

A Novel Protein Gel Route to Synthesize Luminescent $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ Powders Calcined at Lower Temperature

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A novel protein gel method was developed to synthesize composite oxide phosphors, in which ovalbumin was used as gelling agent. By this route, $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ powders were obtained at 700 °C with a size of less than 50 nm. Under ultraviolet excitation, the emission peak is located around 510 nm. This simple method is applicable to high-throughput synthesis.

Recently, lutetium compounds have aroused much interest, especially in scintillator research. That is because most of them have high density, good mechanical properties, good radiative stability, and high light yield. While lutetium oxide, fluoride, silicate, and aluminate single crystal scintillators are being further studied,^{1–3} some translucent lutetium compound ceramics have been also researched^{4,5} for several years. Among the big family of lutetium compounds, rare-earth-doped lutetium aluminum garnet (LuAG:Re) is one of the most important objects of study. Compared with single-crystal scintillators, the advantages of ceramic scintillators are very obvious, with simpler preparation, quite lower cost, higher doping amount, and better homogeneity. In previously reported research, there have been two main problems left to be solved, the first one is that sintering needs to be developed to get a higher transmittance, and the second one is that composition (doping species and amount) should be optimized to obtain higher emission and shorter decay time. Both of the two problems can be cut through the research of precursor powders. Additionally, as lutetium element has low abundance in the crust, its compounds are very expensive. Therefore, a more efficient way is to use a combinatorial approach^{6,7} for a fast screening to optimize the composition of LuAG:Re phosphors. And also, simple and homogenous synthesis methods are required. In the present research, we chose LuAG:Ce³⁺ powders as target material and developed a new “protein gel” preparation method. By using this method, we obtained LuAG:Ce³⁺ powders in a simple way. Compared with sol-gel synthesis, this protein gel method is a simple operation and requires lower reaction temperature. So, this method can be applied in ink-jet combinatorial approaches which require water-soluble starting material, simple reaction, and good homogeneity.

Appropriate amounts of aluminum oxide (Al_2O_3 , 99.99%) and lutetium oxide (Lu_2O_3 , 99.95%) were dissolved in concentrated nitric acid to form $\text{Al}(\text{NO}_3)_3$ and $\text{Lu}(\text{NO}_3)_3$ solutions. The two kinds of solutions were well mixed in stoichiometric ratio (Lu:Al = 3:5), and 1 mol% (relative to Lu) cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.9%) was added. Aqueous ammonia was used to adjust the pH to 7. About 100 mg mL⁻¹ amount of ovalbumin was then added. After intensive stirring, the protein solution was heated at 90 °C in an oven. When the heat denaturation was completed, a stable yellow gel was obtained. The precursor gel

was then vacuum dried at 120 °C and annealed at various temperatures from 600 to 1100 °C for 2 h in a muffle furnace.

The crystalline phase was identified by X-ray diffraction analysis (XRD, Model D/MAX-2550V) using $\text{Cu K}\alpha$ radiation. The thermal reactions were followed in static air by simultaneous TG and DTA with heating rate of 10 °C min⁻¹ (STA449, Netzsch). The microstructure and morphology were examined using a transmission electron microscope (TEM, Model 200CX, JEOL, Tokyo, Japan). Photoluminescence spectra were obtained using a Perkin-Elmer LS-55 luminescence spectrometer with a xenon discharge lamp. The emission spectra under 365 nm Hg lamp of micro samples were examined by an Ocean Optics SD4000 fiber spectrometer; the spot diameter can be adjusted as small as 1.0 mm. All the measurements were performed at room temperature.

Figure 1 presents the XRD patterns of LuAG:Ce³⁺ powders from the protein gel route annealed at different temperatures. It can be seen that the garnet phase was obtained at temperatures as low as 700 °C, and no intermediate phase was observed. With the temperature increasing, continuous refinement of peak shapes and increased intensity are observed, those correspond to the grain growth. Micromorphology of LuAG:Ce³⁺ powders annealed at 800 °C was recorded and is presented in Figure 2. At this temperature, most of the grains appear ellipsoidal with a maximum size of about 50 nm.

It is well known that ovalbumin is a globular egg white protein, with a radius of about 3 nm and a molar mass of 46000 g mol⁻¹. At neutral pH, heating an ovalbumin solution will result in the formation of fibrillar aggregates. The dependence of the interfiber distance (d_{max}) for aggregates on the protein concentration (C) was found to be $d_{\text{max}} \propto C^{-0.51}$, this scaling behavior is in good agreement with that theoretically derived for the distribution of spaces in a random network of

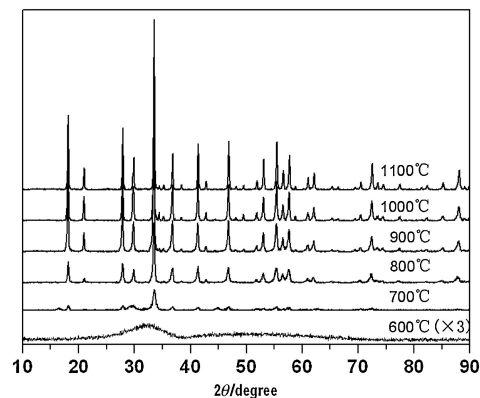


Figure 1. XRD patterns of LuAG:Ce³⁺ powders annealed at various temperature, from 600 to 1100 °C.

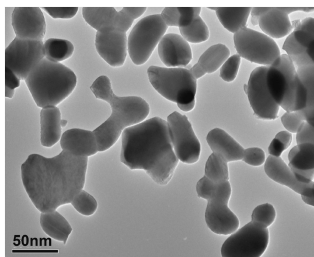


Figure 2. TEM photograph of LuAG:Ce³⁺ powders annealed at 800 °C for 2 h.

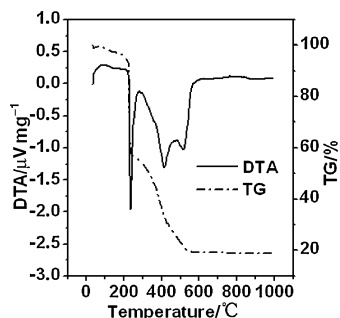


Figure 3. TG-DTA curves of LuAG:Ce³⁺ gel (heating rate: 10 °C min⁻¹, sample weight: ca. 10 mg).

straight fibers.^{8,9} When the protein gel was dried, precursor nitrate powders homogenized in nanoscale were obtained, which benefit from protein polarity and three-dimensional effects of the network. Another role protein gel has played was as a combustion agent during the calcine process. The thermal process may be depicted as in Figure 3, which shows the TG-DTA curves of the xerogel. The exothermic peaks at 400–600 °C arose from the pyrolysis of protein, corresponding to about 40% loss of weight. The intensive combustion evoked formation of microcrystal nucleus, and the subsequent reaction might be induced at a low temperature (700 °C).

Figure 4 shows the excitation and emission spectra of LuAG:Ce_{0.01} powders. Two excitation bands around 460 and 348 nm were observed, corresponding to 4f–5d electron transitions. The emission peak is at 510 nm. We also measured the emission spectrum under excitation of 365 nm, which is the wavelength of a high-pressure Hg lamp.

In order to apply this method to high-throughput synthesis, a primary experiment of eight small samples with different Ce content were prepared. The experiment was as follows: raw material solutions of different stoichiometric ratio were taken by a microsample injector and mixed in a deep-well multiwell plate (capacity volume of each well was 4.0 mL). After being well mixed by vibrator, the solutions were removed to microwells drilled on an Al₂O₃ ceramic plate (capacity volume of each well was about 20 μL). Another ceramic plate of the same shape was put reversely to prevent the mixing of powders during the next steps. The heat treatment was the same as a regular reaction. Annealing temperature was 1100 °C.

A SD4000 fiber spectrometer recorded the emission spectra excited by a 365 nm Hg lamp. The content dependence of relative integral intensity of 450–700 nm emission is presented in Figure 5. In this work, the most intensive emission was obtained with 0.5 mol % Ce doping.

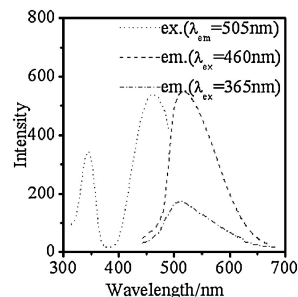


Figure 4. Excitation and emission spectra of LuAG:Ce_{0.01} powders.

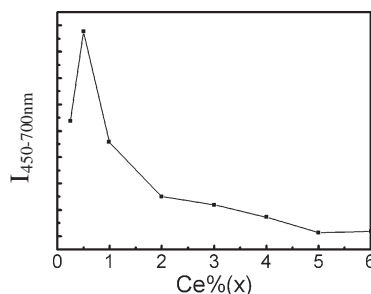


Figure 5. Integral emission intensity of LuAG:Ce³⁺ powders with different doping content (excited by 365 nm Hg lamp).

Certainly more samples could be synthesized on one plate in one process. Additional research on this aspect is not presented in this paper.

In this paper, we report a novel protein gel method for powder preparation. By this method, luminescent LuAG:Ce powders were easily prepared. Compared with normal sol-gel methods, the reaction temperature is much lower (700 °C, compared to 820 °C¹⁰), and the operation is simpler. Eight microsamples with different Ce content were synthesized as parallel on a ceramic plate. Luminescent properties were tested by a fiber spectrometer, and optimal doping content was easily determined. This protein gel method can be widely applied to composite phosphor synthesis, especially used in combinatorial approaches. With combinatorial approaches, starting materials and reaction time could be effectively saved, and reaction conditions can be uniformly controlled.

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