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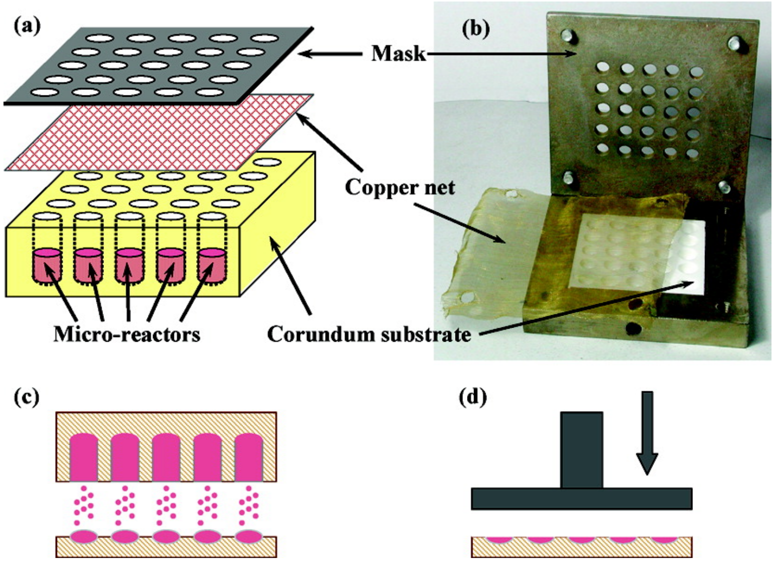

Parallel Solution Combustion Synthesis for Combinatorial Materials Studies

Zhen-Lin Luo,[†,‡] Bin Geng,[†,‡] Jun Bao,[†,‡] and Chen Gao*,[†,‡]

National Synchrotron Radiation Laboratory and Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei, Anhui 230026, China, and Department of Physics, University of Science and Technology of China, Hefei, Anhui 230026, China

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A parallel solution combustion synthesis technique was developed for combinatorial materials studies. The vigorous combustion reactions were successfully limited in the microreactors by using a substrate−net−mask microreactor system and the lowest adoptable furnace temperature. Using this technique, a luminescent materials library of $Y_3Al_5O_{12}/Tb_x$ was synthesized with the aid of an ink-jet delivery system. Structure and luminescence characterizations were implemented using X-ray diffraction and UV/X-ray spectroscopies, respectively. The results show that this technique is reliable and applicable to combinatorial study of powder materials with high synthesis temperature.

Introduction

During the past decade, combinatorial materials science has attracted significant attention due to its potential high efficiency in discovery and optimization of novel materials. Many materials have been studied through this efficient strategy.[1−5] However, the high synthesis temperature required for many inorganic functional materials makes it difficult to apply this strategy to the combinatorial studies of these materials. Compared with the solid-state reaction, wet chemical methods can produce homogeneous materials at relatively low temperature due to the molecular-scale mixing of the precursors in solution. Among them, sol−gel, co-precipitation, and hydrothermal synthesis have been successfully applied to combinatorial studies of catalyst, zeolite, etc.[6−10] The solution combustion (SC) method is an important wet chemical synthesis technique which was first proposed by J. J. Kingsley and K. C. Patil in 1988.[11] This method has the advantage of instantaneous high temperature. This unique characteristic makes it very suitable for efficient synthesis of high-temperature materials. So far, to the best of our knowledge, this method has not been applied to the study of combinatorial materials.

Solution combustion synthesis involves an exothermic reaction between an oxidizer (such as metal nitrates) and an organic fuel (typically urea, glycine, or carbohydrazide). In such a reaction, the precursor mixture of oxidizer, organic fuel, and water decomposes, dehydrates, and ruptures into a flame. The chemical energy released from the exothermic redox reaction can instantaneously heat the reaction system up to a high temperature (>1500 °C) without external heat input. Porous crystalline or amorphous powder can be formed in a gleam. Using this method, various complex ceramics which require high-temperature sintering, such as aluminates, ferrites, and chromites, have been successfully synthesized and studied.[11−15] Since the combustion reaction is so violent that the synthesized fine powder often flies out of the reaction container, how to keep the products in the microreactors and prevent them from mixing with each other becomes a key factor for the materials library synthesis using this method.

In this paper, we describe a combinatorial synthesis technique based on the SC method that we have developed. A microreactor array drilled on a ceramic substrate was used as the parallel solution combustion reactors. To decrease the reaction strength and limit the products inside the microreactors, the lowest adoptable furnace temperature and a substrate−net−mask mechanism were adopted. Using this technique, a $Y_3Al_5O_{12}/Tb_x$ luminescent materials library was synthesized. XRD and UV/X-ray photoluminescence (PL) were implemented for library characterization. The result is in agreement with that from conventional scale synthesis reported in the literature.

Experimental Section

Figure 1a and b show the schematic diagram as well as a photograph of the substrate−net−mask microreactor array system, respectively. The bottom is a corundum substrate with a predrilled miniwell array. The wells are 5 mm in diameter, 8 mm in depth and act as the microreactors. A copper net is covered over the substrate to prevent the reaction products from flying out of the wells. On top of the net is a metal mask with a through-hole array, which has the same diameter and interval as that of the substrate. The mask is pressed firmly against the substrate with four screws at the four corners so that the copper net covers the substrate tightly to prevent the synthesized powders in different microreactors from flying out and mixing with each other. Because the powder in the deep wells is sometimes hard to

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* Corresponding author. E-mail: cgao@ustc.edu.cn.

[†] National Synchrotron Radiation Laboratory and Hefei National Laboratory for Physical Sciences at Microscale.

[‡] Department of Physics.

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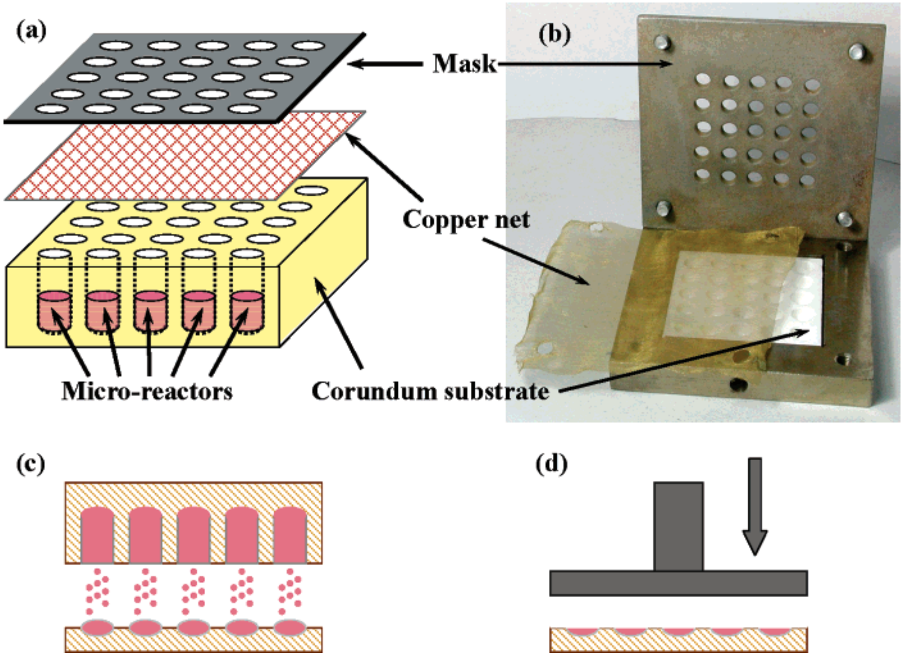

Figure 1. (a) Schematic diagram and (b) photograph of the substrate−net−mask microreactor array system. (c) A plastic substrate with the same predrilled shallow (2 mm in depth) well array was assembled with the library and then flipped over so that the synthesized powder materials drop into the shallow wells. (d) After removal of the corundum substrate, a metal plate was used to compact the powders.

characterize, additional steps may be adopted to transfer the powders to a shallow-well substrate, as shown in Figure 1c and d.

The SC reaction is a complex process and could be affected by many factors, such as the type of fuel, fuel-to-oxidizer ratio, furnace temperature, etc.[16−18] Using low furnace temperature can effectively decrease the strength of the SC reactions. Our previous study shows that the ignition temperatures for the formation of Y_2O_3 (eq 1) and $Y_3Al_5O_{12}$ (eq 2) from the nitrate−glycine combustion are ∼210 and 250 °C, respectively.[19] To achieve the lowest reaction temperature, the furnace temperature in our experiments was held at 200 °C for 30 min and then slowly increased to 300 °C at the rate of 3 °C/min. During this period, the combustion is ignited spontaneously as the temperature reaches the ignition temperature.

$$6Y(NO_3)_3 + 10NH_2CH_2COOH \rightarrow 3Y_2O_3 + 14N_2\uparrow + 25H_2O\uparrow + 20CO_2\uparrow \quad (1)$$

$$9Y(NO_3)_3 + 15Al(NO_3)_3 + 40NH_2CH_2COOH \rightarrow 3Y_3Al_5O_{12} + 56N_2\uparrow + 100H_2O\uparrow + 80CO_2\uparrow \quad (2)$$

Before going to the combinatorial materials study, a test library containing alternatively arranged $Y_2O_3/Eu_{0.01}$ and $Y_2O_3/Tb_{0.01}$ samples was synthesized to check if the reactions and the reaction products could be limited inside the microreactors. With the aid of a homemade ink-jet delivery system,[20] precursor solutions (>99.99% purity) of 0.24 M $Y(NO_3)_3$, 0.024 M $Eu(NO_3)_3$, 0.024 M $Tb(NO_3)_3$, and 1.06 M glycine were dispensed into the microreactors according to the stoichiometric ratio in eq 1 (Eu and Tb were added as dopants to replace Y), and the amount of metal cations in each microreactor was kept constant (6.4×10^{-6}mol). Subsequently, 40 μL of deionized water was added into every microreactor, and the as-deposited library was left in air 10 h for diffusion. After that, the library was assembled with the copper net and the metal mask and placed in an electrical furnace at 200 °C for 30 min. Then the furnace temperature was increased to 300 °C at the rate of 3 °C/min. SC reactions took place in every microreactor during this period. Finally, the library was annealed at 900 °C for 1 h. Figure 2 is a luminescent photograph of the test library under 254-nm UV excitation. Emission spectra from the two materials were acquired using a scanning fiber spectrometer,[20] as shown in Figure 3. From the spectral purity, it was concluded that the SC reactions were successfully limited in the microreactors. The integrated emission intensity of $Y_2O_3/Eu_{0.01}$ and $Y_2O_3/Tb_{0.01}$ from different microreactors is plotted in Figure 4. A fluctuation of ∼9% has been observed. Considering that there is a 10% fluctuation in the ink-jet delivery system,[20] this result is reasonable.

Furthermore, a luminescent library of terbium doped yttrium aluminum garnet, $Y_3Al_5O_{12}/Tb_x$, was synthesized to demonstrate the applicability of the parallel SC synthesis

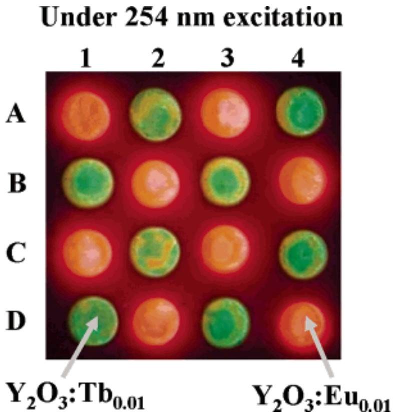

Figure 2. Luminescence photograph of the test library, which consists of alternatively arranged $Y_2O_3/Eu_{0.01}$ (red) and $Y_2O_3/Tb_{0.01}$ (green) samples.

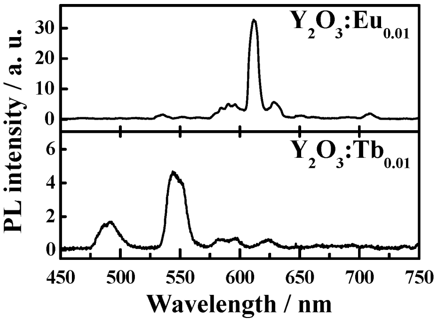

Figure 3. Emission spectra of the $Y_2O_3/Eu_{0.01}$ and $Y_2O_3/Tb_{0.01}$ samples under 254-nm UV excitation.

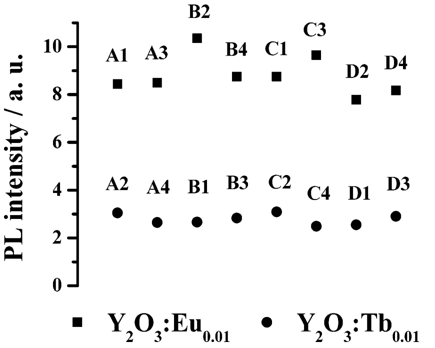

Figure 4. Integrated emission intensity of samples in the test library under 254-nm UV excitation.

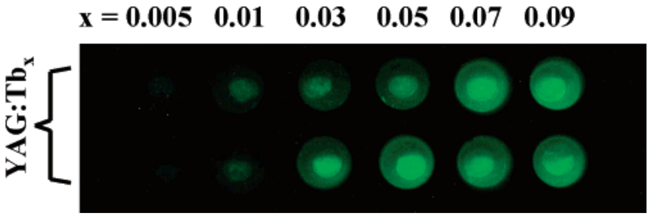

Figure 5. Composition map and luminescent photograph of the YAG/Tb$_x$ library under 254-nm UV excitation.

technique to high-temperature materials. The composition map is shown in Figure 5. The synthesis procedure is similar to the above description except for the following differences: one more precursor, 0.4 M $Al(NO_3)_3$ solution, was used, and the library was calcined at 1000 °C for 1 h. UV PL and X-ray PL of the synthesized library were characterized. Structure analysis on a few selected individual samples was conducted using the conventional X-ray diffraction method on a rotating anode X-ray diffractometer (model MXPAHF, Mac Science) with CuK_α radiation ($\lambda = 0.154\ 19$ nm).

Results and Discussion

$Y_3Al_5O_{12}$ (YAG) is an important luminescent host material, which has a high synthesis temperature for conventional solid-state reaction (typically >1600 °C for several hours).[21] The SC method has the potential to significantly reduce the synthesis temperature and the sintering time. The XRD patterns of two selected samples ($Y_3Al_5O_{12}/Tb_x$, $x = 0.005$ and 0.09) in the library are presented in Figure 6. The two samples exhibit the same diffraction peaks, which can be indexed to the yttrium aluminum garnet phase ($Y_3Al_5O_{12}$, PDF No. 33-0040). This result indicates that pure phase YAG powder had been simultaneously synthesized in the microreactors using the SC reaction with a relatively quick calcination at lower temperature than that of a conventional solid-state reaction.

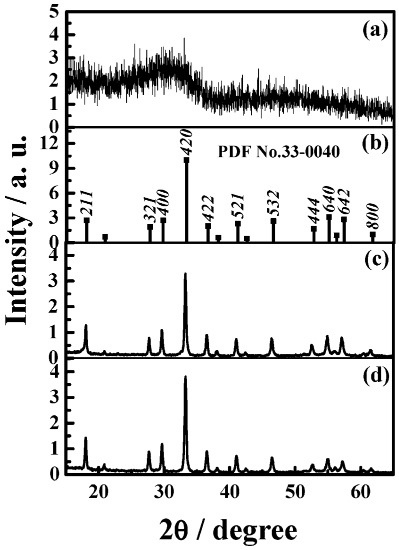

Figure 6. (a) X-ray diffraction pattern of the as-combusted $Y_3Al_5O_{12}/Tb_{0.005}$ powder. The diffuse scattering heap indicates that the as-combusted powder is in an amorphous or highly disordered state. (b) Standard powder diffraction pattern of $Y_3Al_5O_{12}$. (c, d) X-ray diffraction pattern of two selected samples from the $Y_3Al_5O_{12}/Tb_x$ materials library calcined at 1000 °C/1 h: $Y_3Al_5O_{12}/Tb_{0.005}$ and $Y_3Al_5O_{12}/Tb_{0.09}$, respectively.

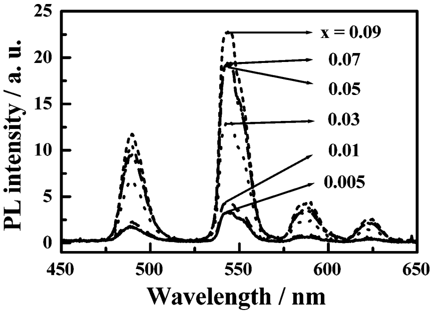

Figure 7. Emission spectra of the YAG/Tb$_x$ samples under 254-nm UV excitation.

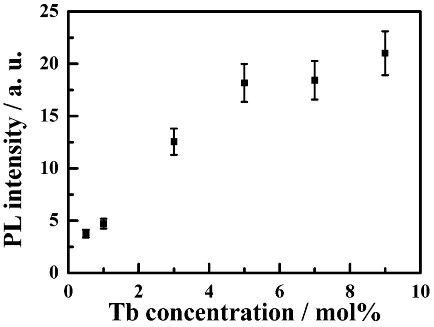

Figure 8. Integrated intensity of the Tb $^5D_4 \rightarrow {}^7F_j$ emission (450−650 nm) of YAG/Tb$_x$ samples as a function of Tb concentration under 254-nm UV excitation.

Figure 5 shows a luminescent photograph of the library under 254-nm UV excitation. The UV PL spectra shown in Figure 7 reveal that Tb $^5D_4 \rightarrow {}^7F_j$ emission (450−650 nm) dominates the spectra, and the emission intensity increases with the Tb concentration. Figure 8 shows the integrated emission intensity of Tb $^5D_4 \rightarrow {}^7F_j$ emission as a function

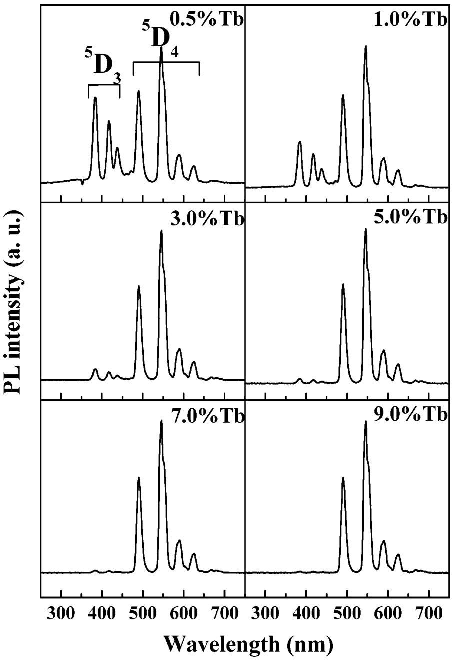

Figure 9. X-ray photoluminescence spectra of the YAG/Tb$_x$ samples.

of Tb concentration. From this figure, it can be concluded that the optimum doping concentration of Tb is ~5 mol %, which fairly agrees with conventional results.[22]

To investigate the influence of Tb concentration on the emission spectral distribution of the YAG/Tb$_x$ under X-ray excitation, the luminescent library was transferred into a shallow-well substrate, and the X-ray PL was characterized using a homemade X-ray characterization system.[23] Figure 9 shows the emission spectra of the YAG/Tb$_x$ samples under hard X-ray excitation. The branch ratio of the integrated emission intensity of $^5D_3 \rightarrow {}^7F_j$ to $^5D_4 \rightarrow {}^7F_j$ as a function of Tb concentration is plotted in Figure 10. The ratio decreases from 0.53 (YAG/Tb$_{0.005}$) to 0.01 (YAG/Tb$_{0.09}$), which coincides with that from the conventional scale SC reaction.[24] The dependence of the branch ratio on the Tb concentration has been extensively studied and is well-explained with the cross-relaxation theory.[22,25] This dependence can be used as intrinsic evidence of the phase formation and uniform doping. The quantitative agreement indicates that the designed materials are synthesized successfully, and the parallel SC microreactions can be applied to a combinatorial study of high-temperature materials.

Conclusion

In conclusion, a parallel SC synthesis technique has been developed and applied to combinatorial materials library synthesis. The vigorous combustion reactions were successfully limited in the microreactors by using a substrate−net−mask reactor system and the lowest adoptable furnace temperature. Using this technique, a luminescent materials library of $Y_3Al_5O_{12}$/Tb$_x$ was synthesized with a relatively quick calcination at relatively low temperature (1000 °C for 1 h). The XRD and UV/X-ray PL results agree well with that from conventional-scale syntheses reported in the literature, indicating good reliability of this synthesis technique.

On the basis of the advantages of SC method, we expect that this parallel SC synthesis technique is also suitable for combinatorial studies of metastable materials and nanoscale materials with large specific surface. Combinatorial studies of catalyst and photocatalyst using this technique are currently underway in our group.

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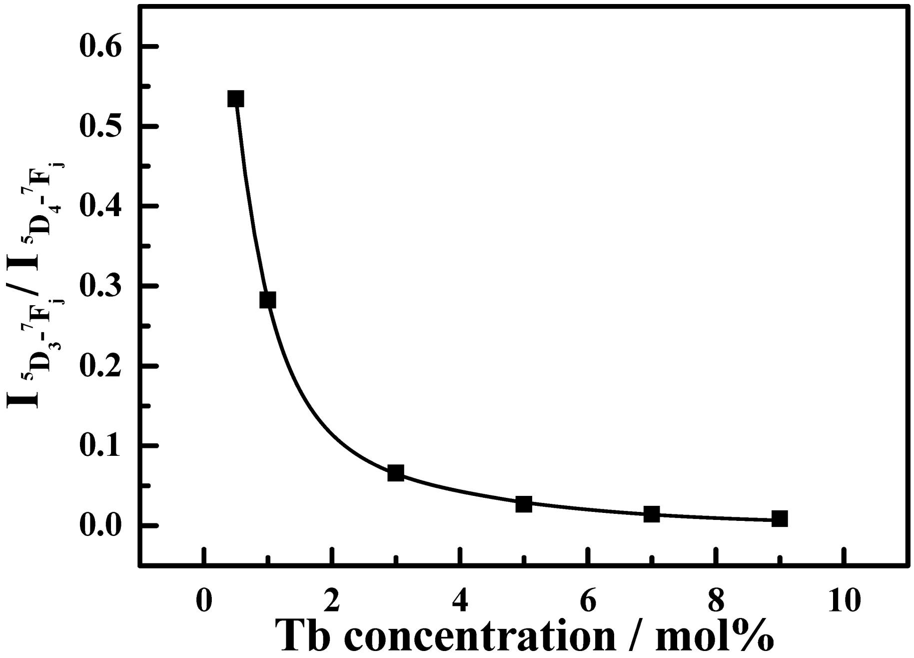

Figure 10. The branch ratio of the integrated intensity of Tb $^5D_3 \rightarrow {}^7F_j$ emission to $^5D_4 \rightarrow {}^7F_j$ emission of YAG/Tb$_x$ samples as a function of Tb concentration (under hard X-ray excitation).

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