Chapter - 6

SUMMARY OF RESULTS & SUGGESTIONS FOR FUTURE WORK
6.1 GENERAL

Presented work deals with the synthesis, characterization and development of luminescent materials. The material selection was crucial because of the limited facilities at the work place. It was decided that the materials that could be selected for their study should be synthesized by simple techniques, which does not involved temperatures more than 1000°C. The required facilities should be within the existing range of the place and not much investment are involved. Secondly, the work should involve such facilities that could be developed indigenously with meager investment. Our aim was to select few TLD materials and Lamp phosphors for the study of their synthesis in view to obtain easier, simple and cost effective techniques; characterization of structure of host, improvement in luminescent properties and development in view of cost reduction.

Accordingly, Lithium Aluminates host materials were selected for TL dosimetric applications specifically personal monitoring. MgB₂O₄·Dy,Na material was first studied in 1983 then in 1993 and very encouraging results are appeared during 2000. This material was accepted principally, as a TLD material for measuring and estimation of personal radiation exposures. The material has Zₘₐₓ value around 8.4 close to tissue equivalent and has all other properties like LiF-TLD 100.

We dealt with phosphor for lighting and presented our own results on the tricolour lamp phosphors, high-pressure mercury vapour pressure lamp phosphors. While going through the literature, it was felt that no systematic work has been done in synthesis of these phosphors and simple method of preparation. Most of the reported methods require stringent experimental conditions involving high temperatures as high as 1600°C. Other recent methods involve use of sol gel technique. Though it offers many advantages such as small particle size, homogeneity of the product etc., a lot of processing is involved to get the final product. Many a times, firing at high temperature is essential to get good crystallinity. In view of this situation need was felt to device, simple and low temperature method to synthesize these phosphors.

While selecting the materials from Lamp phosphors, it was decided to take at least 2 representatives from Red, Green, Blue and UV regions. Specifically, the emphasis was given on the improved methods of their synthesis. For the developmental study we had selected age old RED Correction phosphor Y₂O₃:Eu and an UV emitting phosphor CaSO₄:Eu.
6.2 SUMMARY OF RESULTS

1. In the system of Lithium-aluminium mixed oxide system we prepared all the possible different phases viz. LiAlO$_2$, Li$_3$Al$_2$O$_6$, Li$_3$A$_{11}$O$_9$ and Li$_5$AlO$_4$ doped with 100 ppm Cu as well as Mn. Surprisingly, it was noticed that only Li$_5$AlO$_4$:Cu (100 ppm) and Li$_5$AlO$_4$:Mn (100 ppm) was able to show the TL emission.

2. The phase Li$_5$AlO$_4$ has a $Z_{eff}$ very close to tissue equivalent, and hence this promising material was further tested for rest of the dosimetric parameters. The TL intensity of Li$_5$AlO$_4$:Cu is about 62% of that for TLD-100 whereas the TL intensity for Li$_5$AlO$_4$:Mn was very much less of about 20%.

3. The glow curve (C) for Li$_5$AlO$_4$:Cu consists of a single glow peak mostly symmetrical at about 341°C. Its shape is very simple and relatively at much higher temperature as compared to TLD-100. Its full width at half maximum is relatively higher than that of TLD-100.

4. In case of Li$_5$AlO$_4$:Mn also the similar TL behavior was noticed (Curve E). It has a very low intensity and the peak is very wide. The peak temperature in this case is about 327°C.

5. In case of Mg$_2$O$_7$:Dy,Na we reproduced all the promising results as expected. The glow curve of Li$_5$AlO$_4$:Cu is very simple as compared to all the other three phosphor materials.

6. Looking at the promising features of Li$_5$AlO$_4$:Cu phosphor it was further investigated for various higher doping concentration of Cu. We noticed that the TL intensity decreases remarkably with increasing doping concentration. Cu in higher concentration proved to be 'killer' in the host rather than an activator. Maximum TL intensity was noticed in 100-ppm sample and TL intensity decreases continuously and saturates at doping level of 1000 ppm.

7. The Glow curves for 1000-ppm and 1500-ppm samples are nearly identical. In short, the TL intensity is found to be comparable with that of LiF-TLD100 (with same exposure) only for the doping level of Cu of about 100 ppm. Therefore, the sample having 100 ppm doping of impurity was further investigated in respect of dose dependence. We noticed perfect linear variation of TL peak Intensity with dose.
8. The study is repeated for Mn doped Lithium aluminate here we noticed that the Mn doping proved to be less promising than Cu. Further we noticed perfect linearity only up to 1000 Rad and TL intensity was very much less as compared to that of Cu sample.

9. We made all the TL tests on MgB₄O₇:Dy,Na and we confirmed the literature reports. The synthesis method we used is combustion. All the results are in good agreement with that of the literature. It is noticed that the TL intensity at the peak 163 °C, increases with doping concentration and also increases almost linearly with the increasing exposure.

10. We have further studied the effect of heating rates on the glow curve of MgB₄O₇:Dy,Na we found that the increase in heating rate shifts the TL peak towards high temperatures with the decrease in TL intensity (peak height) and little broadening of the glow peak.

11. TL Response curves: The perfect linearity is observed in Li₅AlO₄:Cu and MgB₄O₇:Dy,Na for the full range of doses used, i.e. 10Rad to 10000 Rad. It is observed that the Li₅AlO₄:Cu (100ppm) is more sensitive than MgB₄O₇:Dy,Na.

12. Reusability and thermal stability were checked and we noticed no change in TL intensity/sensitivity and good thermal stability.

13. In case of the fading test also the Li₅AlO₄:Cu (100ppm) has found to succeed MgB₄O₇:Dy,Na. It has shown fading as low as 1.5 % in 30 days when stored in dark.

14. The main features of Li₅AlO₄:Cu (100 ppm) powder solid thermoluminescent Dosimeters are its nearly tissue equivalence to photon radiation (Zeff. = 8.2), which is measurably lower than MgB₄O₇:Dy,Na ,high sensitivity ,very simple and single well defined yet symmetrical glow curve, low fading about 1.5% in 30 days, excellent reproducibility and reusability and very wide linearity range upto 100Gy.

15. Above mentioned characteristics make this TL material very useful and anytime better than MgB₄O₇:Dy,Na (as reported by Furetta et al 2000) for multimode dosimetric applications, particularly in individual monitoring as well as in various medical dosimetric purposes. High trap depth of this material makes it very stable dosimeter since its single glow peak is at 341°C.
16. Red phosphor is the major component (80%) in the tri-colour lamp and hence extensive research on luminescent properties of $Y_2O_3$: Eu$^{3+}$ has been carried out. Since the charge transfer transition of Eu$^{3+}$ has a good overlap with the most intense mercury discharge line (254 nm), direct excitation of Eu$^{3+}$ is possible. On excitation at 254 nm, $Y_2O_3$: Eu$^{3+}$ shows sharp emission at 611 nm in which maximum intensity is concentrated. For getting good luminescent properties, Eu$^{3+}$ should be doped homogeneously in the host.

17. The $Y_2O_3$: Eu$^{3+}$ phosphor shows the characteristic narrow band emission at 611 nm and its excitation maximum (246nm) overlaps well with the intense line in the Hg discharge, hence this phosphor is most deserving as a red component in lamp applications. The emission spectrum of $Y_2O_3$: Eu$^{3+}$ shows two curves for two different samples prepared by co-precipitation and molten salt method. The intensity of emission was found to be little higher in sample prepared by co-precipitation.

18. PL spectra for YVO$_4$: Eu phosphors. The emission spectrum consists of well-known Eu$^{3+}$ lines around 596nm, 610nm and 618 nm. The first line corresponds to $^5D_0 \rightarrow ^7F_1$ transition and remaining two lines correspond to $^5D_0 \rightarrow ^7F_2$ transition. The 616nm line is most intense as compared to 585nm line in the emission spectrum. The YVO$_4$: Eu sample prepared by solid state reaction method showed slightly higher emission intensity as compared to molten salt method.

19. CeMgAl$_{11}$O$_{19}$: Tb$^{3+}$ phosphor, which is a green emitter in a blend, was synthesized by combustion synthesis. The results in this case are also encouraging because this method is not only time and energy saving but also found to be effective in lowering the cost of manufacture of the phosphor used in the blend.

20. BaMgAl$_{10}$O$_{17}$: Eu$^{2+}$ is another well-known blue emitting lamp phosphor widely used for last 2-3 decades. We applied here combustion synthesis method. We found that this phosphor is prepared within several minuets and the powder so obtained is having a uniform particle size and yet its luminescent properties are not altered. The combustion synthesis is found to be more useful in this case also.
21. Sr$_{4.95}$ Eu$_{0.05}$ (PO$_4$)$_3$Cl phosphors prepared by solid state reaction show the PL emission at 445 nm at the blue region of the spectrum after excitation of 254 nm of emission of Hg vapour. Sr$_{4.95}$ Eu$_{0.05}$ (PO$_4$)$_3$Cl possesses comparable PL intensity with that of commercial leader blue phosphor. Hence, Sr$_{4.95}$ Eu$_{0.05}$ (PO$_4$)$_3$Cl can be used in lamp industry as a blue component of tri-colour lamp.

22. PL spectrum of LaPO$_4$(Ce,Tb). Excitation spectra consist of a broad band centred on 280nm corresponding to the transition 4f$\rightarrow$5d. The spectrum shows a strong absorption having good overlap with Hg radiation. Emission spectrum shows a very strong emission at 543nm ($\lambda_{ex}=254$nm) due to the transition $^5$D$_{4}$ $\rightarrow$ $^7$F$_{5}$ of Tb. The excitation and emission intensities in samples prepared by solid-state reaction and co-precipitation method were found to be almost similar.

23. Eu$^{3+}$ and Eu$^{2+}$ exhibit characteristically different PL. Eu$^{3+}$ emission is weak arising from forbidden transitions $^5$D$_{0}$ $\rightarrow$ $^7$F$_{1}$ (around 590 nm) and $^5$D$_{0}$ $\rightarrow$ $^7$F$_{2}$ (around 611 nm) whereas efficient Eu$^{2+}$ emission corresponding to transition from levels 4f$^6$5d$^1$ configuration to the ground state $^8$S$_{7/2}$ of 4f$^7$ configuration peaks at 385 nm in CaSO$_4$. In the un-irradiated sample there is no Eu$^{2+}$ present, and hence no 385 nm emission.

24. Exposure to ionizing radiation causes some Eu$^{3+}$ $\rightarrow$ Eu$^{2+}$ conversion. Characteristic PL of Eu$^{2+}$ are observed in the irradiated sample. Eu$^{2+}$ concentration in the irradiated sample and thus the PL intensity is proportional to the exposure. Excitation source for RPL lamp using CaSO$_4$:Eu$^{3+}$ is thus capable of exciting Eu$^{2+}$, and it not having component overlapping with Eu$^{2+}$ emission (360-410 nm). In our samples, excitation spectrum of Eu$^{2+}$ is quite broad. However, short wavelength UV itself causes some Eu$^{2+}$ $\rightarrow$ Eu$^{2+}$ conversion. Thus it is suitable in Lamps emitting in UVB region.

25. We have prepared CaO:Bi$^{3+}$ phosphor by co-precipitation method with the subsequent decomposition into oxide. The aqueous solution of Ca(NO$_3$)$_2$.4H$_2$O (4.7135gm) and Bi(NO$_3$)$_3$.5H$_2$O (0.0194gm) was prepared in double distilled water, which was then precipitated by required quantity of (NH$_4$)$_2$CO$_3$, to get ppt of Bi$^{3+}$ doped CaCO$_3$. This ppt was oven dried and decomposed at 1000°C, for 24 hours and a powder sample of CaO:Bi$^{3+}$ was obtained. The emission spectrum showed a single peak at about 395nm, which has the PLLCD application. The excitation spectrum is broad band, covering the UV range and having peaks at 230nm, 310nm and 360nm.
26. One more exemplary phosphor, which has potential for its application in red component of full color thin film electro-luminescent devices was synthesized and its PL spectrum showed the strong emission centered at around 631nm.

27. It is possible to obtain UV emitting materials giving light output in a well-defined spectral region. These phosphors can be used in preparing lamp phosphors based on Hg-discharge. Fast, low cost methods like combustion synthesis can be used for preparing these phosphors. Development of lamps prepared from these phosphors will be desirable for further research in the field such as photo therapy, patients monitoring etc.

28. We prepared CaSO₄ Eu by various co-precipitation routes and also with acid distillation. We found the identical nature of excitation and emission spectra in PL study and also in TL profile. It has clearly indicated good reproducibility of material and consistency of co-precipitation method of synthesis, formation of desired CaSO₄ host and incorporation of activator (Eu²⁺) in the host. The single intense peak at 388 nm (λₑₓ = 254 nm) confirms the existence of Eu²⁺ in the host after UV-irradiation. The various excitation bands corresponding to f-d transition of Eu²⁺ ions further confirm the existence of Eu²⁺ in the host.

29. We performed PL measurements on Y₂O₃: Eu³⁺ phosphor prepared from Y₂O₃ of different purities (99.99%, 99.90% & 99%). Each emission spectrum contains only a dominant line at 611 nm, corresponding to the transition ⁵D₀ → ⁷F₂. The relevant excitation arises from the charge transfer band peaking at 246 nm in the excitation spectrum. Intensity of emission in these samples is same (within ±5%) as that of the sample prepared from 99.99% Y₂O₃, as well as the commercial phosphor. Not withstanding the emphasis on using high purity materials for synthesis of Y₂O₃: Eu³⁺, We find in this study that, the use of yttrium oxide of lower purity does not affect the properties of Y₂O₃: Eu³⁺ phosphor.

30. From the results presented here, it can be concluded that Y₂O₃ of 99% purity can be used for the synthesis of Y₂O₃: Eu³⁺ phosphor. Use of Y₂O₃ of 99% purity in the synthesis of the phosphors mentioned above will help in reducing the cost of production from Rs. 8283/- to Rs. 3262/-. 
31. \( \text{Y}_2\text{O}_3;\text{Eu} \) is further considered for its development. Its Excitation maxima of the spectrum is slightly away from the desired wavelength of Hg discharge i.e., 253.7 nm. La and Y has approximately same ionic size. We obtained most interesting results for the designed experiments on widely used RED phosphor \( \text{Y}_2\text{O}_3;\text{Eu} \). It is clearly seen that best compromise for high intensity and matching of the excitation peak for Hg discharge main line is achieved in \( Y_{1.40} La_{0.65}O_3; Eu_{0.03} \).

32. By incorporation of La in place of Y in a host material there is reduction of the cost of the product simply because of lower cost of La-compound.

33. The investigations on the Y-La system has clearly indicated that the substitution of Y by La in \( \text{Y}_2\text{O}_3;\text{Eu} \) results in shifting of excitation peak from 246 nm to desired 253.7 nm for \( Y_{1.40} La_{0.65}O_3; Eu_{0.03} \). This shift has improved the conversion efficiency of the phosphor by about 25%. It is also further concluded that the incorporation of La in place of Y in a specified ratio has also brought down the cost of the phosphor. If the lower purity Yttrium oxide is used in the phosphor the cost of the modified yet improved phosphor could be brought down from Rs. 8283/- to Rs. 2669/- per kg of the product. The modified yet technologically improved product could be prepared as low as 32.22 % cost.

6.3 SUGGESTIONS FOR FUTURE WORK

1. The investigations on \( \text{Li}_5\text{AlO}_4;\text{Cu} \) (100 ppm) are preliminary. The tailoring of the material, with the choice and control over the co-dopant, to yield high TL intensity and the peak of the glow curve at appropriate temperature is to be carried out. The further study of these systems with respect to dose linearity, fading characteristics, reuse treatment, batch processing will only decide their usefulness in the TL dosimetry.

2. The investigations on our TLD materials has clearly indicated that the TL intensity at the respective peak temperature of our \( \text{Li}_5\text{AlO}_4;\text{Cu} \) (100 ppm) is lower than LiF.TLD-100 but any time very high as compared to that of \( \text{MgB}_4\text{O}_7;\text{Dy}, \text{Na} \). TL peak in our newly tried sample is little broad. The TL intensity could be improved and peak could be made still narrow by giving the right type of annealing/quenching treatment. The investigations in this context will be very promising.
3. Since, the excitation maximum of YVO₄: Eu matches with the intense line in HPMV discharge tube, it is used in high-pressure lamps. Though the intensity of emission in samples prepared by molten salt method is slightly less as compared to other methods, this method can be improved.

4. Significant advantages are expected from the use of narrow band 390 nm phosphor in collimation optics and in polarizers in addition to performance advantages from having higher transmission to the LCD. There are significant benefits in the use of narrow band illumination for PL-LCD. The effect of bandwidth on contrast ratio for a normally black mode TN has been shown. The selection of a phosphor with a peak emission wavelength near 390 nm permits higher transmission (x 1.03) through a standard LCD than the 365 nm emission used in the original disclosure.

5. There is need to improve upon the matching of the wavelength of source of excitation in many phosphors. The experiments that are performed on Y-La system could be carried on CaSO₄:Eu, YVO₄:Eu etc for better luminescent properties at reduced cost.