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Self heat generating synthesis of tri-colour lamp phosphors

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Abstract. The simple method for the preparation of phosphors such as aluminates, Y_2O_3, YVO_4 and $LaPO_4$ by the combustion synthesis described earlier in the literature is reported. It is shown here that the phosphors prepared by such synthesis do not possess all the required characteristics. Suitable modifications by way of annealing at $> 1200°C$ in controlled atmospheres, however, can yield the phosphors with characteristics which may fulfil the demands of lamp industry.

Keywords. Photoluminescence; phosphors; tri-colour lamps; aluminates; rare earth spectra.

1. Introduction

Photoluminescent materials are used in Hg-discharge lamps for converting UV light to visible. Such phosphors have been popularly called as 'lamp phosphors'. In 1971, a lamp with high colour rendition index was proposed which was based on blend of phosphors emitting in three primary colour regions (Koedam and Opstelten 1971). Verstegen *et al* (1974) had demonstrated such lamps for the first time. These lamps have been called tri-colour lamps. Various phosphors used in tri-colour lamps have often been reviewed (Ryan 1981; Pappalardo 1987; Smets 1987, 1991; Welker 1991; Blasse 1995; Ronda 1995). In recent years, some papers have appeared on preparation of these phosphors using self heat generating synthesis, also termed as the combustion synthesis (Ekambaram and Patil 1995 a,b,c; Kingsley *et al* 1990a,b). Phosphors in fine particle (of the order of several microns) form could be prepared by this method. In order to find out the suitability of the phosphors prepared by this method, it is necessary to study the parameters such as excitation and emission spectra, quantum efficiency, quenching temperature, etc. However, these important properties have not been reported. We have prepared some commonly used phosphors by the combustion synthesis and obtained relevant parameters. These results, which could be of real utility to the lamp industry, are presented in this paper.

2. Experimental

The following lamp phosphors were prepared using the combustion synthesis: $YVO_4:Eu^{3+}$ and $Y_2O_3:Eu^{3+}$ (red), $BaMgAl_{10}O_{17}:Eu^{2+}$, $Sr_4Al_{14}O_{25}:Eu^{2+}$ (blue), $Sr_5Eu^{2+}_{0.5}Mg_6Al_{55}O_{94}$ (blue), $CeMgAl_{11}O_{19}:Tb$, $LaPO_4:Ce, Tb$ (green), and $YVO_4:Dy$ (white). The synthesis involved heating of metal nitrates with fuels such as urea at temperatures around 500 °C. The details can be found in the original papers (Kingsley *et al* 1990a,b; Ekambaram and Patil 1995a,b,c). The compounds so prepared were identified using XRD technique. PL characteristics were studied using Hitachi

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F-4000 spectrofluorometer. Quantum efficiencies were obtained on a set up described elsewhere (Alexander *et al* 1993), or by comparing the light output with the standard phosphors.

3. Results and discussion

All the phosphors prepared were in fine particle form. The particle size ($< 7\mu$), which was determined using Malvern particle size analyser, is suitable for lamps.

Figure 1 shows the PL spectra for $Sr_4Al_{14}O_{25}:Eu^{2+}$ phosphor. Emission is obtained around 438 nm and the excitation maximum is observed at 318 nm. This is not characteristic of $Sr_4Al_{14}O_{25}:Eu^{2+}$. Most probably, another phase is formed. We modified the synthesis so as to produce reducing atmosphere. The phosphor prepared with this synthesis exhibited the well known (Smets *et al* 1989) emission in the form of a dominant band around 480 nm and a weak one around 400 nm. The excitation spectrum consists of two bands around 270 nm and 350 nm. The emission, however was very weak, about 25 times weaker than that required for lamp application. We prepared other Sr-aluminate phases. In $SrAl_{12}O_{19}$: Eu^{2+} emission was observed around 390 nm which agrees with the reported value (Kutty *et al* 1990). However, the quantum efficiency was much below the reported efficiencies of the order of 90% (Stevels and Schrama-de Pauw 1976; Kutty *et al* 1990). The aluminate $Sr_5Eu^{2+}_{0.5}Mg_6Al_{55}O_{94}$ was also prepared. Emission in this phosphor was obtained around 463 nm,

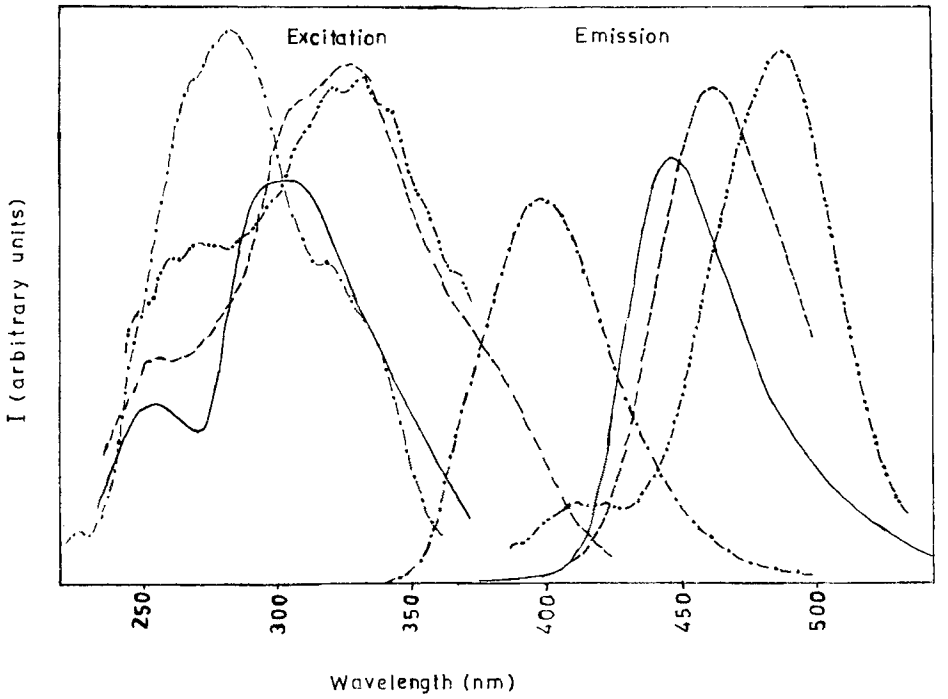

Figure 1. PL spectra for various europium doped Sr-aluminates (–.–.–, $SrAl_{12}O_{19}$; ———, $Sr_4Al_{14}O_{25}$:Eu; –.–.–.–, $Sr_4Al_{14}O_{25}$:Eu (prepared under reducing condition); – – –, $Sr_5Eu_{0.5}Mg_6Al_{55}O_{94}$:Eu).

which was close to the reported value (Verstegen 1974). The quantum efficiency (at 254 nm) was around 25% only. The excitation spectrum consisted of a strong maximum at 331 nm and only a weaker band around 250 nm. Thus, it can be concluded that by starting with different Sr: Al ratio, various Sr-aluminates can be prepared by the combustion synthesis. However, quantum efficiencies of the samples prepared by the combustion synthesis are an order of magnitude lower than those reported for the compounds. Perhaps, full reduction of Eu to the divalent form is not achieved. The temperature attained during the combustion synthesis may not be high enough to yield the phosphors with adequate PL efficiencies.

Figure 2 shows the PL spectra for $BaMgAl_{10}O_{17}$: Eu^{2+}. Intense emission is observed around 450 nm. Quantum efficiency is quite high, around 90%.

Figure 2 also includes PL spectra for $CeMgAl_{11}O_{19}$: Tb phosphor. This phosphor had yellow body colour. Most probably, this occurs due to presence of small amount of tetravalent Ce and Tb ions. Due to strong self-absorption, the apparent quantum efficiency of the phosphor was only 40%. We modified the synthesis so as to produce the phosphor with white body colour with quantum efficiency above 90%. The modified process is based on preparing the sample under reducing atmosphere. The excitation spectrum has a broad maximum around 270 nm, and the overlap with Hg emission at 253·7 nm is satisfactory. Another well known green emitting phosphor $LaPO_4$: Ce, Tb was also prepared by the combustion synthesis. Again, the

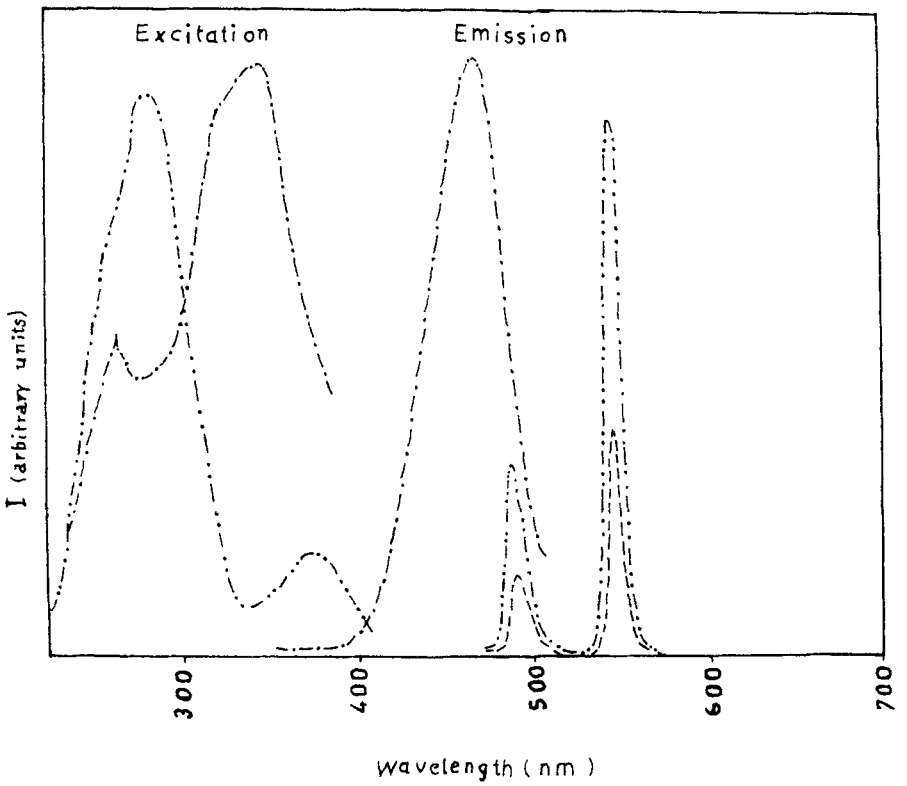

Figure 2. PL spectra for some commonly used lamp phosphors prepared by combustion synthesis (– – –, $LaPO_4$: Ce, Tb; –.–.–., (Ce, Tb) $MgAl_{11}O_{19}$; –.–.–, $BaMgAl_{10}O_{17}$: Eu).

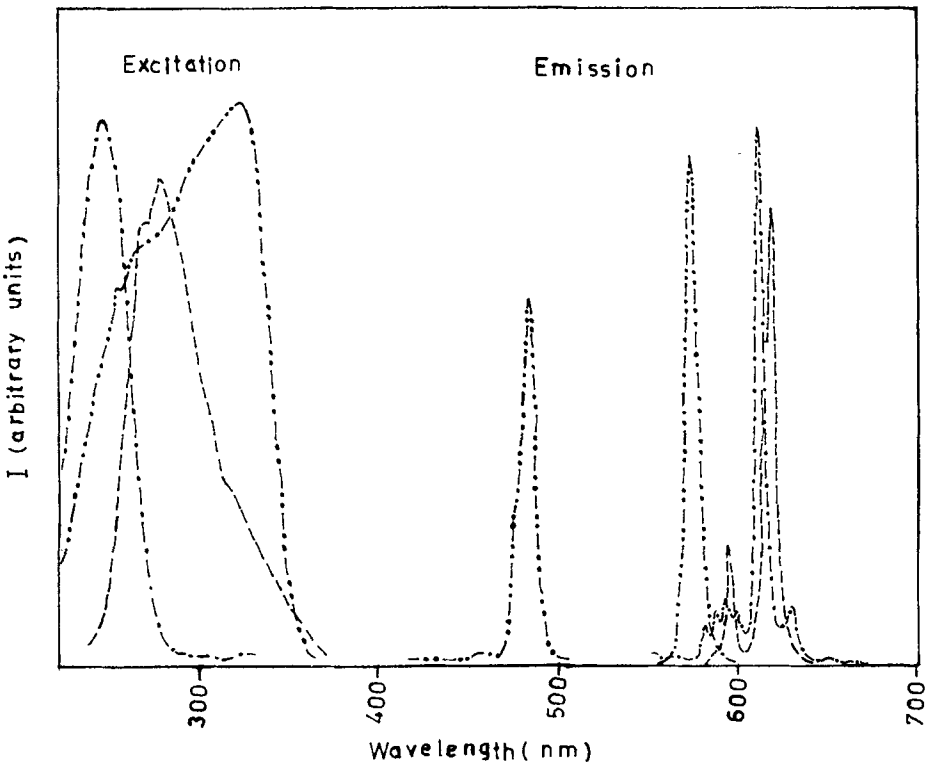

Figure 3. PL spectra for some yttrium based phosphors (.–.–, Y_2O_3: Eu; –..–..–, YVO_4: Dy; – – – YVO_4: Eu).

usual combustion synthesis produced a phosphor with yellow body colour. The modified synthesis involving reheating in reduced atmosphere produced the phosphor with desired properties.

Figure 3 shows PL spectra for Eu^{3+} doped Y_2O_3 and YVO_4 and Dy doped YVO_4 phosphors. In the case of the former, the well known emission around 610 nm is observed. The excitation peaking at 243 nm overlaps well with the Hg emission. However, the light output was only 40%, of that for the commercial phosphor for which 100% quantum efficiency is reported for (Welker 1991). When the Y_2O_3: Eu phosphor prepared by the combustion synthesis was re-annealed at 1400 °C for 1 h, efficiencies approaching 100% were obtained. It seems, that quenching the sample from high temperature phase occurring above 1400 °C is a must for obtaining good quantum efficiency (Schaik and Blasse 1992). Future attempts should be directed at achieving such temperatures during the combustion synthesis e.g. by using additional oxidizer (Gopichandran and Patil 1990). It is known that the temperature attained during the combustion synthesis is well in excess of the initiating temperature. The temperature can be controlled by choice and the quantity of the fuel and oxidizer (Chick *et al* 1990; Kingsley and Pederson 1993).

YVO_4: Eu and YVO_4: Dy phosphors prepared by combustion synthesis had a yellow body colour. These phosphors had to be re-heated at temperatures around 1200 °C for removing the body colour. High quantum efficiency of the order of 90%

was then observed for both the phosphors. YVO_4: Eu emission is in the form of narrow lines around 595 and 616 nm in the orange red region of the spectrum corresponding to transitions $^5D_0 \rightarrow {}^7F_1, {}^7F_2$. YVO_4: Dy emission is white, consisting of yellow (573 nm) and blue (483 nm) bands corresponding to $^4F_{9/2} \rightarrow {}^6H_{13/2}$ and $^6H_{15/2}$ transitions.

4. Conclusions

Lamp phosphors in fine particle form were obtained by the combustion synthesis. However, the quantum efficiencies, body colour, excitation spectrum, etc of the phosphors obtained by the method described in the literature are not suitable for application in lamps. Some modifications, such as reheating in the reducing atmosphere, of the synthesis, however, seem to be possible. These modified methods can lead to synthesis of phosphors with characteristics acceptable to lamp industry. Future efforts may be directed towards achieving these modifications.

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References

Alexander G, Ramakrishna P, Mukherjee T K and Nambi K S V 1993 *Indian J. Pure Appl. Phys.* **31** 531
Blasse G 1995 *J. Alloy Comp.* **225** 529
Chick L A, Pederson L R, Maupin G D, Bates J L, Thomas L F and Exarhos G J 1990 *Mater. Letts* **10** 6
Ekambaram S and Patil K C 1995a *J. Alloy Comp.* **217** 104
Ekambaram S and Patil K C 1995b *J. Mater. Chem.* **5** 905
Ekambaram S and Patil K C 1995c *Bull. Mater. Sci.* **18** 921
Gopichandran K and Patil K C 1990 *Mater. Letts* **10** 291
Kingsley J J and Pederson L R 1993 *Mater. Letts* **18** 89
Kingsley J J, Suresh K and Patil K C 1990a *J. Mater. Sci.* **25** 1305
Kingsley J J, Manickam N and Patil K C 1990b *Bull. Mater. Sci.* **13** 179
Koedam M and Opstelten J J 1971 *Light Res. Tech.* **3** 205
Kutty T R N, Jagannathan R and Rao R P 1990 *Mater. Res. Bull.* **25** 1355
Pappalardo R G 1987 in *Spectroscopy of solid state laser type materials* (ed.) Di Bartolo (New York: Plenum Press) pp 397–429
Ronda C R 1995 *J. Alloy Comp.* **225** 534
Ryan F M 1981 *J. Lum.* **24/25** 827
Schaik V W and Blasse G 1992 *Chem. Mater.* **4** 410
Smets B M J 1987 *Mater. Chem. Phys.* **16** 283
Smets B M J 1991 in *Adv. non-radiative processes in solids* (ed.) Di Bartolo (New York: Plenum Press) pp 353–386
Smets B M J, Ratlen J, Hoeks G and Verlijsdonk 1989 *J. Electrochem. Soc.* **136** 2119
Stevels A L N and Schrama-de Pauw A D P 1976 *J. Electrochem. Soc.* **123** 691
Verstegen J M P J 1974 *J. Electrochem. Soc.* **121** 1623
Verstegen J M P J, Radielovic D and Vrenken L E 1974 *J. Electrochem. Soc.* **121** 1627
Welker T 1991 *J. Lum.* **48/49** 49