

Direct Synthesis of BaAl₂S₄:Eu²⁺ Blue Emission Phosphor by One-Step Sulfurization of Highly Homogeneous Oxide Precursor Prepared via a Solution-Based Method

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Eu²⁺-activated barium thioaluminate (BaAl₂S₄:Eu) is a key blue emission phosphor material for full color inorganic electroluminescence display technology.¹ BaAl₂S₄:Eu demonstrates excellent emission brightness and a short decay time; its color coordinates match the NTSC (National Television System Committee) standard for blue color. Although blue fluorescence of BaAl₂S₄:Eu was reported more than 30 years ago by Donohue and Hanlon,² this compound has attracted significant attention only recently after Miura et al. reported³ that blue emission from a thin-film electroluminescence device employing BaAl₂S₄:Eu exhibited high brightness, and this material is a promising blue phosphor for applications in inorganic EL devices. The prototype of a high-definition 34 in., full color display using this compound and pilot industrial technology were developed by iFire a few years later.⁴ The proposed thick dielectric electroluminescent (TDEL) display technology utilizing the color-by-blue (CBB) scheme, which uses only one high brightness BaAl₂S₄:Eu EL phosphor together with green and red color conversion pigments, allowed for the achievement of ~1000 cd/m² display brightness.⁴ Although iFire has experienced difficulties in terms of rapid commercialization of this technology because of a relatively lower color depth and contrast of the TDEL screens when compared to the modern liquid crystal (LCD) and plasma displays, the low manufacturing cost and low target price of a large screen high definition televisions make this technology attractive for next-generation full color flat panel displays.⁵

The synthesis of good quality BaAl₂S₄:Eu still presents certain challenges. Currently, the solid-state reaction between

individual metal sulfides in evacuated quartz ampoules^{6–9} or in a flow of H₂S^{10,11} is the main method for synthesis of BaAl₂S₄:Eu material. Annealing in a gas flow is more common for preparation of thin films either by two-source deposition^{3,10,12} or by sulfurization of Ba–Al–Eu alloy.⁴ Although it is recognized that kinetics of the interaction between BaS and Al₂S₃ is relatively rapid,^{6,10} one can hardly expect that homogeneous distribution of the Eu²⁺ activator in a BaAl₂S₄ host can be achieved after just a few hours of conventional sintering.

The application of soft solution methods for the synthesis of BaAl₂S₄:Eu could be an appealing alternative to the conventional ceramic method. Nevertheless, to the best of our knowledge, solution techniques have not been used for the synthesis of this inorganic EL phosphor, with the exception of our previous study¹³ on a two-step synthesis strategy, which made use of a BaS:Eu intermediate for the reaction with Al₂S₃. One may expect that solvothermal synthesis of chalcogenides in organic solvents,¹⁴ ammonothermal preparation of sulfides,¹⁵ or reactions with sulfur in hydrazine solutions¹⁶ applied for the synthesis of various sulfide materials may provide the key for the development of a solution technique for the synthesis of BaAl₂S₄:Eu. However, up to now, no direct synthesis of BaAl₂S₄ by any solution based method has been reported.

We believe that a convenient application of solution synthesis may be connected with the preparation of a multicomponent homogeneous oxide precursor and its direct conversion into a sulfide by final annealing. Although sulfurization in H₂S gas flow is frequently used for the preparation of strontium and barium thiogallates^{17,18} by conventional solid-state reactions starting from metal oxides and carbonates, the same sulfurization approach is inappropriate for BaAl₂S₄:Eu because of the higher stability of Al₂O₃ compared to Ga₂O₃. Nevertheless, it provides a useful hint for the development of solution synthesis of BaAl₂S₄.

This paper describes a simple synthesis of BaAl₂S₄:Eu phosphor material employing a solution method. A fine

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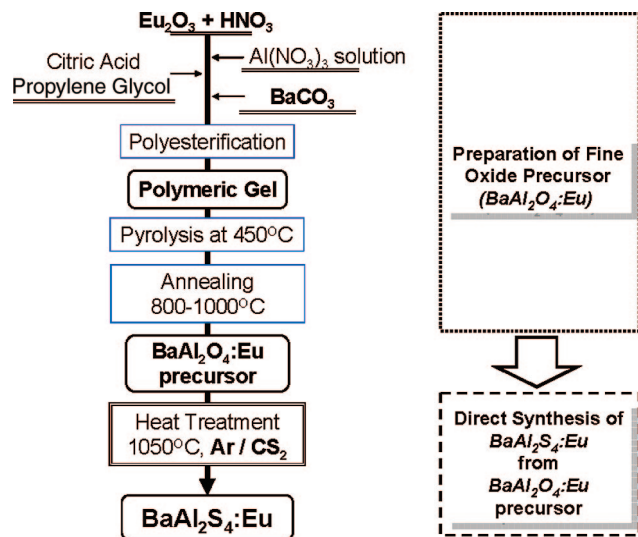


Figure 1. Flowchart of $\text{BaAl}_2\text{S}_4:\text{Eu}$ synthesis employing polymerizable complex method and sulfurization-reduction.

oxide-carbonate precursor was prepared by the polymerizable complex method.¹⁹ This technique provides a superior means for obtaining fine multicomponent oxide powders with excellent homogeneity of cation distribution. In addition, pyrolysis of the polymeric gel very frequently occurs below the crystallization temperature of the target oxide, which allows for the preparation of very active precursors for oxide or sulfide materials. Such a fine oxide was transformed into $\text{BaAl}_2\text{S}_4:\text{Eu}$ by annealing in a CS_2 atmosphere. The experimental procedures are provided in the Supporting Information. The schematic description of this synthesis is displayed in the flowchart in Figure 1.

Appropriate metal salts are dissolved in a solution of citric acid in glycol in the required stoichiometry. Citric acid chelates metal ions to form stable complexes. The temperature of the solution is gradually increased to 130–200 °C to promote the polyesterification reaction between free citric acid and glycol. The metal complex species trapped by the polymeric network remain uniformly mixed as in the solution. Pyrolysis of the polymer starts at around 400 °C, and the remaining carbon is eliminated by annealing above 600 °C. Thermogravimetric analysis of the sample after pyrolysis at 450 °C is included in the Supporting Information. The sample loses weight continuously up to 600 °C by the release of absorbed water followed by the oxidation of residual organic compounds. In the range of 600–890 °C, the weight remains almost constant. Annealing of the sample at 800 °C yields a fine white powder; the XRD pattern for this powder is shown in Figure 2a. Such a sample consists of amorphous oxide and carbonate phases with a small amount of BaAl_2O_4 , whose diffraction peaks start to appear in the XRD. The formation of the BaAl_2O_4 phase occurs above 890 °C, accompanied by CO_2 release resulting in weight loss in the TG curve. The precursor annealed at 1000 °C yields BaAl_2O_4 as a single phase (Figure 2b). For sulfurization by CS_2 , we selected the fine oxide precursor prepared at 800 °C.

Caution! CS_2 is a toxic and flammable compound. It affects the human nervous and reproductive systems and

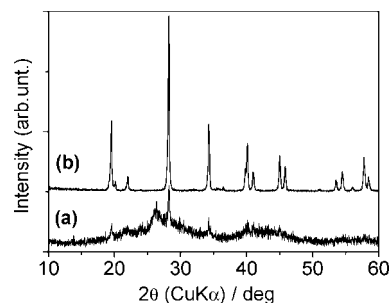


Figure 2. XRD patterns of the $\text{BaAl}_2\text{O}_4:\text{Eu}$ fine precursor obtained by annealing at (a) 800 and (b) 1000 °C.

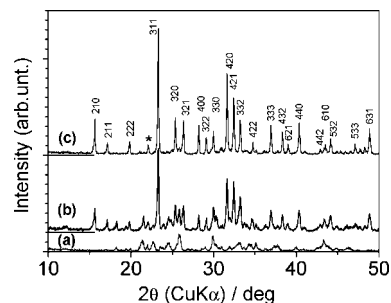


Figure 3. XRD patterns of the powders obtained from fine $\text{BaAl}_2\text{O}_4:\text{Eu}$ precursor after (a) one, (b) two, and (c) three times annealing in the Ar/CS_2 gas flow at 1050 °C. The diffraction peaks (c) are indexed as belonging to the cubic BaAl_2S_4 phase with $a = 12.6286(2)$ Å.

large intake is fatal. One should protect skin from direct contact with CS_2 because it penetrates skin. Experiments should be carried out in a room with good ventilation. Ignition of CS_2 occurs upon heating, because of contact with strong oxidizers or Zn dust.

This fine powder was annealed at 1050 °C for 6 h in a tube furnace in an Ar/CS_2 gas flow created by bubbling Ar carrier gas through CS_2 at room temperature. After sulfurization, the powder emitted green-blue light upon excitation by a UV lamp, indicating reduction of Eu^{3+} to the Eu^{2+} state. The XRD pattern of this sample is presented in Figure 3a. The intensities of the XRD peaks are low and the crystalline phase does not have a match in the PDF database. However, all strong reflections can be identified as belonging to the monoclinic phase ($a = 15.0452(7)$ Å, $b = 14.8541(7)$ Å, $c = 8.7182(4)$ Å, $\beta = 106.46(3)^\circ$), and its lattice parameters are close to those of $\text{Ba}_2\text{Al}_2\text{S}_5$ reported by Le Thi et al.⁹ Moreover, the distribution of the intensities resembles the XRD pattern of the $\text{Sr}_2\text{Ga}_2\text{S}_5$ phase (PDF card 79–1955), which may suggest a similar crystal structure. However, SEM-EDS characterization of the sample revealed neither the presence of $\text{Ba}_2\text{Al}_2\text{S}_5$ nor the formation of Al-rich phases, which would be expected to accompany the Ba-rich phase considering the starting stoichiometry. Moreover, the Ba:Al ratio in 10 randomly selected regions of the sample showed a reproducible composition close to 1:2. In addition, in each analyzed region, the oxygen peak in the EDS spectrum was rather strong compared to the typical intensity for pure sulfides, whereas the sulfur content with respect to the metals was below the expected value. Combining the metal and sulfur ratios determined by EDS with the charge neutrality, and assuming the presence of oxygen in this compound, the approximate bulk composition of this phase

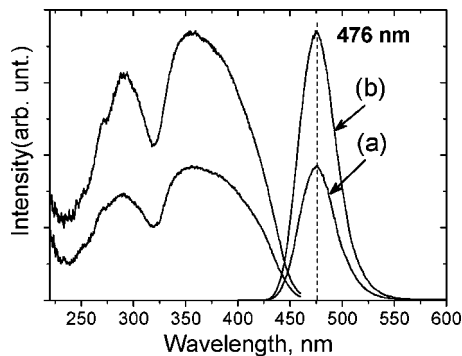


Figure 4. Excitation ($\lambda_{em} = 475$ nm) and emission ($\lambda_{ex} = 305$ nm) spectra of (a) as-prepared and (b) ground powders of $BaAl_2S_4:Eu$ synthesized by the sulfurization-reduction method.

was obtained as $BaAl_{2.43}S_{2.17}O_{2.48}$. Thus, it was concluded that sulfurization does occur, though it is not complete, and an oxysulfide phase forms as an intermediate compound. We therefore concluded that additional annealing in the Ar/CS_2 gas flow was necessary. Patterns b and c in Figure 3 present XRD patterns of the samples after the second and third annealing. $BaAl_2S_4:Eu$ was found to be the main phase after the second annealing, whereas the third annealing yielded an almost single phase cubic $BaAl_2S_4:Eu$. The secondary phase present in a small amount and marked by an asterisk in Figure 3c could not be identified. According to EDS analysis in 10 randomly selected regions of the obtained material, the average Ba/Al ratio was 2.03 and the standard deviation was 1.28 times smaller than for the sample prepared by the conventional method. This result indicates substantially better homogeneity of the material prepared by the solution method compared to $BaAl_2S_4$ synthesized by the solid state reaction.

The fluorescence spectra of the sample after the final annealing are presented in Figure 4. The emission spectrum consists of a single peak centered at 476 nm corresponding to the $4f^6(7F)5d-4f^7(8S_{7/2})$ transition of Eu^{2+} in the $BaAl_2S_4$ host.²⁰ No peaks are seen at longer wavelengths, suggesting that other barium thioaluminates, which could form because of competing reactions, are absent. The “as-prepared” powders had a gray color. After short grinding, the color of the powder became lighter and the emission intensity significantly improved, as shown in plots a and b in Figure 4, reaching 30% of the intensity of commercial $BaMgAl_{10}O_{17}:Eu$. The dark color can be explained by carbon deposition on the powder surface during the reduction, whereas the stronger emission after the grinding is a result of the breaking of weakly agglomerated particles and exposure of fresh surface to the excitation light. The presence of carbon was confirmed by Raman spectroscopy (Figure 5), which revealed relatively strong peaks corresponding to the sp^2 -hybridized

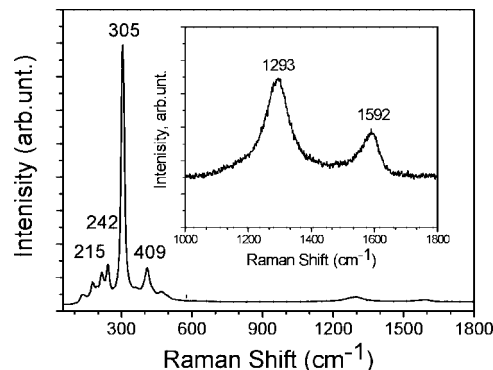
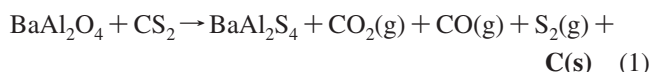


Figure 5. Raman spectrum of $BaAl_2S_4:Eu$ prepared by sulfurization-reduction method. Inset displays the spectrum range between 1000 and 1800 cm^{-1} with the characteristic peaks of sp^2 carbon (graphite).

carbon (graphite)²¹ in the as-prepared samples. The presence of carbon on the $BaAl_2S_4:Eu$ surface is a result of the reduction process that occurs according to the following scheme:



We are currently unable to carry out reduction without the simultaneous formation of carbon; however, further progress can be expected after the process parameters are fine-tuned that primarily affect the $CO_2 + C = 2CO$ equilibrium.

We should emphasize the significance of the active precursor consisting of preferably amorphous phases for the described sulfurization process. When the $BaAl_2O_4:Eu$ powder obtained at 1000 °C (Figure 2b) was used in this synthesis, the final product always contained a considerable amount of secondary phases. The XRD pattern of the resultant sample is available as Supporting Information.

The synthesis route described here is insensitive to ambient humidity because it does not have to deal with unstable sulfides such as BaS and Al_2S_3 used in the usual ceramic method. Therefore, the utilization of a glovebox for sample handling or annealing in ampoules is not required. The overall cost of reagents for the proposed solution based synthesis is $\sim 70\%$ lower than the cost of the sulfides needed for the conventional solid state reaction.

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Supporting Information Available: Experimental procedures, TG-DTA of the precursor, XRD pattern of the sample obtained by sulfurization of crystalline $BaAl_2O_4$ (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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