Parallel Synthetic Exploration of Tm^{3+} -Doped Alkaline-Earth Gallate Phosphors by use of Polymerizable Complex Method

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The methodology of parallel synthesis based on the polymerizable complex method is described in this work. A model system such as $\text{A}_x\text{Ga}_y\text{O}_z$ ($\text{A} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$) was used to test the proposed approach and to find potential hosts for Tm^{3+} activated blue light emission phosphor materials. It was found that Ca-containing compounds as hosts are superior to the other alkaline-earth containing materials in this system. The composition $\text{Ca}_5\text{Ga}_6\text{O}_{14}:\text{Tm}^{3+}$ demonstrated excellent color purity with CIE coordinates $x = 0.16$, $y = 0.12$ and it had emission intensity corresponding to the 68% peak intensity of commercial BAM ($(\text{Ba}, \text{Eu})\text{MgAl}_{10}\text{O}_{17}$)-one of the strongest blue emission phosphor.

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1. Introduction

The parallel synthesis is the concept originating from combinatorial chemistry, and it is one of the most efficient ways to search for new phosphor materials.¹⁾ Selection of the particular preparation method for the whole parallel synthesis scheme is very important, since a choice of the inadequate method may result in preparation of materials with sizable amounts of impurities, inhomogeneities and extended defects possibly leading to exclusion of potentially promising compositions during the initial screening. Thus parallel synthesis approach combined with the polymerizable complex (PC) method^{2)–4)} can be regarded as the most suitable methodology for this purpose, since the PC method has great advantage over other conventional methods in preparation of high-performance materials with excellent homogeneity in the precise and reproducible way and, in addition, PC method is neither time-consuming nor it requires unique or expensive equipment. Although this particular combination can not compete in the number of trial compositions with the thin film combinatorial methods, it provides sizable amounts of samples sufficient for characterization by conventional laboratory methods.

In this work we applied the PC method for the parallel synthesis of a series of oxides in the $\text{A}_x\text{Ga}_y\text{O}_z$ system ($\text{A} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$) to search for the potential host material in which Tm^{3+} can act as an efficient blue light emitting fluorescence center. Previously known Tm^{3+} -activated phosphors include $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Tm}^{3+}$,^{5)–6)} $\text{YVO}_4:\text{Tm}^{3+}$,^{7)–8)} $\text{LaPO}_4:\text{Tm}^{3+}$,⁹⁾ $\text{LnOCl}:\text{Tm}^{3+}$ ($\text{Ln} = \text{Y}, \text{La}, \text{Gd}$),¹⁰⁾ $\text{Ca}_4\text{GdO}(\text{BO}_3)_3:\text{Tm}^{3+}$,¹¹⁾ $\text{Y}_3\text{GaO}_6:\text{Tm}^{3+}$,¹²⁾ and $\text{KLa}(\text{WO}_4)_2:\text{Tm}^{3+}$,¹³⁾ all of which exhibited relatively weak brightness when we examined their photoluminescence properties using samples prepared in our laboratory. Tm^{3+} -doped samples of $\text{A}_x\text{Ga}_y\text{O}_z$ with 20 different compositions were simultaneously prepared through the parallel synthesis scheme, and their fluorescence properties were visually screened. The best performing composition was more carefully examined. A new phosphor material $\text{Ca}_5\text{Ga}_6\text{O}_{14}:\text{Tm}^{3+}$ with a strong blue emission at 454 nm was discovered by this approach and its fluorescence properties are briefly discussed in this paper.

2. Experimental section

The idea of the parallel synthesis approach combined with the polymerizable complex (PC) method is shown in Fig. 1.

Stock solutions containing Mg^{2+} , Ca^{2+} and Sr^{2+} ions with concentration of 1 mol/dm³ were prepared by dissolving their nitrates into water. Due to relatively low solubility of $\text{Ba}(\text{NO}_3)_2$ barium acetate was used as a source of Ba^{2+} ions. Stock solutions containing Ga^{3+} or Tm^{3+} ions were prepared by dissolving Ga_2O_3 or Tm_2O_3 into nitric acid followed by dilution of water to adjust solution concentration to 1 mol/dm³. Another stock solution containing citric acid with concentration of 2 mol/dm³ was prepared by dissolving it into water (a). The required amounts of solutions corresponding to a given composition of the target compound were delivered by a digital pipette into test tubes with a size of $\phi 30$ mm-height 200 mm. The stock solution of citric acid with a volume 2 times larger than the total volume of metals solution was added into the test tube. In this way, an array of solutions having individually set metal composition for each element of the array was prepared in a respective test tube (b). These test tubes had been kept in an oven at 80°C for 2 h until solutions became transparent. Then propylene glycol with a stoichiometric ratio of 1:1 with respect to citric acid was added into each test tube, followed by stirring on a vibrating stirrer. Then the set of the test tubes was placed again into an oven at 120°C for 12 h in order to promote polyesterification between citric acid and propylene glycol (c). The test tubes containing transparent polyester-type resins were heated in a sand bath set at 500°C for 2 h in order to eliminate organic matters (d), followed by heat treatment in a furnace set at 550°C for 4 h (e). The resulting precursors were transferred from the test tubes to alumina crucibles (f) and heat treated in a furnace at 800°C for 12 h (g). Finally the resulting white powders were heat treated at 1200°C in a box furnace for 2 h to produce the final samples (h).

The sample compositions examined in this work are shown in Table 1. We chose Ga as a key element combined with alkaline earth metals such as Mg, Ca, Sr and Ba. In total 20 different compounds including simple oxides of Ga_2O_3 , MgO, CaO, SrO were chosen, whose crystal structures are known but the corresponding Tm^{3+} -activated materials were not well studied. The amount of Tm doping in all samples was 1 mol% with respect to the alkaline-earth elements (for Ga_2O_3 , the nominal composition was $(\text{Ga}_{0.99}\text{Tm}_{0.01})_2\text{O}_3$).

The rapid screening of the obtained products was carried out by visual observation of the emission light under the excitation by a UV-lamp using 254 nm wavelength (i). The sam-

Fig. 1. Parallel synthesis scheme for exploration of new phosphors. (a) stock solutions, (b) mixing of stock solutions, (c) formation of polyester-type resins, (d) elimination of organic matters, (e) formation of powder precursors, (f) presursors put in crucibles, (g) decomposition of carbonate, (h) final products after high temperature heat treatment and (i) visual observation of emission light under illumination of UV light.

Table 1. Chemical Compositions of Binary Metal Systems in Alkaline-earth Elements and Ga Investigated

Ratios of AE and Ga		Alkaline-Earth (AE) elements			
AE	Ga	Mg	Ca	Sr	Ba
0.0	100	Ga ₂ O ₃	Ga ₂ O ₃	Ga ₂ O ₃	Ga ₂ O ₃
7.7	92.3	-	-	SrGa ₁₂ O ₁₉	BaGa ₁₂ O ₁₉
20.0	80.0	-	CaGa ₄ O ₇	SrGa ₄ O ₇	-
33.3	66.6	MgGa ₂ O ₄	CaGa ₂ O ₄	SrGa ₂ O ₄	BaGa ₂ O ₄
42.9	57.1	-	Ca ₃ Ga ₄ O ₉	Sr ₃ Ga ₄ O ₉	-
45.5	54.5	-	Ca ₅ Ga ₆ O ₁₄	-	-
50.0	50.0	-	Ca ₂ Ga ₂ O ₅	-	-
60.0	40.0	-	-	Sr ₃ Ga ₂ O ₆	Ba ₃ Ga ₂ O ₆
62.5	37.5	-	-	Sr ₁₀ Ga ₆ O ₁₉	-
66.6	33.3	-	-	-	Ba ₄ Ga ₂ O ₇
100	0.0	MgO	CaO	SrO	-

ples with high emission brightness were characterized further by means of a fluorescence spectrometer (F-4500, Hitachi-Co.). The phase purity was examined by use of a powder

Table 2. Phase Purity of Host Compounds and their Tm-doped Samples

Number	Formula	Host	Phase purity	
			Tm ³⁺ -doped compound	
			Tm ₂ O ₃	Others
#1	Ga ₂ O ₃	○	Detected	Detected
#2	MgGa ₂ O ₄	○	Detected	Detected
#3	MgO	○	Detected	Detected
#4	CaGa ₄ O ₇	○	None	None
#5	CaGa ₂ O ₄	○	None	None
#6	Ca ₃ Ga ₄ O ₉	○	Detected	None
#7	Ca ₅ Ga ₆ O ₁₄	○	None	None
#8	Ca ₂ Ga ₂ O ₅	×	None	Detected
#9	CaO	○	None	None
#10	SrGa ₁₂ O ₁₉	○	None	None
#11	SrGa ₄ O ₇	○	None	None
#12	SrGa ₂ O ₄	△	None	Detected
#13	Sr ₃ Ga ₄ O ₉	○	None	None
#14	Sr ₃ Ga ₂ O ₆	○	None	None
#15	Sr ₁₀ Ga ₆ O ₁₉	○	None	None
#16	SrO	○	None	None
#17	BaGa ₁₂ O ₁₉	×	None	Detected
#18	BaGa ₂ O ₄	○	None	None
#19	Ba ₃ Ga ₂ O ₆	○	None	None
#20	Ba ₄ Ga ₂ O ₇	○	None	None

○ : Single phase
 △ : Mixture of two phases
 × : No formation of the target compound

Fig. 2. Visual observation of fluorescence for a set of the final samples under UV (254 nm) illumination; the numbers correspond to those in Table 2.

X-ray diffractometer (RINT-2200, Rigaku Co.).

3. Results and discussion

Table 2 summarizes information on the phase purity of each host compound synthesized by the parallel synthesis scheme and results of Tm doping. Except for Ca₂Ga₂O₅, SrGa₂O₄ and BaGa₁₂O₁₉ (sample #8, #12 and #17), all host compounds studied were obtained in their pure form. Ca₂Ga₂O₅ is known as a high-pressure phase and its synthesis under ambient pressure was unsuccessful. As for Tm doping, it has turned out that not all crystals were successfully doped with Tm³⁺. Detection of Tm₂O₃ indicates that the amount of Tm would be at least beyond the solubility limit for compounds such as Ga₂O₃, MgGa₂O₄, MgO and Ca₃Ga₄O₉ (sample #1, #2, #3 and #6, respectively).

Figure 2 shows visual observation of fluorescence for a set of the final samples under UV (254 nm) illumination. One

Table 3. Excitation and Emission Wavelength and Relative Emission Intensity in Selected Ca–Ga–O Systems

Number	Compounds Formula	Wavelength/nm		Emission Intensity (%) [*]
		Excitation	Emission	
#4	CaGa_4O_7	248	457	16
#5	CaGa_2O_4	252	458	7
#6	$\text{Ca}_3\text{Ga}_4\text{O}_9$	240	454	16
#7	$\text{Ca}_5\text{Ga}_6\text{O}_{14}$	240	454	68
#8	$\text{Ca}_2\text{Ga}_2\text{O}_5$	240	454	39

^{*}Relative to the peak intensity of a commercial $(\text{Ba},\text{Eu})\text{MgAl}_{10}\text{O}_{17}$ (BAM)

Fig. 3. Excitation and emission spectra of $\text{Ca}_5\text{Ga}_6\text{O}_{14}:\text{Tm}^{3+}$; asterisks (*) correspond to the reflection incident or over tone light by the surface of sample.

may clearly see that binary Ca–Ga complex oxides can be good host materials for Tm^{3+} acting as efficient blue light emitting fluorescence center. Thus we have picked up five Ca–Ga complex oxides (#4–#8) for further characterization by fluorescence spectroscopy. **Table 3** shows the excitation wavelength at which a given sample exhibits the maximum emission intensity, the emission wavelength and the corresponding emission intensity. The emission intensity was normalized in such a way that the intensity of a commercial $(\text{Ba}, \text{Eu})\text{MgAl}_{10}\text{O}_{17}$ (BAM) is defined as 100%.

The most prominent result was obtained for $\text{Ca}_5\text{Ga}_6\text{O}_{14}:\text{Tm}^{3+}$, which emission intensity reached 68% of that of BAM. The excitation and emission spectra of $\text{Ca}_5\text{Ga}_6\text{O}_{14}:\text{Tm}^{3+}$ are shown in **Fig 3**. Upon excitation by 240 nm light, two major emission peaks showed up at 360 and 454 nm. The excitation peak at 240 nm is most likely associated with light absorption arising from the host $\text{Ca}_5\text{Ga}_6\text{O}_{14}$ compound. The emission peaks at 360 and 454 nm can be assigned to the $^1\text{D}_2 \rightarrow ^3\text{H}_6$ and $^1\text{D}_2 \rightarrow ^3\text{F}_4$ transitions of Tm^{3+} activator, respectively. Peaks at 480 and 225 nm marked with asterisks in the emission and excitation spectra are not intrinsic to the sample, but they are due to the reflection of light by the surface of sample and higher order diffraction in the monochromator. The FWHM of the emission peak corresponding to the $^1\text{D}_2 \rightarrow ^3\text{F}_4$ transition was approximately 20 nm, which is much narrower than typical emission peaks of other blue emission phosphors such as BAM. The CIE color chromaticity x and y values of our $\text{Ca}_5\text{Ga}_6\text{O}_{14}:\text{Tm}^{3+}$ were estimated to be 0.16 and 0.12, which

indicates excellent blue color purity. There is a fundamental question why particularly the calcium (Ca–Ga–O) compounds rather than other systems involving Mg, Sr or Ba are suited as superior hosts for Tm^{3+} .

Ca^{2+} has ionic radius close to Tm^{3+} , thus Ca is substituted for Tm easily and crystal lattice distortion is small compared to Mg, Sr and Ba compounds. However the reason why Ga compound was suitable host for Tm emission needs further study.

Investigation of this question is currently in progress and it will be extensively discussed elsewhere.

4. Conclusion

In this work we present a methodology of the parallel synthesis employing a sol-gel technique-polymerizable complex method. In the model system such as $\text{A}_x\text{Ga}_y\text{O}_z$ ($\text{A} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$) we discovered a series of complex oxides which can act as outstanding host compounds for Tm activator to produce blue emission. It was demonstrated that Ca-containing compounds are superior to the other alkaline-earth containing materials in the system. In particular it was found that $\text{Ca}_5\text{Ga}_6\text{O}_{14}:\text{Tm}^{3+}$ emission intensity corresponds to the 68% peak intensity of commercial BAM $((\text{Ba}, \text{Eu})\text{MgAl}_{10}\text{O}_{17})$ one of the strongest blue emission phosphor and it demonstrated good color purity.

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