000 °C, and (c) 1100 °C in a sulfur atmosphere provided by a Na_2CO_3−S mixture.

Table 1. Characteristics of Y_2O_2S Sub-micrometer Powders Prepared by Homogeneous Precipitation Method Compared against High-Performance Commercial Samples[a]

sample	temp (°C)	particle size (nm)	chromaticity coordinates (*x*/*y*)	luminosity (cd/m^2)	relative brightness (%)
water	1100	170	0.652/0.339	248.4	84
EG	1100	109	0.651/0.340	165.6	56
PG	1100	142	0.653/0.338	171.5	58
HG	1100	269	0.652/0.340	275.0	93
HG	1200	620	0.650/0.341	310.5	105
HG Tb 13 ppm	1200	600	0.649/0.342	331.2	112
HG Tb 30.8 ppm	1200	660	0.649/0.342	334.1	113
HG Tb 64.5 ppm	1200	580	0.653/0.339	310.5	105
commercial Y_2O_2S:Eu		4500	0.644/0.346	275.0	93
commercial Y_2O_2S:Eu,Tb			0.657/0.338	295.7	100

[a] 20 kV electron beam with the current density of 1 mkA/cm^2 was applied for excitation. EG: ethylene glycol; PG: propylene glycol (propan-1,2-diol); HG: hexamethylene glycol (hexane-1,6-diol).

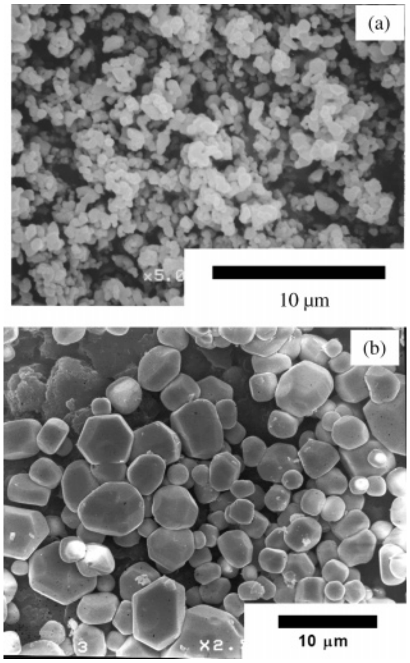

Figure 5. SEM photographs of (a) Y_2O_2S:Eu sample prepared by homogeneous precipitation from water−hexamethylene glycol solution and annealed at 1200 °C in a sulfur atmosphere over a Na_2CO_3−S mixture and of (b) commercial Y_2O_2S:Eu phosphor used as a reference.

concentration we observed a slight quenching of luminescence. Above 1200 °C we were not able to obtain single-phase Y_2O_2S by this synthesis setup. It is interesting to notice that although we could prepare samples with sub-micrometer size particles and emission intensity superior to that of the commercial 4.5 μm Y_2O_2S phosphor (its morphology is presented in Figure 5b), the decrease of particles below 300 nm did result in a gradual decline of the luminescence brightness. The samples with the average particle size close to 100 nm demonstrated <60% of the reference sample's intensity.

To understand the presented results, we have to recall that coprecipitation, which became one of the conventional techniques for synthesis of multicomponent materials, including Y_2O_2S:Eu,[6,8−11] is carried out in such a way that high supersaturation is created and it guarantees rapid formation of fine particles, final high homogeneity and precise stoichiometry of the target compound. When solubility product is achieved, formation of the precipitate becomes spontaneous. At high supersaturation, formation of solid phase is fast and it leaves very narrow room for control of particle size and shape. In the case of hydroxides, they tend to yield a fluffy, almost continuous mass with entrapped mother liquor. Therefore, the usual procedure is not very powerful when particle morphology is the primary issue.

In this work we have carried out slow precipitation of yttrium and europium hydroxides and/or oxocarbonates during the hydrolysis of urea near the boiling point of solutions. This process has apparent similarity with hydrolysis of alkoxides because the metal−oxygen network is growing steadily during decomposition of urea, when the pH slowly changes. It is not surprising that the "homogeneous precipitation" method faces challenges similar to those of the classic sol−gel method: difference in hydrolysis rate and solubility products for different metals as well as difficulty in controlling precipitate morphology. Therefore, we checked the effect of different glycols on the formation of precipitate. In this case, the presence of glycols make the "homogeneous precipitation" technique similar to the so-called "polyol process", which was proposed for the reduction synthesis of metal particles[16] and then has been extended to the preparation of fine metal oxides.[17] Here, glycols play two roles: they inhibit coagulation and change surface tension, which determines change of surface free energy and eventually the critical size of nuclei of the solid phase. Thus, hydrolysis of urea provided hydroxyl and carbonate groups and the system slowly and homogeneously approaches saturation and supersaturation state. At this stage the supersaturation is reduced by the formation of the nuclei of the new phase and their growth. However, glycol prevents nuclei of the new phase from the coagulation and they continue to grow homogeneously.[18] The next difficulty in processing of the powders is related to the possible sintering of the obtained fine particles during high-temperature annealing. Fortunately, yttrium oxide, sulfide, and oxosulfide have very high melting points (2439, 1925, and ∼2200 °C, respectively) and according to Tamman's rule one should expect that noticeable sintering will start above 1200 °C, which is quite consistent with available reports. However, to use this advantage, one should exclude the possibility of a liquid-assisted process in the flux. For this reason, we separated the solid and sulfur-containing flux and carried out the sulfurization using sulfur transferred through the gas phase. Indeed, in this case the pronounced particle growth was observed only for the powders annealed at 1200 °C.

We believe high emission intensity for these Y_2O_2S submicrometer powders became possible due to the interplay of several following factors: (i) application of solution methods allows excellent control of homogeneity of Eu and Tb doping into Y_2O_2S; (ii) formation of the precipitate without high supersaturation during an almost equilibrium process is essential for the low concentration of extended defects in the precursor particles; (iii) sulfurization at relatively high temperature results in further decrease of defect concentration due to the defects annealing; (iv) separation of flux from the solid and topochemical reaction with sulfur in the gas phase allows one to avoid pronounced sintering and obtain fine particles without additional milling.

Conclusion

The complex homogeneous precipitation carried out in the presence of glycol can yield Y_2O_2S:Eu fine particles with excellent morphology and emission intensities superior to one of the best commercial materials with much larger particles and poorly controlled morphology.

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Supporting Information Available: SEM photographs of Y_2O_2S:Eu with additional Tb doping after synthesis at 1200 °C in the sulfur atmosphere. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Sun, S.; Murray, C. B.; Weller, D.; Folks, L.; Moser, A. *Science* **2000**, *287*, 1989.
(17) Feldmann, C.; Jungk, H. O. *Angew. Chem., Int. Ed.* **2001**, *40*, 359.
(18) Fievet, F.; Lagier, J. P.; Figlarz, M. *MRS Bull.* **1989**, Dec, 29.