

# Luminescent Properties of the Tb<sup>3+</sup>-Activated ABCO<sub>4</sub> and ABC<sub>3</sub>O<sub>7</sub> Phosphors (A=Ca, Sr ; B=Y, RE ; C=Al, Ga)

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## Abstract

In ABCO<sub>4</sub> and ABC<sub>3</sub>O<sub>7</sub> (A=Ca, Sr; B=Y, Rare earth; C=Al, Ga), random distribution of static crystalline fields in activator sites results in inhomogeneous broadening of spectral lines of luminescent materials. In this study, we investigated luminescent properties of above-mentioned materials by excitation and emission spectra. In result, both ABCO<sub>4</sub>:Tb and ABC<sub>3</sub>O<sub>7</sub>:Tb phosphors emit the green light. ABC<sub>3</sub>O<sub>7</sub>:Tb phosphors absorbed shorter wavelength energy than ABCO<sub>4</sub>:Tb phosphors so that the emission efficiencies of ABC<sub>3</sub>O<sub>7</sub>:Tb phosphors were higher than those of ABCO<sub>4</sub>:Tb phosphors under vacuum UV.

## 1. Introduction

ABCO<sub>4</sub> compounds form tetragonal crystals with the K<sub>2</sub>NiF<sub>4</sub> type of structure I4/mmm. The crystals are built up from CO<sub>6</sub> layers formed in the ab plane. Between the layers divalent A cations and trivalent B cations are distributed randomly in nine coordinated sites with C<sub>4v</sub> symmetry. ABC<sub>3</sub>O<sub>7</sub> compounds form tetragonal crystals belonging to the space group P4<sub>2</sub>m. The crystal structure is built up from CO<sub>4</sub> layers formed in the ab plane. Between the layers the divalent A cations and trivalent B cations are distributed randomly in eight coordinated sites with C<sub>s</sub> symmetry. The spectral-energy distributions of rare-earth ion usually consist of sharp line transitions. But above compounds, the B<sup>3+</sup> ions are partly replaced by Tb<sup>3+</sup> ions. The A<sup>2+</sup> and B<sup>3+</sup> ions are distributed at random over one crystallographic lattice, therefore the crystal field at the Tb<sup>3+</sup> ions varies from site to site, resulting in slightly different wavelength positions of the emission transitions, so that our spectral-energy distribution shows broad lines in this case [1].

In this study, we investigated the characteristics of the excitation and emission spectra of ABCO<sub>4</sub> and ABC<sub>3</sub>O<sub>7</sub> (A=Ca, Sr; B=Y, Rare earth; C=Al, Ga)

prepared by a complex-polymeric method.

## 2. Experiments

The phosphor samples were prepared by a complex-polymeric method as can be seen in Fig. 1. The aliquots of each solution including Gd<sup>3+</sup>, Ca<sup>2+</sup>, Al<sup>3+</sup>, Tb<sup>3+</sup> metal ion, citric acid and ethylene glycol solution were injected into 6ml-test tubes according to the composition of samples to be prepared. The mixed solution was heated at 135°C for hydrolysis and polymerization, and then transparent solution-complex polymeric precursor was obtained. The phosphors were obtained by burning-out of precursors which contains the removal of organic materials at 600°C for 3hrs in the furnace and heating at 1000-1200°C for 3hrs in reducing atmosphere (5% H<sub>2</sub>/N<sub>2</sub>). In order to examine the luminescent efficiency of the several sample, we used the UV and vacuum UV excitation. The structure and the crystallinity of the fired samples are investigated by X-ray diffraction patterns.

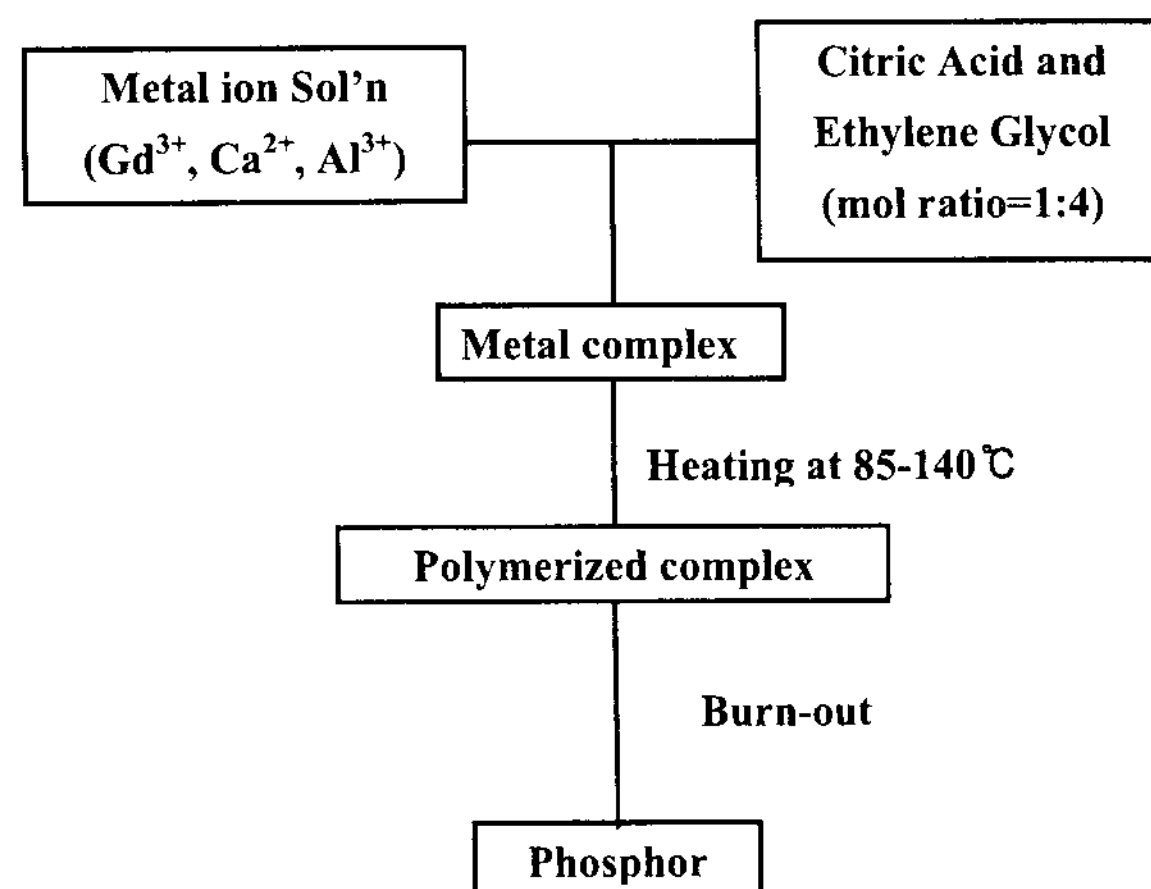


Fig. 1 Complex-polymeric method

### 3. Results and Discussions

Fig. 2 and Fig. 3 show the excitation spectra of  ${}^5D_4 \rightarrow {}^7F_5$  transition in  $\text{CaYAlO}_4$  and  $\text{CaGdAlO}_4$  samples and in  $\text{CaYAl}_3\text{O}_7$  and  $\text{CaGdAl}_3\text{O}_7$  samples, respectively.

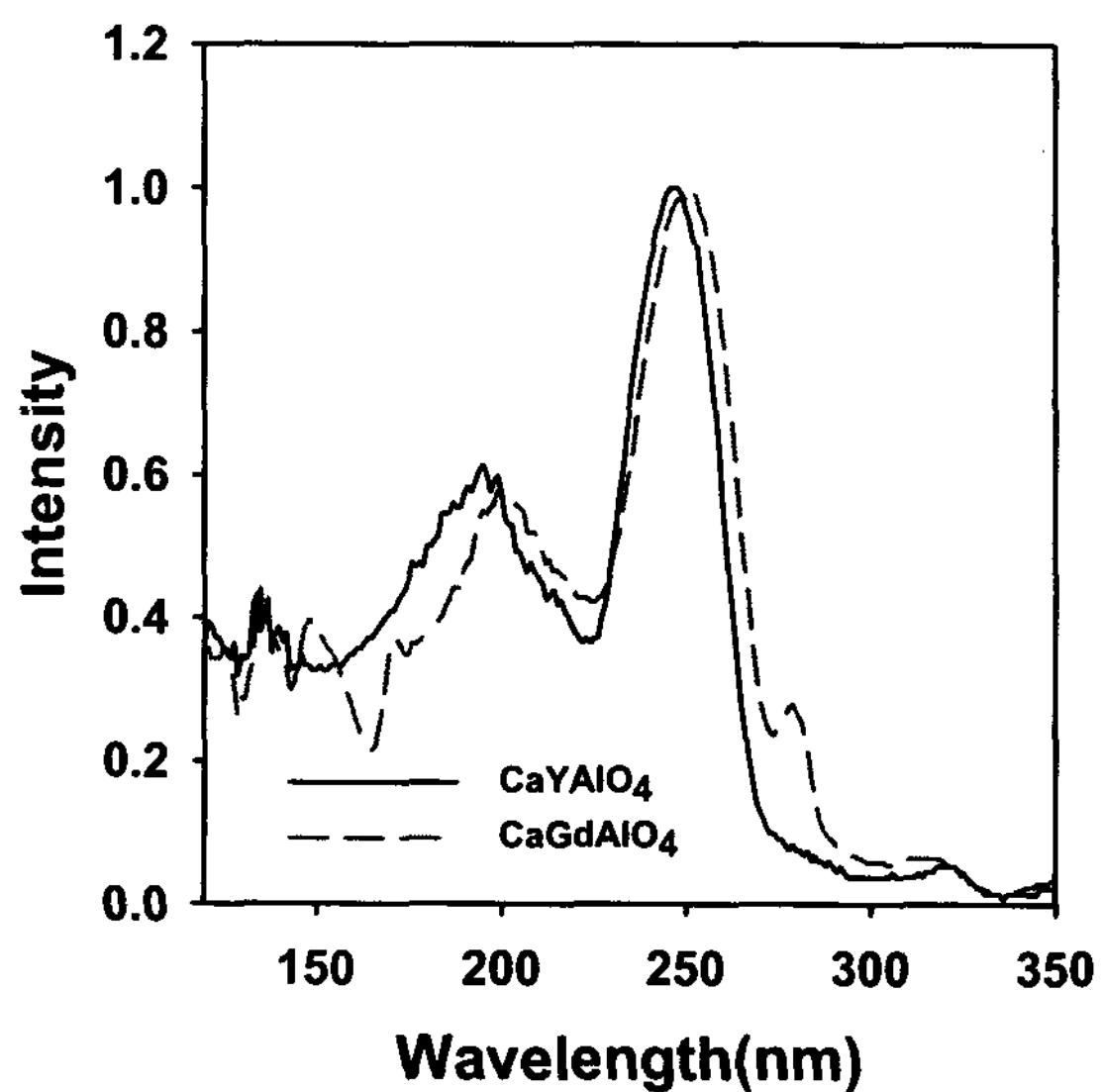


Fig. 2 Excitation spectra of  $\text{CaYAlO}_4\text{:Tb}$  and  $\text{CaGdAlO}_4\text{:Tb}$

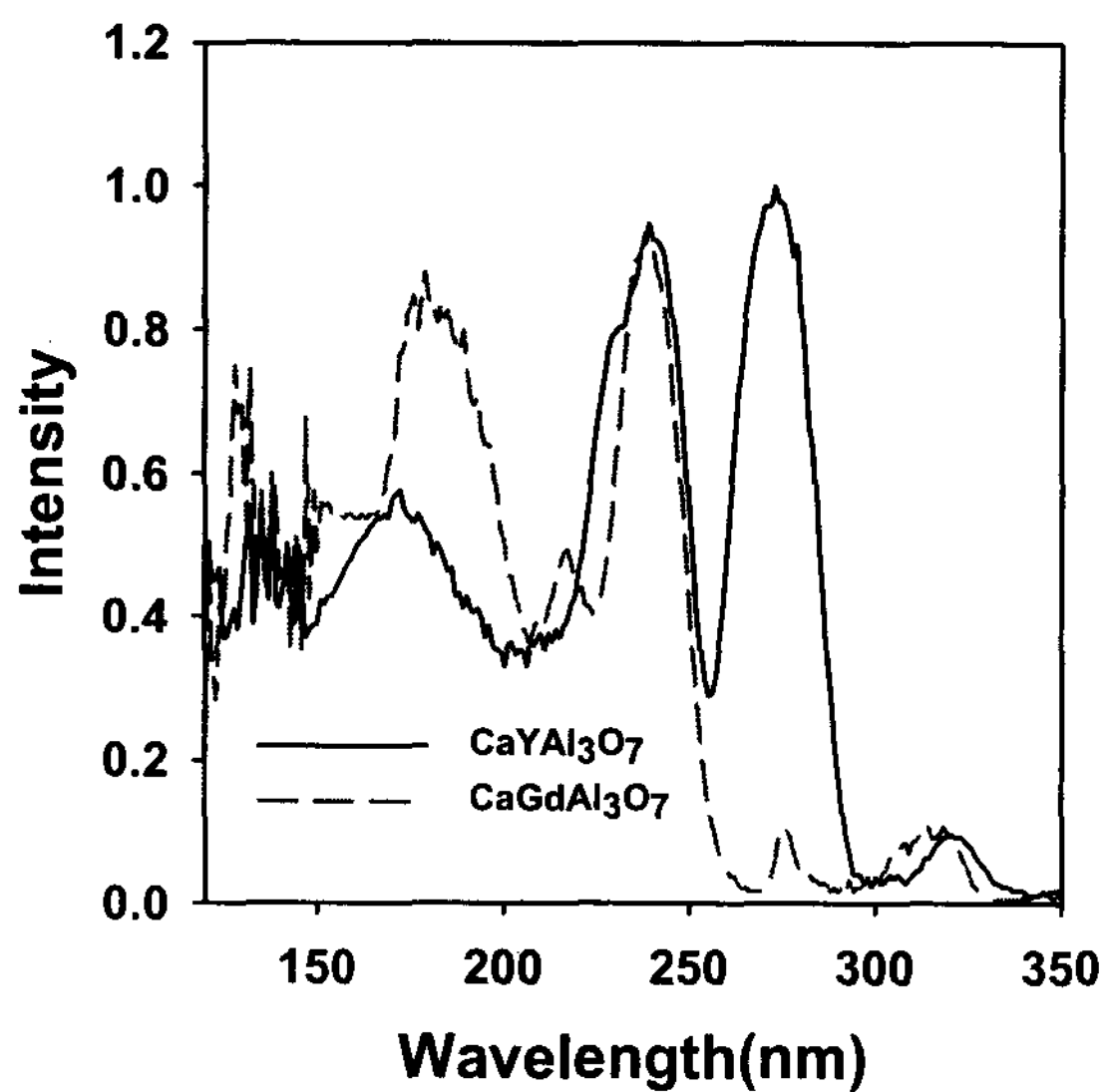


Fig. 3 Excitation spectra of  $\text{CaYAl}_3\text{O}_7\text{:Tb}$  and  $\text{CaGdAl}_3\text{O}_7\text{:Tb}$

In Fig. 2, the excitation spectra show one broad peak in the range between 200 and 300nm, which is believed to be attributed to the 4f-5d transition of in the nine coordinated sites with  $C_{4v}$  symmetry. In Fig. 3, the excitation spectra show several broad peaks in the range between 200 and 300nm, which are believed to be attributed to the 4f-5d transition of in the eight coordinated sites with  $C_s$  symmetry. The  $\text{Tb}^{3+}$  site in the host lattice is 8-coordinated to oxygen atoms (symmetry  $D_{2d}$ ) [4-6]. It is thus assumed that several conspicuous peaks in the excitation spectra could be the splitting of the  ${}^7D$  and  ${}^9D$  levels due to crystal field splitting as well as to non-cubic terms in the crystal-field expansion [2].

The strong peaks in the low-energy regime below 250nm could be assigned to  ${}^9D$  levels, the strong intensity of which can be assigned to the  $C_s$  symmetry compared to the  $D_{2d}$  symmetry in some host which has the weak peak.

The factors influencing the position of this band are the nephelauxetic effect and crystal-field splitting. In the series, Ca than Sr and Al than Ga, the 4f-5d band shifts to higher energies. This may be ascribed to the fact that the next nearest neighbour cations ( $\text{Ga}^{3+}$ ,  $\text{Al}^{3+}$ ) show increasing polarizing action on the  $\text{O}^{2-}$  ions surrounding the  $\text{Tb}^{3+}$  ions, so that the influence of  $\text{O}^{2-}$  on the  $\text{Tb}^{3+}$  ion becomes less. The excitation bands above 320nm result from 4f-4f transition of the rare-earth ions. The strong band coincides with a strong absorption band is not due to the host lattice and must therefore be ascribed to transitions in the  $\text{Tb}^{3+}$  center.

The green emission of  $\text{Tb}^{3+}$  - activated  $\text{ABCO}_4$  and  $\text{ABC}_3\text{O}_7$  phosphors is mainly due to transitions from the  ${}^5D_4$  level to the  ${}^7F_5$  at appropriate concentration. The intensity of  ${}^5D_4 \rightarrow {}^7F_5$  transition (at about 545nm) dominates by the cross-relaxation process of  ${}^5D_3 \rightarrow {}^5D_4$  and  ${}^7F_6 \rightarrow {}^7F_0$  or  ${}^5D_3 \rightarrow {}^5D_0$  and  ${}^7F_6 \rightarrow {}^7F_4$ . In other word, these transitions involve nearly the same energy, so that energy transfer from the  ${}^5D_3$  level of one  $\text{Tb}^{3+}$  ion to another  $\text{Tb}^{3+}$  ion is possible. We detected green emission spectrum in all compounds.

Fig. 4 shows the emission spectra of the some phosphors under vacuum UV excitation (147nm). Typical transitions from both  ${}^5D_3$  and  ${}^5D_4$  levels down to  ${}^7F_j$  levels of  $4f^8$  configuration were assigned in Fig. 4. All of  $\text{ABCO}_4$ -typed and  $\text{ABC}_3\text{O}_7$ -typed phosphors shows the similar patterns as shown in Fig. 4.

In case of  $\text{ABCO}_4$  compounds, the energy of VUV region is absorbed by host lattice. But the absorbed

energy does not efficiently transfer to  $Tb^{3+}$  energy level. But in  $ABC_3O_7$  compounds, the energy absorbed by host lattice transfers to activator by charge-transfer of  $O^{2-}$ . According to the results,  $ABC_3O_7$  phosphors excited effectively at 147nm wavelength than  $ABCO_4$  phosphors.

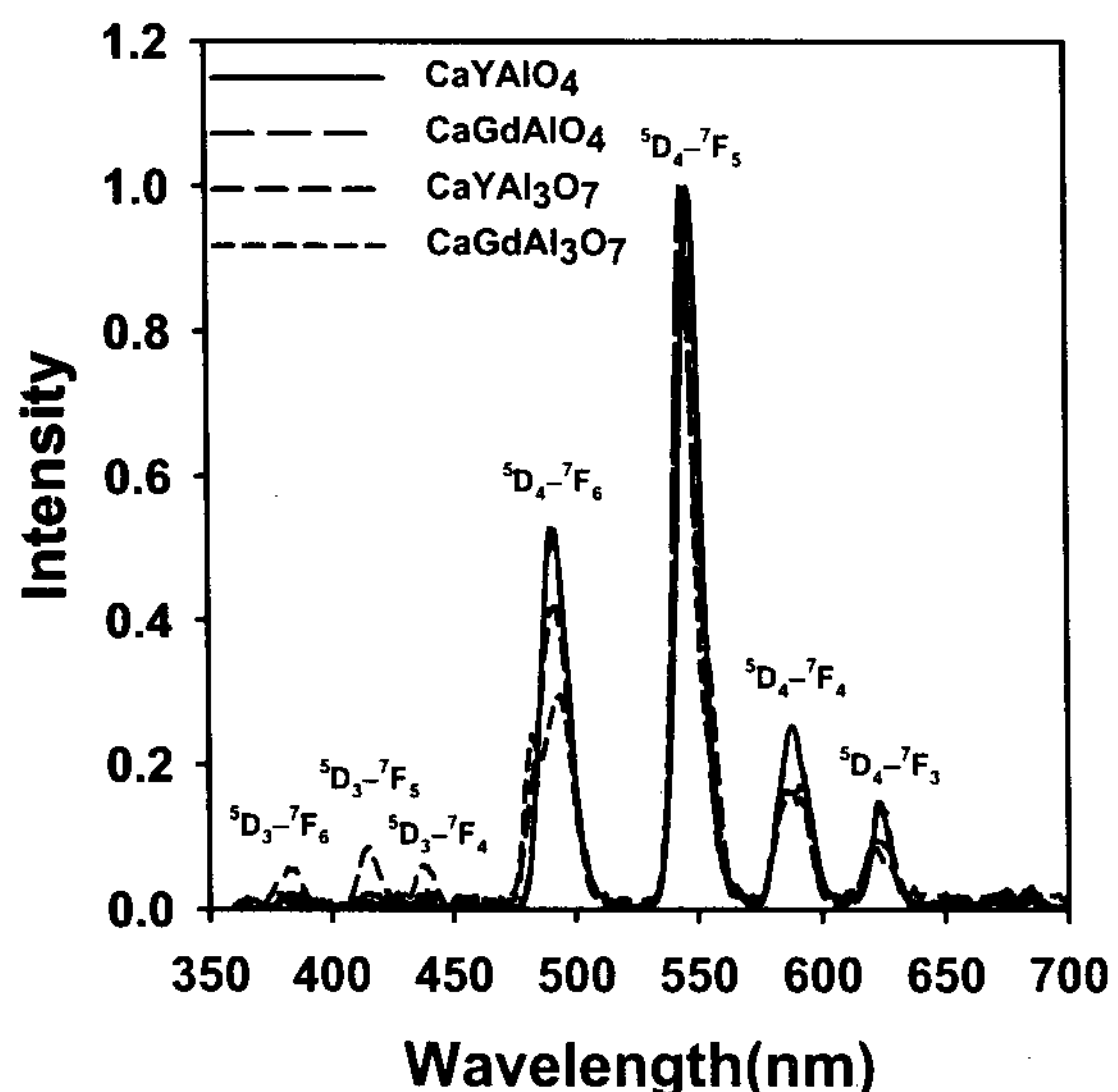


Fig. 4 Emission spectra of some phosphors under 147nm

Fig. 5 shows the concentration quenching behaviors of  $^5D_3-^7F_5$  emission,  $^5D_4-^7F_5$  emission and luminance in  $CaGdAlO_4$  and  $CaGdAl_3O_7$  phosphors under 147nm. The 147nm light could excite photons at ground state to lattice absorption level as well as charge transfer band. Therefore, the photons excited to lattice absorption level could migrate into other ions more randomly, so that they could be quenched at even lower  $Tb^{3+}$  concentration. The 147nm data are very important from the practical point of view, in that the actual PDP application adopts this wavelength as an excitation source. The maximum intensity of  $^5D_3-^7F_5$  and  $^5D_4-^7F_5$  emissions in  $CaGd_{1-x}Tb_xAlO_4$  was obtained at about  $x=0.005$  and  $x=0.05$ , and in  $CaGd_{1-x}Tb_xAl_3O_7$  at about  $x=0.01$  and  $x=0.07$ , respectively.

In particular, it is very interesting that  $CaTbAl_3O_7$  ( $x=1$ ) have some luminescence. This phenomenon could be explained from that  $Tb^{3+}$  ion separated from others by  $AlO_4$  layer as seen in Fig. 7. The ionic distance between  $Tb^{3+}$  ions is long so that the

concentration quenching could not detect in  $CaTbAl_3O_7$  phosphors.

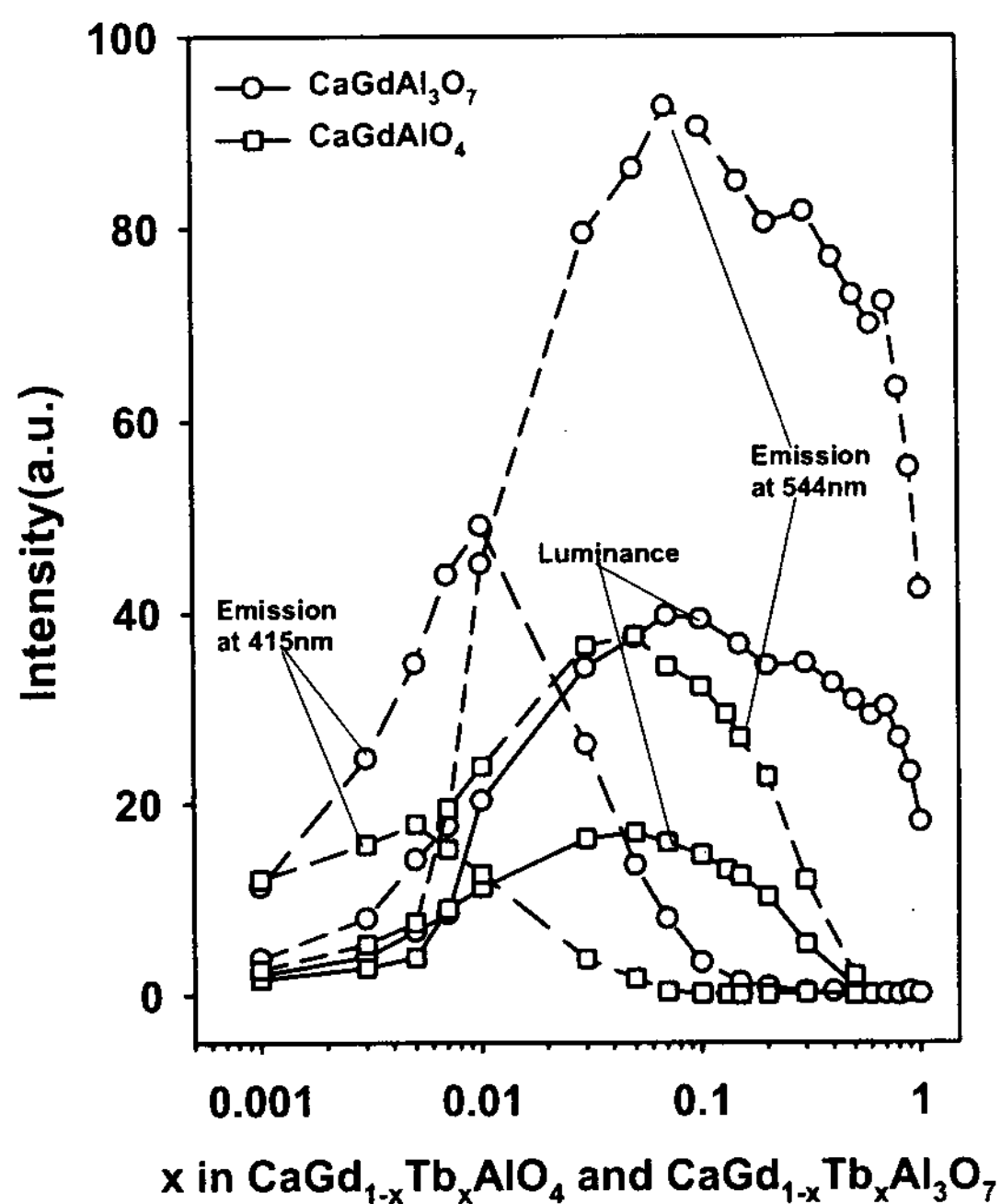


Fig. 5 Concentration quenching behaviors under 147nm

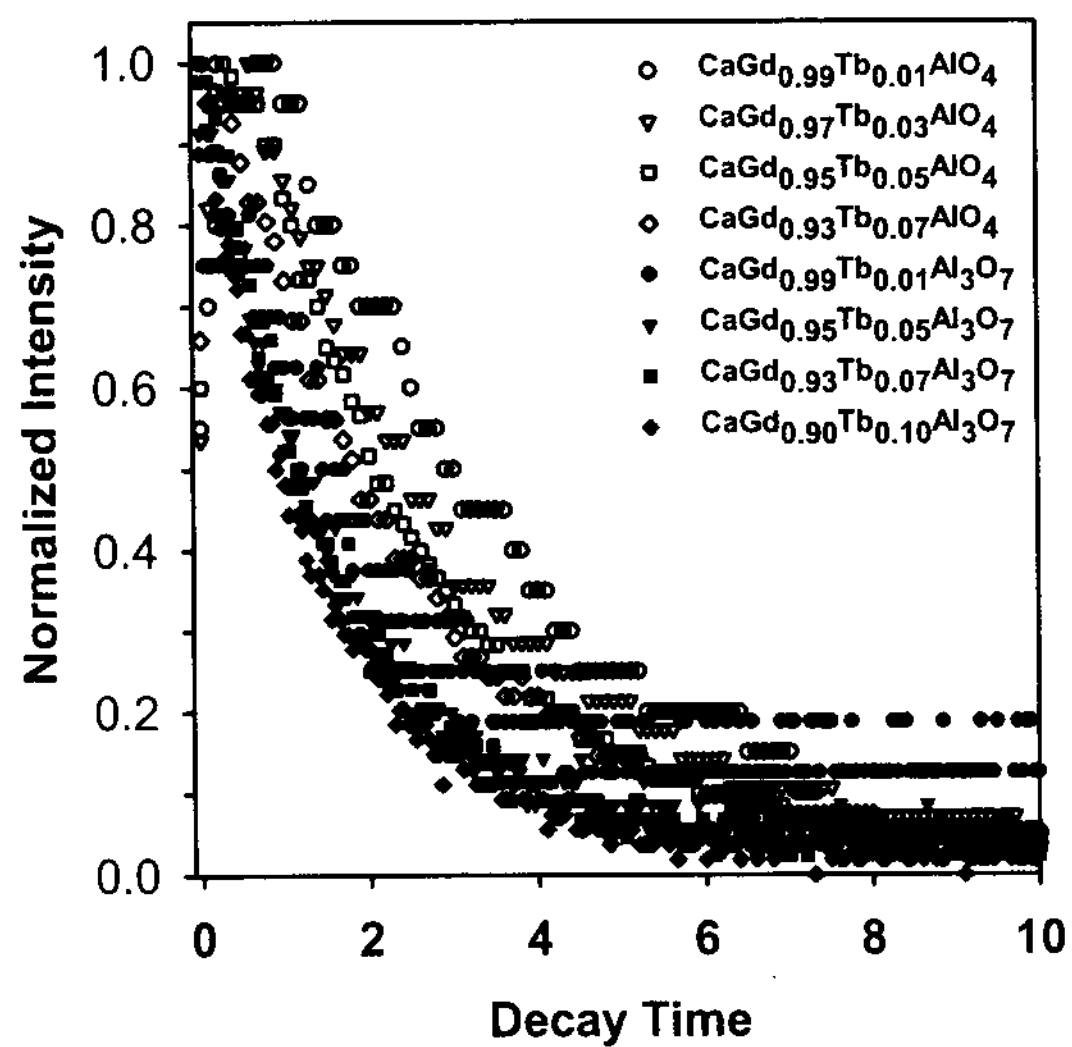


Fig. 6 Normalized decay curves of  $^5D_4-^7F_5$  emission under 254nm.

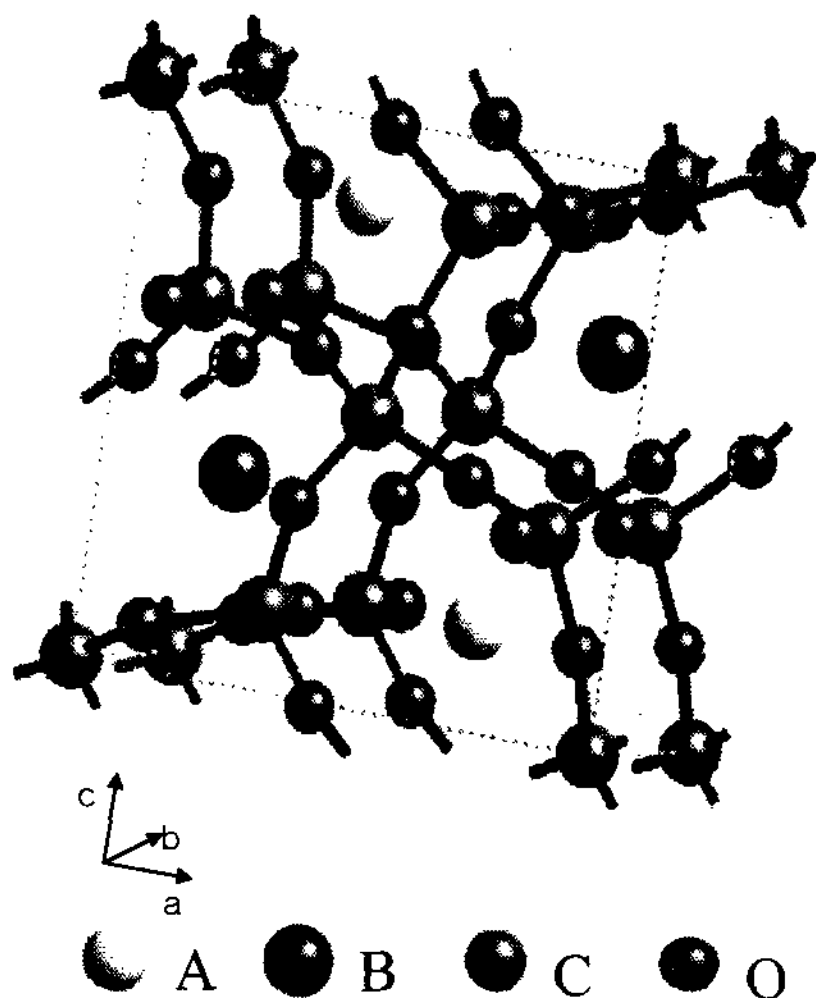


Fig. 7 The structure of  $ABC_3O_7$

Fig. 6 shows the normalized decay curves of  ${}^5D_4$ - ${}^7F_5$  emission under 254nm as a function of Tb concentration. The decay time (about 6ms, 10%) of  $CaGdAl_3O_7$  phosphors with maximum luminance is longer than that (4ms) of  $CaGdAlO_4$  phosphors.

According to the results, the decay time of  $ABC_3O_7$  phosphors with maximum luminance is longer than that of  $ABCO_4$  phosphors.

The radiative decay time of  ${}^5D_3$  level is much shorter than that of  ${}^5D_4$  level. Such a difference could be described to the intrinsic nature of each level but one cannot ignore the possibility of a nonradiative transition from  ${}^5D_3$  level to  ${}^5D_4$  level with the assist of phonon vibration.

The concentration quenching process gives rise to the decreases in  ${}^5D_4$  decay time with increasing the  $Tb^{3+}$  concentration and produces a non-exponential decay component in the initial regime of the decay curves. As can be seen in Fig. 5, the concentration quenching begins at about 0.07 mol of  $Tb^{3+}$  in  $CaGdAl_3O_7$  phosphors. For  $x < 0.07$  the decay curves show a certain extent of rising in the initial part of decay curves, which is associated with the radiationless process involving cross relaxation [7, 8]. But in  $CaGdAlO_4$  phosphors we could not detected the rising phenomena at the lower concentration of Tb.

Finally, the intensity of luminance under 147 nm in  $ABC_3O_7$  compounds resulted in the same as follows;  $CaYAl_3O_7 > CaLaAl_3O_7 \approx SrLaAl_3O_7 > SrLaGa_3O_7 >$

$SrGdGa_3O_7$ , and the intensity of luminance of under 254 nm in  $ABCO_4$  compounds;  $SrGdAlO_4 > CaYAlO_4 > SrLaGaO_4 \approx CaLaAlO_4 > SrLaAlO_4$ .

#### 4. Conclusions

We investigated luminescent properties of  $ABCO_4:Tb$  and  $ABC_3O_7:Tb$  compounds by excitation and emission spectra. In result, both  $ABCO_4:Tb$  and  $ABC_3O_7:Tb$  phosphors emit the green light.  $ABC_3O_7:Tb$  phosphors absorbed shorter wavelength energy than  $ABCO_4:Tb$  phosphors so that the emission efficiencies of  $ABC_3O_7:Tb$  phosphors were higher than those of  $ABCO_4:Tb$  phosphors under vacuum UV (147 nm). In case of  $ABC_3O_7$  compared with  $ABCO_4$ , the absorbed energy of VUV wavelength region is more efficiently transferred to  $Tb^{3+}$  ion. So, the luminescent efficiency of  $ABC_3O_7$  phosphors is higher in VUV region. Moreover, the high luminance is detected in high activator concentration due to structural effect. The decay time of  $ABC_3O_7$  phosphors with maximum luminance is longer than that of  $ABCO_4$  phosphors.

#### 5. References

- [1] Ryba-Romanowski, W., Golab, S. Pisarski, W. A. Dominiak-Dzik, G. Berkowski, M. and Pajczkowska, A. J. Phys. Chem Solids, **58**(4), 639 (1997)
- [2] Blasse, G. and Bril, A. Philips Res. Repts **22**, 481 (1967)
- [3] Berdowski, P.A.M. Lammers, M.J.J. and Blasse, G. J. Chem. Phys., **83**, 476 (1985)
- [4] Feigelman, R.S. J. Am. Ceram. Soc., **47**, 257 (1964)
- [5] Milligan, W.O., Mullica, D.F., Beall, G.W. and Boatner, L.A. Inorg. Chim. Acta., **60**, 39 (1982)
- [6] Louis-Achille, V., De Windt, L. and Defranceschi, M. J. Mol. Struct., **426**, 217 (1998)
- [7] Sohn, K-S., Choi, Y. G., Choi, Y.Y., and Park, H.D. J. Electrochem. Soc., **147** (9) 3552 (2000)
- [8] Sohn, K-S., Choi, Y.Y., Park, H.D. and Choi, Y. G., J. Electrochem. Soc., **146** (6) 2375 (2000)