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New phosphor discovery by the single particle diagnosis approach

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ABSTRACT

New phosphors are required for the advancement of lighting and display technologies. One of the most effective ways for new phosphors is to employ new materials for host materials. It takes much time and labor to develop new materials from powder synthesis or single crystal growth. However, even if the powder product is a mixture phase, each particle is a single phase and a single crystal. The single particle diagnosis approach focuses on the tiny single crystal particle. Here we show the concept of the single particle diagnosis approach and some examples of new phosphor discovery by this approach.

1. Introduction

New materials are always needed and in the field of phosphor research new phosphors are required for white light emitting diodes (white LEDs) application. White LEDs are now rapidly spreading to many applications (lighting, display backlight, car headlamp, etc.). It is composed of blue LED and phosphor. The mixture of luminescence from phosphor excited by LED and emission from the LED produce white light. The phosphor is a key material for governing the color characteristics of white LEDs (color rendering in the lighting, color reproduction in the backlight). Although the conventional white LED phosphor YAG:Ce has a high luminescence intensity, the luminescence spectrum is not suitable for high color rendering white LEDs in the lighting and the matching to the color filter is not good in the backlight. Alternative phosphors have been searched, and some Eu^{2+}-doped Si, Al containing nitride and oxynitride (nitridosilicate, oxynitridosilicate, nitridoaluminosilicate, oxynitridoaluminosilicate) phosphors were found to have excellent luminescence properties for better color rendering and matching, and they have been commercialized [1–4]. New phosphors are still required for (1) the wide variation of emission spectra (peak position, peak width) to produce various types of white LEDs, (2) the coming change of emission wavelength of LEDs (near-UV LED) and (3) the high power LEDs where the thermal quenching of luminescence is more predominant.

In the synthesis of phosphors, a luminescent center is doped to a host material in small amount to obtain a luminescence. The luminescence property of Eu^{2+} or Ce^{3+} doped phosphor is so affected by the coordination environment of luminescent center. That is to say, the usage of different host material leads to new phosphor. The search for new phosphor is roughly classified to two methods. One is to employ a known crystal structure that is suitable for luminescent center doping and is not studied for host crystal [1–4]. The other is to find new host material by analyzing single crystals [5–14] or powder products [15]. Both methods, however, are definitely slow and labor intensive. In the single crystal analysis, a large size crystal with high purity and high quality (typically larger than 50–100 μm in all dimensions) is necessary to determine the crystal structure. It requires much time to grow the crystal especially for the material with high melting temperature or with no liquid phase. In the powder process, at least it is necessary to synthesize the new material as single phase to solve the crystal structure from powder XRD data. Even if the powder is single phase of new material, the complicated crystal structure is difficult to solve (i.e. crystal structure with large lattice parameter and low symmetry, crystal structure containing disorder). Therefore, it is desirable to find a way that allows the high-speed discovery of new phosphors, removing the need to prepare a perfect single crystal or a phase-pure powder. The combinatorial chemistry approach has been successfully utilized to high-throughput screening and optimizing luminescent materials [16–19]. However, the luminescent materials discovered so far cannot be considered as real “novel” phosphors as the crystal structure of end members are already known. The improved combinatorial synthesis method (huristic

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optimization) greatly speeds up the discovery of new phosphors [20–22], but it still requires much times of synthesis for pure phase.

We have recently reported a highly effective method to discover new phosphor without special process for crystal growth and single phase powder, and named the new method "single particle diagnosis approach" [23,24]. Here we show the concept of the approach and some new phosphors discovered by this method.

2. Materials and methods

2.1. Concept and procedure of the approach

A single phase powder is obtained by synthesizing a single-phase composition in a phase diagram in a suitable synthesis condition. If the synthesized composition is a region of mixture phase, the product contains the particles of each phase. Actually, due to the non-homogeneity and non-equilibrium condition in a reaction vessel, the tendency to mixture phase will be increased. In the stage of new material research, most of the product is obtained as a mixture phase. However, even if the powder product is a mixture phase, focusing on each (isolated) particle, it is a single phase and a single crystal. In the single particle diagnosis approach, such particle is treated as a candidate of new phosphor. The schematic of single particle diagnosis approach is shown in Fig. 1.

Fig. 1(a) shows the powder samples of various compositions synthesized under standard process and they appear various types of emission by UV-LED excitation depending on the starting compositions. A microscope image of the powder in one crucible is shown in Fig. 1(b). Although the product seems to have a uniform orange luminescence, it consists of different types of luminescence (yellow, orange, green, cyan, etc.), size and form in a micro-scale observation. Single crystal particles are picked and mounted on the glass capillary for the screening by single crystal XRD measurement (Fig. 1(c)). The lattice parameters and Bravais lattice are determined and compared to the database (ICSD, ICDD-PDF, etc.), and the candidates of new phosphor particle are selected. Emission spectrum by UV-LED excitation is supplementary used to judge the novelty of the particle. The glass particle and single crystal-like aggregate are ruled out in this stage.

The crystal structure of the new phosphor is then explored in detail with the EDS analysis (Fig. 1(d)). Due to the recent development of commercially available single crystal X-ray diffractometer (CCD or CMOS detector, focusing mirror), we can determine the crystal structure of a tiny microcrystal down to 5–10 μm. This microcrystal corresponds to the size synthesized by standard synthesis conditions. The special experiment for crystal growth is not necessary. Although much smaller crystal is analyzed by synchrotron XRD, there are many candidates in the single particle diagnosis approach and it is important to characterize them by the laboratory equipment.

Luminescent properties are also measured by single particle (Fig. 1(e)). Because the signal intensity from single particle is so weak, a microscopic observation is employed. We build a single particle fluorescence spectroscopy system to perform photoluminescence property measurements (emission and excitation spectra, thermal quenching, quantum efficiency (QE), decay) of a luminescent particle (Fig. 2). The accuracy of the system is acceptable for a fine particle, which is confirmed by using Ca-α-sialon:Eu^{2+} phosphor as a reference. Here the emission and QE results are shown. Due to the absence of reabsorption by other particles, the single

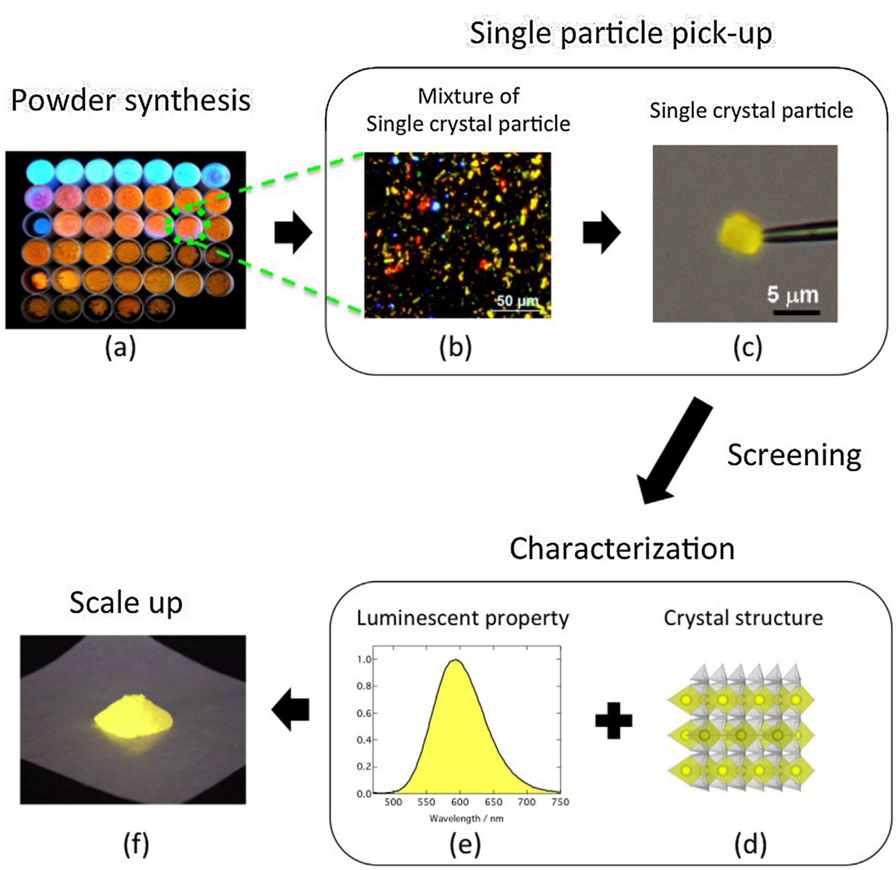

Fig. 1. Schematic of single particle diagnosis approach.
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