Combinatorial Synthesis and Screening of the Tb-activated Phosphors in the System CaO-Y_2O_3-Al_2O_3

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Abstract

We have synthesized some phosphors in the system CaO-Y_2O_3-Al_2O_3 by combinatorial polymerized-complex method. Composition and synthetic temperature of phosphors in the liblary was screened from the emission intensities of individual samples under VUV excitation. In Tb^{3+}-activated CaO-Y_2O_3-Al_2O_3, green phosphors showing good intensity were found to be $CaYAl_3O_7$, $CaYAlO_4$, $YAlO_3$, $Y_3Al_5O_{12}$, $Y_4Al_2O_9$, Ca_3Al_2O6.

1. Introduction

Combinatorial synthesis and screening of vary large numbers of compounds has been widely applied in the pharmaceutical industry for discovery. The application of combinatorial synthesis and characterization of luminescent materials has been enlarged to identification and optimization in interesting new phosphors. But, because the conventional way to synthesize phosphor based on the solid-state reaction is dealt with founded on thin film technology, this had the defect such as a very large scale, an amounts of each compound, too small to be characterized properly, and etc. So, the present investigation aims at applying the liquid-state combinatorial chemistry method to the synthesis of phosphor powders.

In the study, we adopt a polymerizable complex precursor routs, which has been widely applied to the systhesis of a variety materials such as various inorgarnic functional materials. The polymerized-complex combinatorial chemistry method makes it possible to the same that is adopted for the conventional powder sample. Thus, general measurement; PL, XRD, SEM, decay, is possible in a powder state.

In the work, we were synthesized Tb^{3+}-activated phosphors in the system CaO-Y_2O_3-Al_2O_3 by Pechni-Type polymerizable complex technique based on polyesterification between citric acid (CA) and ethylene glycohol (EG), screened the higher luminescent composition at VUV (Vaccum Ultervialet; 147nm) excitation and characterized the phosphors of a optimized compostion such as $Y_3Al_2O_3$, $Y_3Al_5O_{12}$, $CaYAlO_4$, $CaYAl_3O_7$, $CaAl_4O_7$, $Ca_3Al_2O_6$, $CaAl_{12}O_{19}$, $Ca_{12}Al_{14}O_{33}$,.

2. Experiments

First, to synthesize phosphors, which are exciting at VUV, a combinatorial table composed of 210 different compositions was prepared. In accordance with the table, each material sample could be tested with

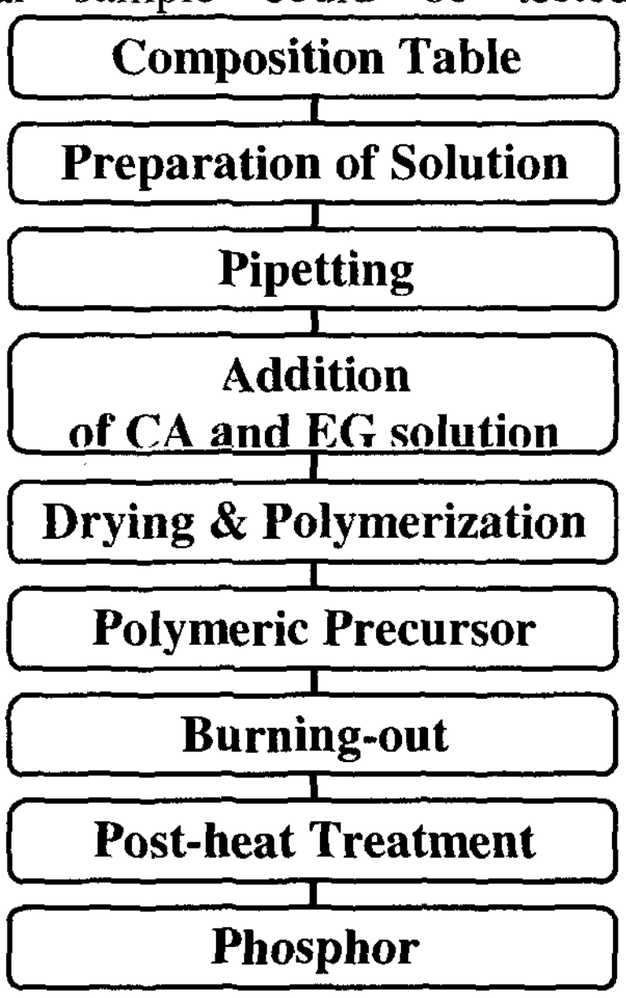

Table 1. Flow diagram of complex-polymeric combinatorial chemistry method

compositions of Ca, Y, and Al components that is in the range from 0 to 1 in 0.05 increments respectively.

The synthesizing process by complex-polymeric combinatorial chemistry method was summarized in Table 1.

The solutions of Ca^{3+}, Y^{3+}, and Tb^{3+} were prepared by dissolving $CaCO_3$, Y_2O_3, and Tb_4O_7 with nitric acid, and the solution of Al^{3+} by dissolving $Al(NO_3)_3 \cdot 6H_2O$ in a deionized water. Each ionic solution was injected to 6ml test tube by using micropippetes according to each composition of the combinatorial table. Then, citric acid and ethylene glycohol were added as 2.5 ~ 3.0 times and 5 times to the equivalence of total metal ions at each test tube. After the removal of water, the polymerization of excess citric acid containing metal-citrate complex and ethylene glycohol occur the complex-polymeric precursors. The burning-out step contains the removal of organic materials at 600 ~ 700°C for 3-5h in furnace.

The post-heat treatment be sequently conducted at 900 ~ 1300°C for 3h in an oxidizing or reducing atmosphere. The final weight of the samples is in the range of 0.1g to 0.2g.

3. Result and Discussion

Figure 1 shows the luminance library for the Tb^{3+} ion the ternary CaO-Y_2O_3-Al_2O_3 system under 147nm excitation. As the filled color in the circle becomes darker, the emission intensity of the luminance becomes brighter. The libraries were made in air or reduction atmosphere at from 900℃ to 1300℃. 3 samples which gives high luminance among them shows in figure 1.

According to the Figure 1, the compositions showing good emission intensity were $Ca_{0.35}Y_{0.2}Tb_{0.05}Al_{0.4}O_6$, $Y_{0.45}Tb_{0.05}Al_{0.55}O_6$, and $Ca_{0.4}Tb_{0.05}Al_{0.55}O_6$.

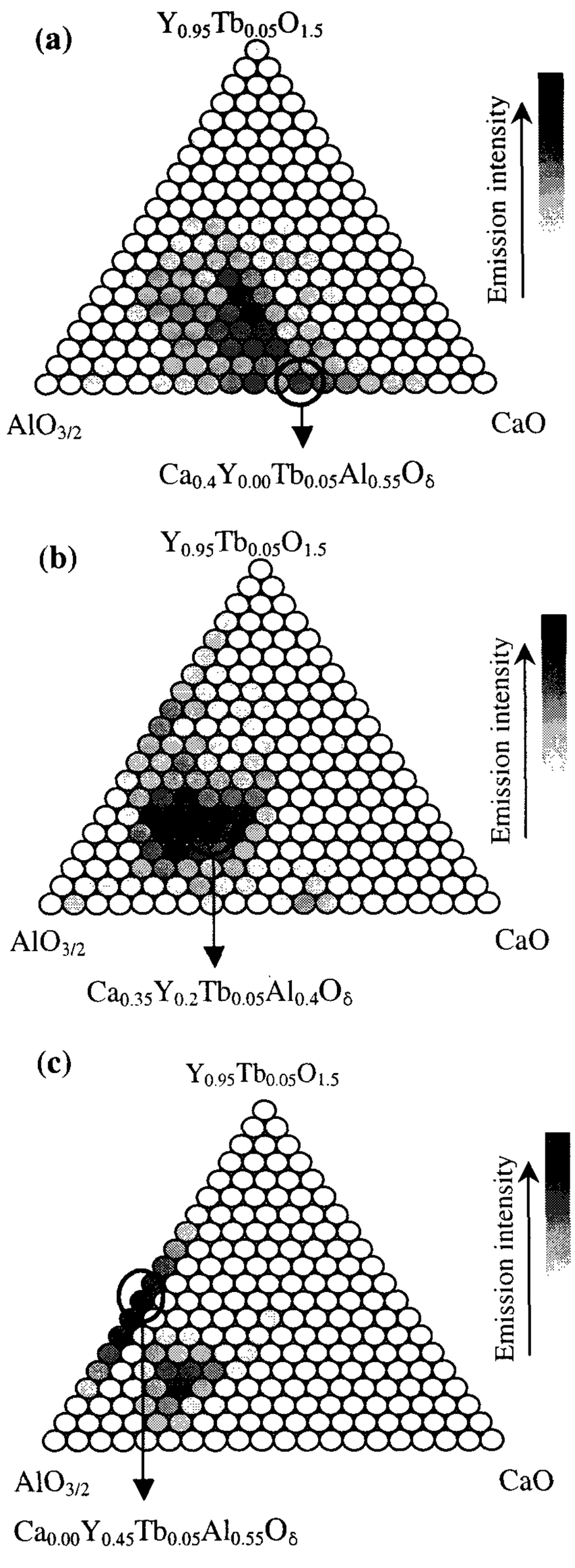

Figure 1. Library for Tb^{3+} ion in the ternary CaO-Y_2O_3-Al_2O_3 system under 147nm excitation. (a) at 900°C in 5% H_2, (b) at 1100°C in air, (c) at 1200°C in Air

From XRD analysis, their structures were identified to the mixtures of $CaYAl_3O_7$ and $CaYAlO_4$, the mixtures of $YAlO_3$ and $Y_3Al_5O_{12}$, $Ca_3Al_2O_6$. By comparing the XRD data with standard data from the JCPDS cards, a quantitative analysis enabled us to identify the compounds and make an estimate of the relative fractions.

In order to investigate the spectral behavior of the compounds searched by XRD, we synthesized the single-phased compounds by the conventional polymeric precursor method. In the work, also we pay attention to Y-Al-O compounds and Ca-Y-Al-O

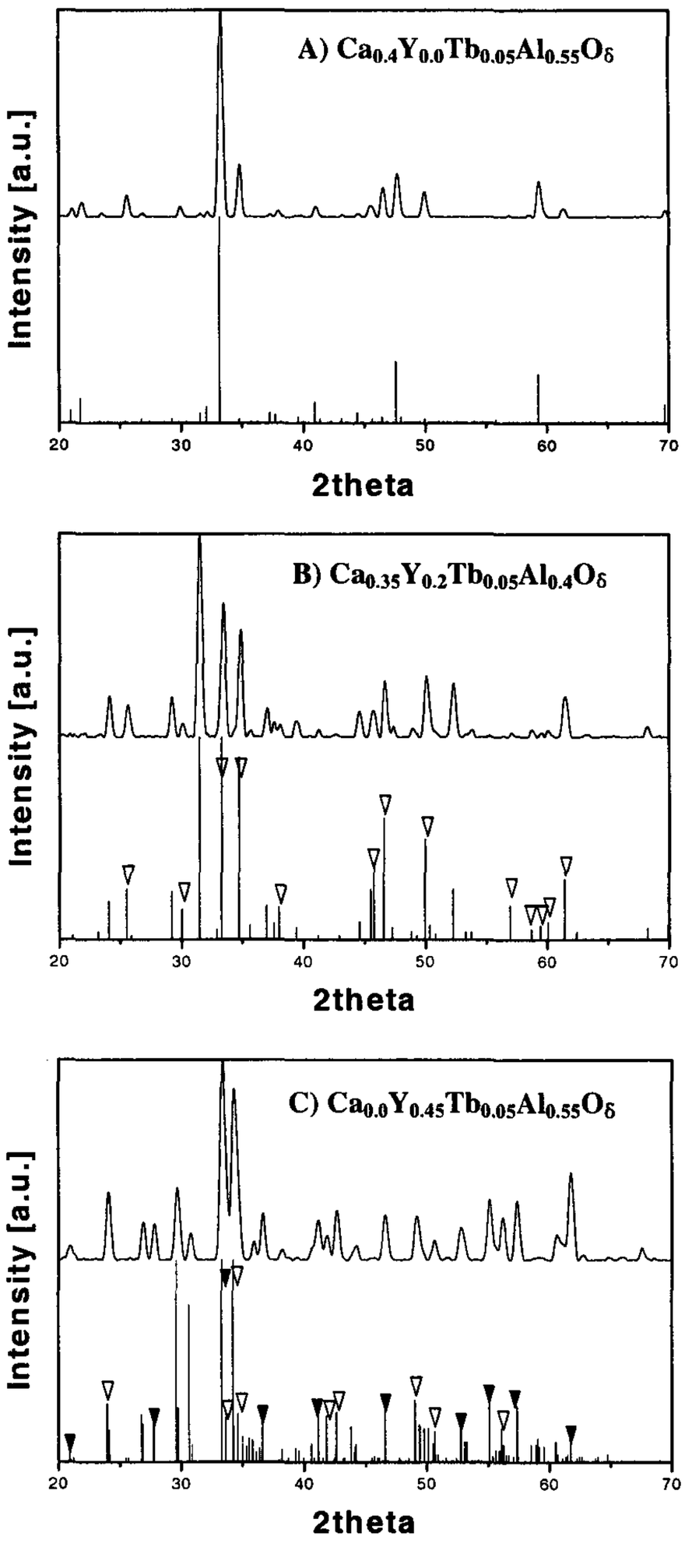

Figure 2. XRD patterns of some samples with different composition. a) 38-1429 $Ca_3Al_2O_6$, b) ▽ : 24-0221 $CaYAlO_4$, 49-0605 $CaYAl_3O_7$, c) ▽ : 33-0041 $YAlO_3$, ▼ : 33-0040 $Y_3Al_5O_{12}$, 34-0368 $Y_4Al_2O_9$

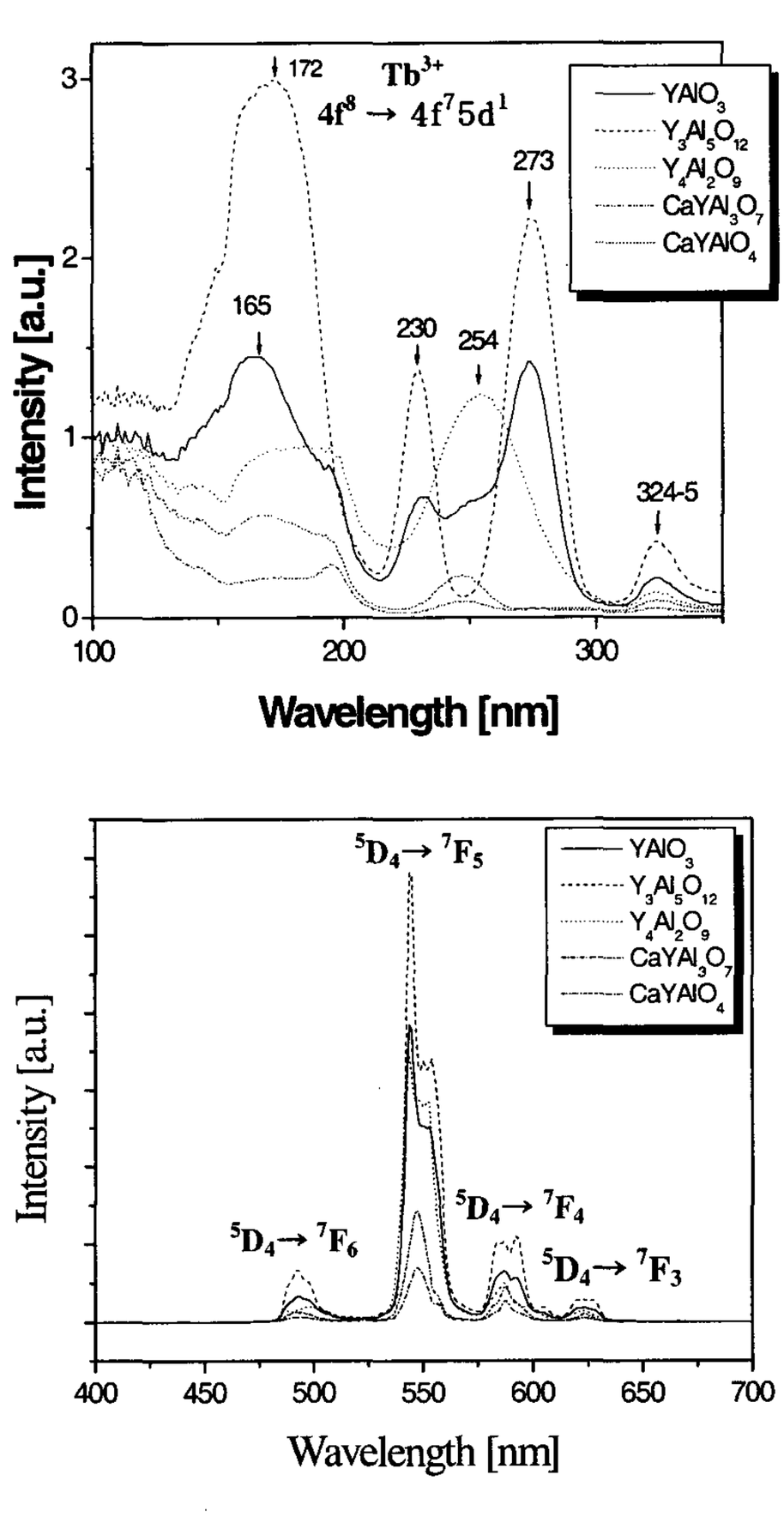

Figure 3. Excitation and emission spectra of synthesized phosphors; a) $YAlO_2$, b) $Y_3Al_5O_{12}$, c) $Y_4Al_2O_9$, d) $CaYAl_3O_7$, e) $CaYAlO_4$

compounds than Ca-Al-O compounds.
Figure 3 shows the excitation and emission spectra of the single-phased compounds. The excitation spectra of each compound was observed the $4f^8$-$4f^75d^1$ transition of Tb^{3+} as to be known much. The green light at 545nm as can be seen in Figure 3 are based on $^5D_4$-^7F_J transition of Tb^{3+}.

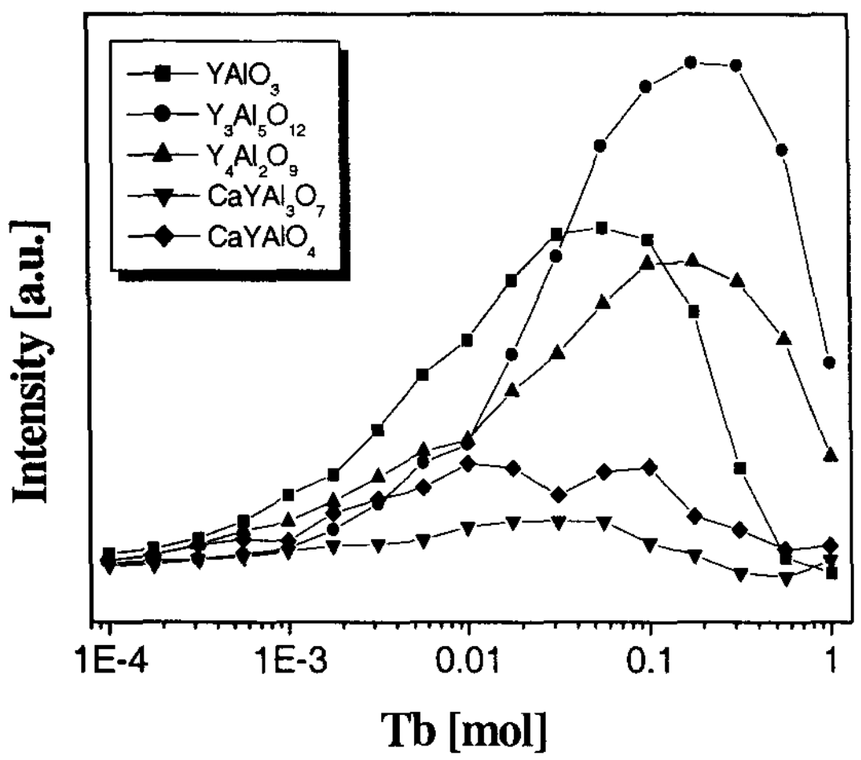

Figure 4. The concentration quenching behavior $^5D_4 \rightarrow {}^7F_5$ emission of synthesized phosphors; a) $YAlO_2$, b) $Y_3Al_5O_{12}$, c) $Y_4Al_2O_9$, d) $CaYAl_3O_7$, e) $CaYAlO_4$

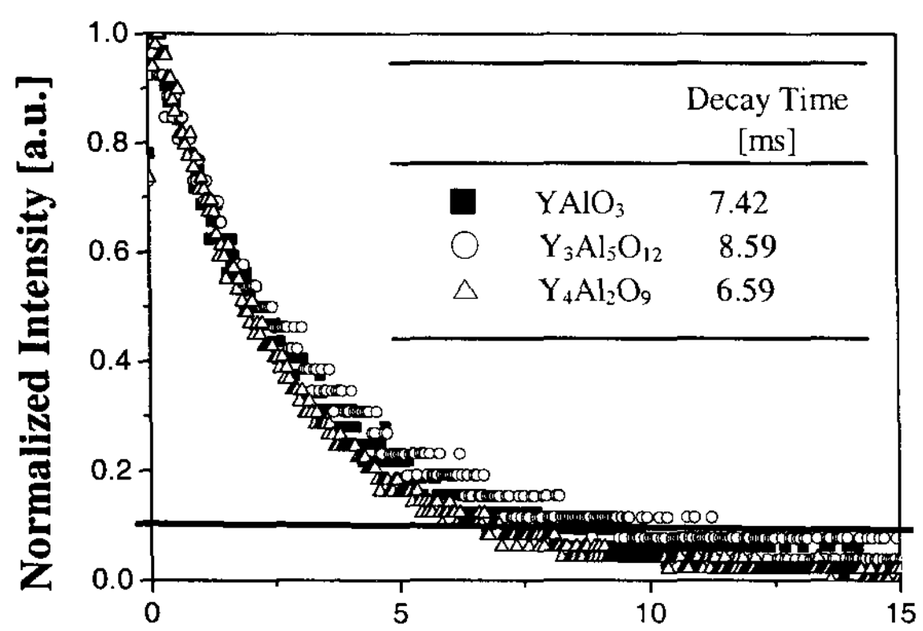

Figure 5. Decay behavior of $^5D_4 \rightarrow {}^7F_5$ emission of synthesized phosphors; a) $YAlO_2$, b) $Y_3Al_5O_{12}$, c) $Y_4Al_2O_9$

Figure 4 shows the result optimized the concentration of Tb^{3+} in each the single-phase compounds.
The 1/10 decay time of phosphors optimazed the concentration of Tb^{3+} under the excitation of 254nm shows in Figure 5. $CaYAl_3O_7$ and $CaYAlO_4$ did not have the meaning even though it measured because of the very low level of emission intensity.

4. Conclusion

A combinatorial polymerized-complex method was used in order to search for new Tb^{3+} activated green phosphors based on the CaO-Y_2O_3-Al_2O_3 ternary system. And we found out that the candidate might be $YAlO_3$, $Y_3Al_5O_{12}$ and $Y_4Al_2O_9$ as the green phosphors for PDPs

5. Reference

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