Synthesis of Sulfide-based Phosphors by Multiply Combined Methods Based Upon Inorganic Chemistry

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Abstract

We developed a panel of innovative solution-based approaches for synthesis of multicomponent sulfide phosphor materials. The application of these synthesis strategies allowed for preparation of high-purity and high-brightness $BaAl_2S_4$:Eu and Ba_2SiS_4:Eu phosphors and led to the discovery of new phosphors suitable for application in the LED-based lighting including Sr_2ZnS_3:Eu, $CaBaSiS_4$:Eu and $(Ba,Sr)_2ZnS_3$:Eu.

1. Introduction

Homogenous distribution of a small amount of activator ions in the host compounds is critical for achieving high brightness and color purity of emission from fluorescent materials. Although this task can be performed efficiently for multicomponent oxides by various solution technologies, preparation of complex sulfides by solution-based methods still remains a considerable challenge. The objective of our work was to develop a range of solution based synthesis techniques, which can be applicable for synthesis of high performance multicomponent sulfide based phosphor materials. In this paper we present synthesis of Eu(II) activated $BaAl_2S_4$ electroluminescent phosphor material ($BaAl_2S_4$:Eu) by a partial solution method and by direct reductive sulfurization of fine oxide precursor to illustrate the essential points of the developed synthesis methods.

2. Experimental

2.1 Partial solution method employing freeze drying.

For freeze drying synthesis 0.5172 g of Eu_2O_3 (Furuchi Chemicals, 99.9%) was dissolved in 10% excess of HNO_3 (Kanto Kagaku, 60-61%) and the solvent was evaporated completely on the hot plate set at 80°C. Then the solid europium nitrate was dissolved in ~50 ml of water and 14.2627 g of $Ba(CH_3COO)_2$ (Wako, 99%) was added to this solution. After complete dissolution of the acetate the total volume was adjusted to 100 ml. The prepared solution was sprayed directly into the liquid nitrogen, which allowed for high cooling speed. The obtained ice in liquid nitrogen was transferred to the freeze-dryer pre-cooled at –30°C and after evaporation of most of liquid nitrogen the vacuum pump was switched on. The following freeze-drying temperature regime was used: 3h at -25°C, 5h at -20°C, 8h at -15°C followed by 5h at 30°C. After sublimation of ice, the product was transferred into the large alumina crucible and inserted directly into the box furnace pre-heated to 400°C. Temperature of box furnace was increased to 800°C within one hour and the powder was calcined for 5 hours. The obtained $BaCO_3$:Eu product was ground mildly in the mortar to break coarse aggregates and heat treated in H_2S-Ar (Tanuma Sanso, 10%H_2S) flow at 950°C for 10 hours. Then, the synthesized BaS:Eu precursor was mixed in N_2 filled glove box with the stoichiometric amount of Al_2S_3 (High Purity Chemicals, 99.99%) to form ~1.5g pellet of 14 mm diameter. The pellet was cut into several pieces and sealed under vacuum into the quartz ampoule. Such samples were annealed at 900°C and 1000°C for 12 hours. After the synthesis the ampoules were opened and a piece of a pellet was crashed to obtain powder for XRD analysis and fluorescence measurements.

2.2 Reductive sulfurization of oxide precursors.

The fine oxide precursor for $BaAl_2S_4$:Eu material was prepared by the polymerizable complex method [1]. In the typical synthesis Eu_2O_3 was dissolved in nitric acid solution; the excess of HNO_3 was evaporated and europium nitrate was re-dissolved in water followed by addition of propylene glycol

(Kanto Kagaku, 99%) and citric acid (Wako, 98%). Then appropriate amounts of $BaCO_3$ (Kanto Kagaku, 99.9%) and $Al(NO_3)_3$ stock solution were added. After dissolution of the carbonate the hot plate temperature was set at $130^{O}C$ and gradually increased to $200^{O}C$ to promote polyesterification reaction between citric acid and propylene glycol. The obtained polymerized gel was subjected to pyrolysis at $450^{O}C$, and the product was annealed in air at $800^{O}C$ for 5 h. The reduction sulfurization reaction was carried out at $1000^{O}C$-$1050^{O}C$ for 2h in the constant flow of Ar passing through CS_2 (Wako, 99%) liquid at the rate of 50 ml/min. The ratio of [All metals] : [Citric Acid] : [Propylene Glycol] was 1:4:10. The concentration of Eu in all synthesized materials was 5 mol%.

The obtained materials were characterized by XRD phase analysis using RINT-2200 (Rigaku) with CuKα irradiation in the continuous scan mode operating at 2^{O}/min scanning speed. The fluorescence spectroscopy measurements were carried out by F-4500 (Hitachi) spectrafluorometer. The internal quantum efficiency values of the prepared phosphor powders were evaluated with the help of JASCO F-6500 fluorescence spectrometer equipped with the ISF-513 attachment properly calibrated using a standard light source (ESC-333, JASCO).

3. Results and discussion

Two principle approaches were proposed in this work for synthesis of multicomponent sulfide materials by use of solution methods. The first synthesis strategy referred to as a partial solution method makes use of the sulfide precursor with homogeneously distributed Eu(II) activator ions prepared by the spray-freezing and freeze-drying method for the reaction with the second sulfide component to produce a target material. The synthesis involves three steps: i) preparation of a carbonate precursor with homogeneous distribution of the activator ion by a solution method; ii) sulfurization of the carbonate precursor in the H_2S atmosphere at elevated temperature; iii) solid state reaction of the sulfide precursor containing the activator ion with the additional component(s) in the sealed volume. During the first step, the homogeneous mixing is achieved in the solution, and it is preserved during rapid freezing of the spray in liquid nitrogen. The sublimation of ice takes place in the solid phase, and therefore the homogeneity of the dry product is expected to be close to the homogeneity in the solution. $BaCO_3$:Eu forms in the first step as a result of the thermal decomposition of the acetate powder obtained after the sublimation of ice. The XRD pattern of this product corresponds to the single phase $BaCO_3$ and one can not identify any impurity phases containing Eu even for relatively high degrees of doping, which means that activator ions are uniformly distributed in the carbonate matrix, and they are not involved in any stand alone phases. Sulfurization of the carbonate phase in the H_2S atmosphere can be understood as an acid-base reaction combined with the reduction of the Eu ions. The corresponding reaction can be expressed by the following chemical equation:

$$\text{“}BaCO_3\cdot{}^{x}/_{2}Eu_2O_3\text{”} + (1+{}^{x}/_{2})H_2S \rightarrow BaS\cdot xEuS + CO_2 + (1+{}^{x}/_{2})H_2O + {}^{x}/_{2}SO_2$$

The XRD pattern of the obtained BaS·xEuS (BaS:Eu) solid product reveals formation of BaS as the main phase, which is accompanied by 2-3% of BaS_2. It should be emphasized that if EuS is present as a secondary phase in the diffraction pattern after sulfurization, it indicates poor homogeneity of the sulfide precursor and can be used as a benchmark for the successful solution processes. The solid state reaction between the BaS:Eu precursor and Al_2S_3 yields the target $BaAl_2S_4$:Eu phosphor material. The XRD pattern of the typical powder is shown in Fig.1a. most of the XRD peaks can be identified as belonging to $BaAl_2S_4$ compound (ICSD #35136). One can also identify an additional peak at 25.81^{O} for the samples synthesized in ampoules. Although there is no reasonable reference for such a phase in the powder diffraction database, we believe [2] that it corresponds to an oxysulfide by-product, which may appear either due to the presence of residual oxygen in the evacuated ampoules or partial reaction between Al_2S_3 and SiO_2. Usually small amount of such an impurity does not affect fluorescent properties of the $BaAl_2S_4$:Eu materials. The corresponding excitation and emission spectra of the $BaAl_2S_4$:Eu phosphor prepared by use of spray-freezing and freeze-dried precursor is shown in Fig. 2a. The emission spectrum contains only one symmetric peak centered at 479nm corresponding to the $4f^6(^7F)5d$-$4f^7(^8S_{7/2})$ transition of Eu^{2+} in $BaAl_2S_4$ [3] and this value of the emission wavelength is an indication of the excellent phase purity of $BaAl_2S_4$:Eu. The excitation spectrum contains two broad bands. The peak at 355 nm is assigned to 4f→5d transition of Eu^{2+}. The second peak at shorter wavelength with the maximum at 290 nm is due to the excitation of host material. The absolute emission intensity for this type of samples was 30-33% compared to one of the best

commercially available (Ba,Eu)$MgAl_{10}O_{17}$ BAM, and it did not change much with the ampoule annealing temperature or synthesis time. The internal quantum efficiency demonstrated by this material was 18%.

The second synthesis method described in this work consists of two steps: i) preparation of the homogeneous oxide precursor by a solution method that involves all metal ions in the correct stoichiometry and ii) reduction-sulfurization of the fine oxide precursor in the atmosphere containing CS_2 at elevated temperatures. The XRD pattern of the typical $BaAl_2S_4$:Eu material obtained by the reduction sulfurization is presented in Fig. 1b. One may easily notice that reflections of only one phase are present in the diffractogram demonstrating high phase quality of the prepared samples. In fact, the single phase material can be synthesized in the rather narrow temperature range of 1030-1070°C, and even under optimal annealing conditions one may obtain products contaminated by an oxysulfide (similar to ampoule synthesis) after short annealing times or insufficient flow-rate of the Ar-CS_2 gas. The excitation and emission spectra in Fig.2b for the samples prepared by reductive sulfurization in CS_2 atmosphere resemble closely the spectra of the materials prepared by partial solution method. However, one may notice that the emission peak is narrower, and it is slightly shifted to shorter wavelength indicating slightly better phase purity of the material. The fluorescence intensity demonstrated by the materials prepared via reductive sulfurization of the oxide precursors typically ranges between 30-35% with the corresponding internal quantum efficiency of 21-24%.

This work presents two main synthesis strategies for preparation of multicomponent sulfide materials employing solution based methods. $BaAl_2S_4$:Eu phosphor was used as a model compound to demonstrate the background of each technique. Although both methods yield comparable results in terms of phase composition and fluorescence emission intensities, these approaches should be clearly distinguished.

The partial solution method (the first process) is generally suitable for synthesis of sulfide materials involving volatile or low-melting point components, when one may not be able to process all metal sulfides simultaneously due to drastic differences in their chemistry. Besides, it should be mentioned that synthesis of the sulfide intermediate is not limited by the freeze-drying method. In contrast one may implement a polymerizable complex method [4],

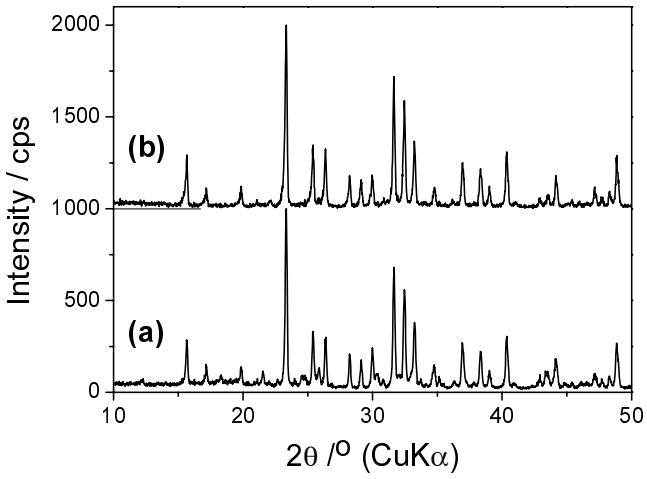

Fig. 1. XRD patterns of $BaAl_2S_4$:Eu phosphor materials synthesized by (a) partial solution method employing freeze-drying and (b) reductive sulfurization of the fine oxide precursor.

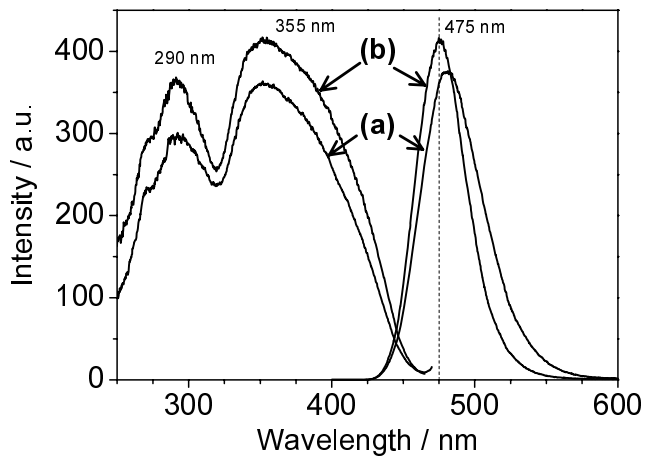

Fig. 2. Excitation and emission spectra of $BaAl_2S_4$:Eu phosphor materials synthesized by (a) partial solution method employing freeze-drying and (b) reductive sulfurization of the fine oxide precursor.

spray-drying or co-precipitation techniques [5], which can lead to the formation of an alkali-earth metal carbonate together with the dispersed activator ions. The three steps synthesis was successfully implemented for search and discovery of new fluorescent materials such as yellow emission Sr_2ZnS_3:Eu [6], $CaBaSiS_4$:Eu [7] phosphors and red emission $(Ba,Sr)_2ZnS_3$:Eu [8] fluorescence material, with the strong potential for application in the LED-based lightning. In all of these compounds the alkali-earth sulfides are combined with an unstable or a volatile sulfide, when direct reductive sulfurization of a corresponding oxide precursor does not work. The

second synthesis approach, which is based on the conversion of the oxide precursor into sulfide in CS_2 atmosphere is more straightforward; however it is more limited at the same time and can be used only for the systems far from the melting point of possible eutectic compositions or volatilization of a reduced product. We successfully applied this technique for synthesis of single phase $BaAl_2S_4$:Eu [2], Ba_2SiS_4:Eu [9] and $SrGa_2S_4$:Eu [10] phosphors. Moreover, the combination of a solution synthesis of solid state materials and a sulfurization of oxide precursors was used for preparation of high quality sulfides of multiple compositions in the parallel way and screening their fluorescent properties to discover new phosphor materials with improved functional properties. As a result of this work the unexpected nanocomposite $CaGa_2S_4$-SiO_2 phosphor material was found in which considerable enhancement of the fluorescence intensity can be realized due to a peculiar microstructure formed on the submicron scale during sulfurization of the highly homogeneous precursor powder.

4. Summary

For the first time a systematic and universal approach was proposed for preparation of multicomponent sulfide materials employing solution based techniques to achieve high homogeneity of cations distribution, excellent phase purity and capable of parallel synthesis of materials of multiple compositions for efficient discovery of new phosphors. The synthesis conditions were refined for preparation of practically important phosphors such as $BaAl_2S_4$:Eu, Ba_2SiS_4:Eu and $SrGa_2S_4$:Eu. A panel of new materials suitable for application in LED lighting was found including Sr_2ZnS_3:Eu, $CaBaSiS_4$:Eu and $(Ba,Sr)_2ZnS_3$:Eu phosphors.

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