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Combinatorial synthesis of phosphors using arc-imaging furnace

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Abstract

We have applied a novel 'melt synthesis technique' rather than a conventional solid-state reaction to rapidly synthesize phosphor materials. During a synthesis, the mixture of oxides or their precursors is melted by light pulses (10–60 s) in an arc-imaging furnace on a water-cooled copper hearth to form a globule of 1–5 mm diameter, which is then rapidly cooled by turning off the light. Using this method, we synthesized several phosphor compounds including $Y_3Al_5O_{12}$: Ce(YAG) and $SrAl_2O_4$: Eu,Dy. Complex phosphor oxides are difficult to produce by conventional solid-state reaction techniques because of the slow reaction rates among solid oxides; as a result, the oxides form homogeneous compounds or solid solutions. On the other hand, melt reactions are very fast (10–60 s) and result in homogeneous compounds owing to rapid diffusion and mixing in the liquid phase. Therefore, melt synthesis techniques are suitable for preparing multi component homogeneous compounds and solid solutions.

Keywords: phosphor, arc-imaging furnace, melt, combinatorial

1. Introduction

In many white-light emitting diodes (W-LEDs), a blue-emitting GaN or ultraviolet -emitting InGaN chip pumps a phosphor that emits a broad spectrum of light [1, 2]. Therefore, novel W-LED phosphors have significant practical interest. Several authors have applied combinatorial chemistry techniques to synthesize such phosphors, and one of the pertinent problems has been the analysis of a large number of prepared samples. The analysis can be facilitated by using a charge-coupled device (CCD) camera to rapidly evaluate the emission color of each phosphor.

Most previous studies used conventional solid-state synthesis to form phosphors, which requires many hours of a diffusion reaction at a high temperature to achieve a homogeneous composition.

In comparison with solid-state reactions, melt processes result in rapid and homogeneous mixing in the liquid phase. Therefore, they are more suitable for synthesizing materials where the homogeneous mixing of elements is required, such as phosphors [3, 4]. Melt synthesis requires higher temperatures than the solid-state routes; it is a rapid-cooling solidification process, whereas the solid-state reactions rely on diffusion. It is possible to obtain a metastable phase from the melt. For example, Araki and Yoshimura prepared a transparent polycrystalline ceramic with a nanostructured metastable phase of HfO_2–$GdAlO_3$–Al_2O_3 using an arc-imaging furnace [5, 6].

In this paper, we report the combinatorial synthesis of phosphors using an arc-imaging furnace. A typical arc-imaging furnace has only one hot spot. Therefore, to enable combinatorial synthesis we designed a turntable holder supporting 24 samples in the furnace. The starting materials were placed in the furnace immediately after mixing and 24 samples were prepared within 30 min.

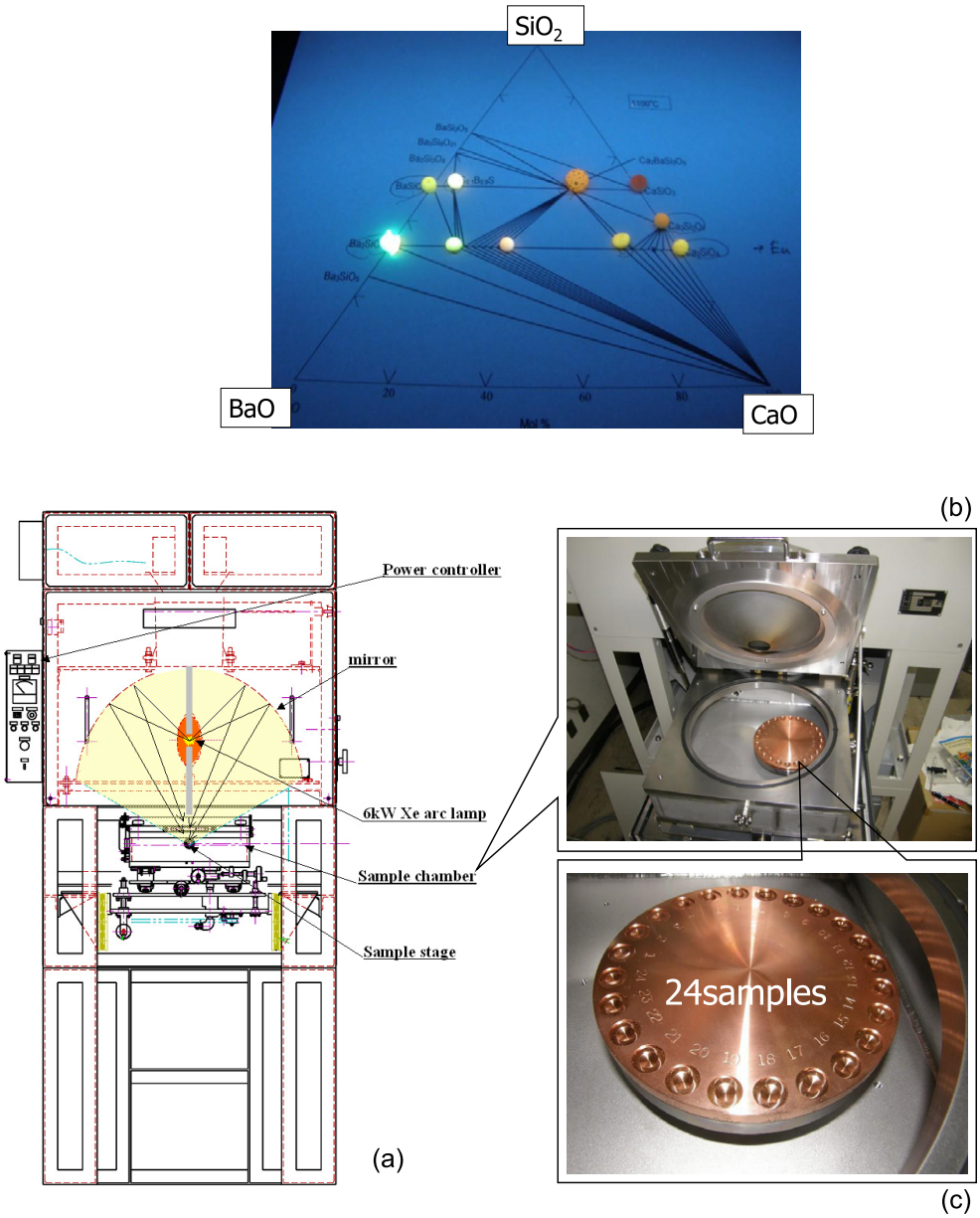

Figure 1. Combinatorial arc-imaging furnace system (a). Light from a 6 kW air-cooled xenon arc lamp is reflected by a collection mirror and emission mirror through the quartz window of the chamber (b) to the sample stage (c). Numbers in (a): 1, power controller; 2, mirror; 3, xenon lamp; 4, sample chamber; 5, 24-sample stage.

2. Experimental details

Our combinatorial arc-imaging furnace was designed to heat small samples to above 2000 °C under clean conditions. As shown in figure 1, the light emitted from a 6 kW xenon lamp is collected by an ellipsoidal mirror (collector) and directed to the sample. A molded sample (3–8 mm size) of mixed oxide or carbonate powder is placed on a water-cooled 24-sample Cu hearth in the sample chamber. The sample can be heated in various atmospheres within a few seconds then rapidly cooled by switching off the light and removing the sample stage from the focus of the collector mirror. In this study, each sample was melted within 30–60 s. By mixing different raw material components, 24 homogeneously melted samples can be prepared within 30 min using this equipment. Details of the furnace have been reported elsewhere [7–9]. When a sample is melted, it forms a globule of 1–5 mm diameter owing to the surface tension; this reduces the contact area with the Cu hearth, and thus the heat exchange. If part of the sample near the contact area with the hearth is not melted, the sample can be turned over and remelted.

3. Results and discussion

3.1. BaO–Si O$_2$–Ca O : Eu phosphors

The barium silicate phosphor $Ba_2SiO_4 : Eu^{2+}$ is well known for its green emission [10]. Owing to its absorption of blue light, this phosphor has been recently used in LEDs. Alkaline-earth silicates have various compositions;

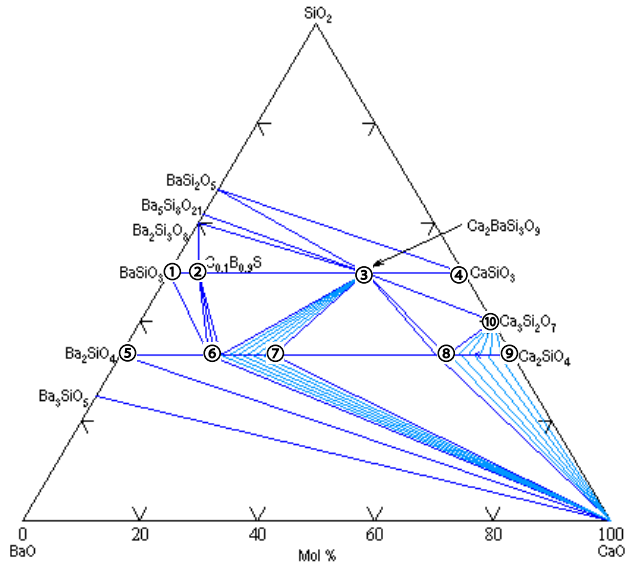

Figure 2. The BaO–SiO_2–CaO phase diagram (a) and phase diagram with superimposed Ba–Si–Ca oxide phosphor sample prepared in this study (b).

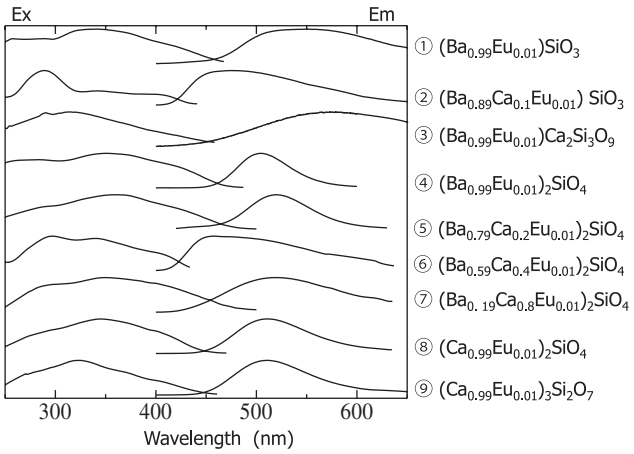

Figure 3. Excitation and emission spectra of the Ba–Ca–Si oxide : Eu phosphors.

for example, there are over 10 compounds within the BaO–SiO_2–CaO phase diagram (figure 2(a)). In figure 2(b), the ten Ba–Si–Ca oxide phosphor samples prepared in this work are superimposed on the BaO–SiO_2–CaO phase diagram. In these phosphors, the luminescent Eu^{2+} ion can substitute for Ba or Ca owing to the similarity of the ionic radii, namely, 1.25, 1.42 and 1.12 Å for Eu^{2+}, Ba^{2+} and Ca^{2+}, respectively [11].

Using this process, all the host compounds were obtained within 1 min. They did not exhibit Eu^{3+} emission because the Eu ions were reduced from the trivalent state to the divalent state owing to the short duration of the synthesis. All samples were well crystallized except for $Ca_2BaSi_3O_9$ (walstromite), which formed a yellow amorphous globule that emitted yellowish-red light under 310 nm excitation. A broad emission spectrum of Eu^{2+} was observed between 400 and 700 nm for each phosphor as shown in figure 3. The $(Ca_{0.99}Eu_{0.01})_3Si_2O_7$ sample contained a single Ca_2SiO_4 phase. Note that, contrary

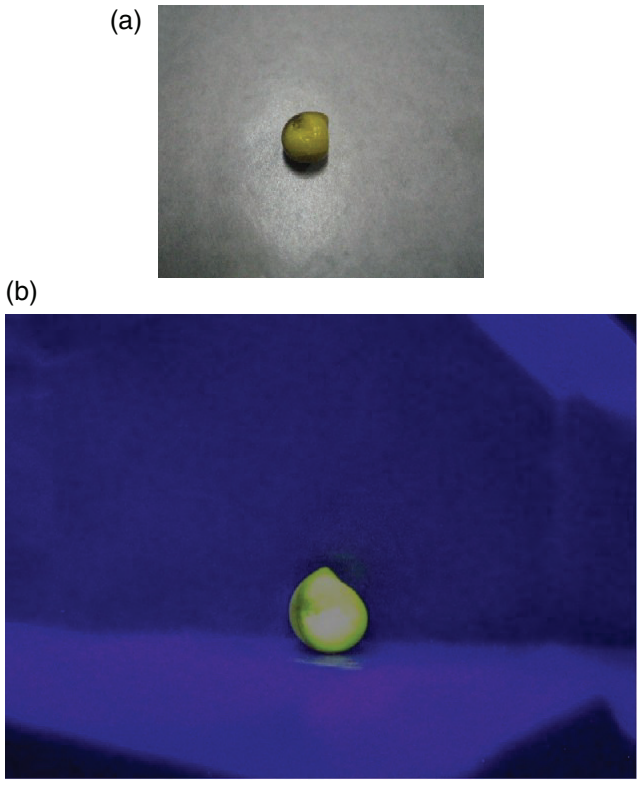

Figure 4. YAG : Ce molten globule: under sunlight (a) and under UV light (b).

to the conventional solid-state reaction, the melt process occurs at relatively low temperatures and therefore results in the most stable phase [5, 6].

We also prepared a series of Ba_2SiO_4–Ca_2SiO_4 phosphors (samples 5–9). Ca_2SiO_4 forms hexagonal, orthorhombic and monoclinic structures depending on the temperature [12, 13]. In contrast, Ba_2SiO_4 has only an orthorhombic phase, whereas $BaCaSiO_4$ was hexagonal [14]. Because of their different crystal structures, samples 5–9 emitted green light centered at about 500 nm [15], whereas sample 7 exhibited a 450 nm peak superimposed on a broad band.

3.2. YAG : Ce

Yttrium aluminum garnet (YAG, $Y_3Al_5O_{12}$) : Ce is one of the most well-known phosphors used in blue LEDs to generate white light.

Figure 4 shows a YAG : Ce sample, which was synthesized from the melt within 15 s in a 5% H_2/Ar gas mixture. In contrast, a solid-state synthesis would generally require several steps: molding into a pellet, heating to a high temperature in a reducing atmosphere and grinding; for example, pure YAG : Ce [16] can be prepared by annealing at 1300 °C for 1 h in CO gas after several intermediate grinding and molding steps. Furthermore, the melt synthesis might prevent contamination from grinding media and containers. For comparison, we prepared a YAG : Ce sample by a solid-state reaction at 1500 °C for 2 h in a 5% H_2/Ar atmosphere. Figure 5 shows XRD patterns of the samples

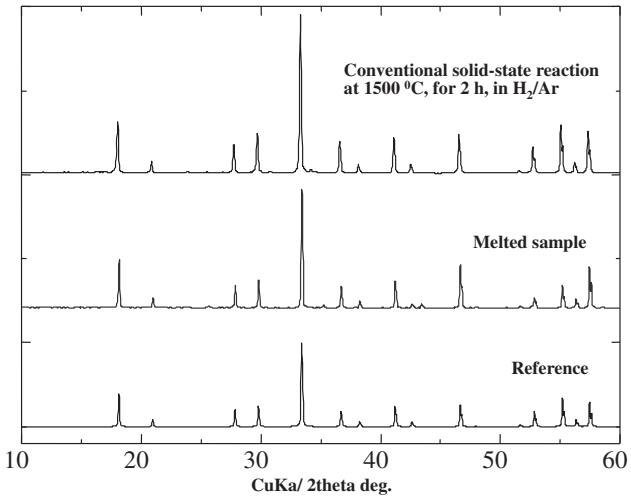

Figure 5. XRD patterns of YAG : Ce samples: (top) prepared by a solid-state reaction at 1500 °C for 2 h in a 5% H_2/Ar atmosphere, (middle) melt sample, (bottom) reference XRD pattern ICSD#20090.

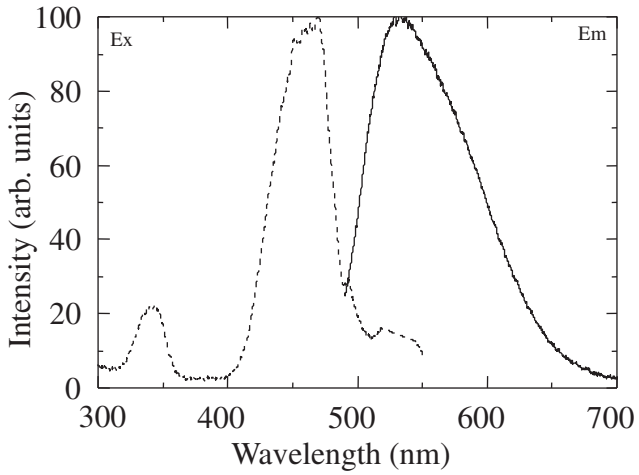

Figure 6. Excitation and emission spectra of the YAG : Ce phosphor.

produced via the melt and solid-state routes. The full widths at half maximum are almost the same for these samples: 0.16° for the solid-state sample and 0.14° for the melt sample at the 420 reflection. Thus, a sample of similar crystallinity was prepared 100 times faster by melt synthesis than by the solid-state route.

Figure 6 shows the excitation and emission spectra of the melt sample, which are the same as those of a commercial sample (P-46). Note that this sample had a grain size of about 300 μm (figure 7), which is specific to the melt-cooling process. Therefore, this method can yield micron-size phosphor lenses.

4. Conclusions

From both scientific and engineering view points, the melt-solidification method is suitable for phosphor research, combinatorial chemistry and high-temperature synthesis. It results in 300 μm grains that can be used as microlenses in optical systems.

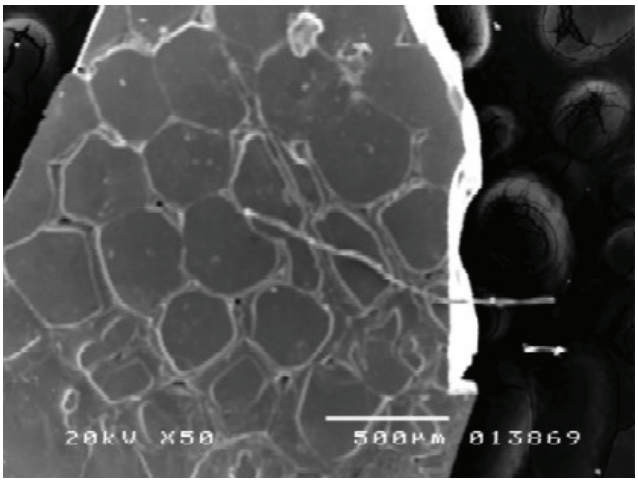

Figure 7. SEM cross-sectional image of the YAG : Ce phosphor.

Acknowledgments

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References

[1] Kaufmann U *et al* 2001 *Phys. Status Solidi* A **188** 143
[2] Feldmann C, Jüstel T, Ronda C R and Schmidt P J 2003 *Adv. Funct. Mater.* **13** 511
[3] Ishigaki T, Toda K, Watanabe T, Sakamoto N, Matsushita N and Yoshimura M 2008 *J. Mater. Sci.* **43** 4749
[4] Ishigaki T, Yoshimura M, Matsushita N, Uematsu K, Toda K and Sato M 2010 *J. Eur. Ceram. Soc.* **30** 165
[5] Araki S and Yoshimura M 2004 *Int. J. Appl. Ceram. Technol.* **1** 155
[6] Araki S and Yoshimura M 2006 *J. Eur. Ceram. Soc.* **26** 3295
[7] Yoshimura M 1974 *Bull. Tokyo Inst. Technol.* **120** 13
[8] Ishigaki T, Seki K, Nishimura E, Watanabe T and Yoshimura M 2006 *J. Alloys Compd.* **408–412** 1177
[9] Ishigaki T, Nishimura E, Seki K, Watanabe T and Yoshimura M 2006 *J. Electroceram.* **17** 885
[10] Barry T L 1968 *J. Electrochem. Soc.* **115** 1181
[11] Shannon R D 1976 *Acta Crystallogr.* A **32** 751
[12] Uchikawa H and Tsukiyama K 1965 *J. Ceram . Assoc. Japan* **73** 100
[13] Phillips B and Muan A 1959 *J. Am. Ceram. Soc.* **42** 413
[14] Thompson J G, Withers R L and Hyde B G 1987 *J. Am. Ceram. Soc.* **70** C383
[15] Barry T L 1968 *J. Electrochem. Soc.* **115** 1181
[16] Yen W M and Weber M J (eds) 2004 *Inorganic Phosphors* (Boca Raton, FL: CRC Press) p 182