CHAPTER V

SUMMARY AND CONCLUSIONS
5.1 Summary

There is renewed interest in manganese doped zinc silicate, a well-established green emitting phosphor with high luminescent efficiency, for use in plasma display panels.

The synthesis and photoluminescence study of Zn$_2$SiO$_4$·Mn phosphor by different methods for comparative analysis was carried out. The Zn$_2$SiO$_4$·Mn phosphor was prepared by Sol-gel, CGUPS and combustion synthesis methods. Samples prepared by these methods exhibit good intensities. In Sol-gel and CGUPS methods, it was necessary to heat the sample above 1100 °C in a reducing atmosphere. In contrast, the combustion method is quick; the reaction is completed within few minutes and the reheating at 1000 °C, even in air, produces the samples of desired intensity.

The emission in synthesized Zn$_2$SiO$_4$·Mn, which corresponds to the transition $^4T_{1g} (^4G) \rightarrow ^5A_{1g} (^6S)$, has a maximum situated at 523 nm with half width of 37 nm, which agrees with the literature value. The corresponding excitation spectrum shows a maximum around 243 nm corresponding to CT transition of Mn$^{2+}$. The emission shows that Zn$_2$SiO$_4$ is formed during the combustion synthesis itself. This is also confirmed from the powder photographs that match well with file JCPDS 37-1485, corresponding to Willemite. This result is significant for obtaining Zn$_2$SiO$_4$·Mn phosphor in fine particle form; as it is known that combustion synthesis yields fine particles. Re-heating at 900 °C removes the colour and increases the intensity. Zn$_2$SiO$_4$·Mn phosphor with intense green emission was obtained by the combustion methods using urea or 3MP5O as fuels. Of the two combustion syntheses used, the one using ZnO as source of zinc and urea as fuel was found most suitable. PL intensities matching the commercial samples were obtained in a sample with optimised fuel to oxidiser ratio with ZnO, Silicic acid, MnSO$_4$, ammonium nitrate and urea in molar ratio 1.92 : 1 : 0.08 : 20 : 20. It was also found that with the Ge co-doping in Zn$_2$SiO$_4$·Mn, the peak of the emission maximum shifts towards the longer wavelength side.

In Eu$^{2+}$ activated silicate hosts, the excitation can be achieved by long wavelength UV bordering onto visible region and the emission is in blue or green region of the spectrum. Such phosphors can be useful for photoluminescent liquid crystal display (PLLCD) applications.
The fluorescence of Eu\(^{2+}\)-activated binary and ternary silicates was, therefore, studied. In the present study some of the alkaline earth silicates doped with divalent europium were prepared by combustion synthesis using the readily available starting materials. Urea was used as a fuel and ammonium nitrate as oxidizer in the optimised ratio.

The phosphors by one-step combustion synthesis did not show intense emission, probably the activator Eu is not incorporated in divalent form. The phosphors were reheated, in the reducing atmosphere provided by heating in a closed box with charcoal, at 900 °C for 1 hour.

In BaSi\(_2\)O\(_5\):Eu\(^{2+}\) efficient broad band emission with maximum at 500 nm is observed for 254 nm excitation. But it does not have efficient excitation at 385-390 nm. Similarly the characteristics emission of Eu\(^{2+}\) was observed in many binary and ternary alkaline earth silicates. Efficient excitation by 385 nm, which is required for PLLCD applications, was observed for some Eu\(^{2+}\) doped disilicates. Their excitation spectrum shows considerable intensity at 385 nm. Emission in Sr\(_2\)MgSi\(_2\)O\(_7\):Eu\(^{2+}\) peaks around 457 nm. Sr\(_2\)MgSi\(_2\)O\(_7\):Eu\(^{2+}\) appears to be suitable as a blue phosphor for PLLCD applications.

The excitation spectrum for Sr\(_3\)MgSi\(_2\)O\(_8\):Eu\(^{2+}\) show very good absorption at 390 nm and it has a sharp edge in the absorption at 400 nm. For both, 254 and 385 nm, excitations, the emission is identical except the intensity. The intensity of emission is 3-times more for excitation at 385 nm than that at 254 nm. The emission band is centred at 454 nm with a bandwidth (FWHM) of 40 nm. The characteristic emission of Eu\(^{2+}\) is corresponding to parity-allowed electric dipole transitions between \(^5S\_{7/2}\)\(\rightarrow\)4f\(^7\) ground state and crystal field components of 4f\(^5\)5d excited state configuration, with the lifetime of the order of 0.6 μs. It was observed that, Sr\(_3\)MgSi\(_2\)O\(_8\):Eu\(^{2+}\) can meet the condition of efficient absorption at 390 nm and transparency to entire visible range. The emission intensity is compared with the blue standard for lamp phosphor BaMgAl\(_{10}\)O\(_{17}:\)Eu\(^{2+}\) and the quantum efficiency of the order of 90% is estimated.

The phosphor Sr\(_3\)MgSi\(_2\)O\(_8\):Eu\(^{2+}\) appears to be a most suitable material as a visible blue emitter in the PI-LCD application. Also it has very good absorption at 370 nm, the emission of GaN based UV laser, and can be a promising blue
component for white light generation using the GaN UV laser and the RGB emitters having excitation at 370 nm.

In the search of efficient UV emitters, some alkaline earth silicates activated with \( \text{Pb}^{2+} \) were prepared by the combustion synthesis. It was observed that \( \text{Pb}^{2+} \) exhibits very efficient emission in \( \text{BaSi}_2\text{O}_5 \) host. Emission in \( \text{BaSi}_2\text{O}_5;\text{Pb} \) is in the form of a broad band around 350 nm and a shoulder at longer wavelengths. The excitation maximum is around 245 nm. The spectra correspond to \( ^1\text{S}_0 \rightarrow ^1\text{P}_1 \) transitions. Luminescence of \( \text{Pb}^{2+} \) (1 mol.%), in some alkaline earth silicates was also studied. The \( \text{Pb}^{2+} \) doped AE silicates can be the promising candidates for UV phototherapy. The \( \text{Ca}_2\text{ZnSi}_2\text{O}_7;\text{Pb}^{2+} \) shows strong emission intensity when excited with 254 nm radiation with a peak at 360 nm.

The lithium silicate system was investigated for TLD application using several activators. The lithium orthosilicate was used as the host material and the activators, such as \( \text{Mn}, \text{Pb}, \text{or Cu} \), from transition metals and \( \text{Eu}, \text{Dy}, \text{Ce} \text{ or Tb} \) from rare earths, with and without the co-dopants such as \( \text{P} \) and \( \text{Mg} \), were tried. There exists a series of solid solutions in the system (Li_2O – MgO – SiO_2) such as Li_2SiO_4, Li_3Mg_0.5SiO_4, Li_2MgSiO_4, and Mg_2SiO_4. The materials were prepared by combustion methods. Some samples were prepared by precipitation method and few samples were also prepared by Sol-gel method. The powder photograph for the lithium silicate matched with the JCPDS file 37-1472 corresponding to Li_2SiO_4. Thermoluminescence glow curves were recorded with the usual set-up.

The materials prepared by sol-gel and precipitation method do not show appreciable TL intensity. The particle size and phase purity may be the reasons. The combustion synthesis with subsequent sintering, does yield interesting results in some systems. The effective-Z value for Li_2SiO_4 is 9.04, which is nearer to the tissue equivalent value of 7.4. Preliminary investigations suggest that Ce can be an efficient activator for developing the TLD material based on the Li_2SiO_4 system, subject to the optimisation of the several parameters. The highest intensity and simplest glow curve in the systems studied in this work was observed with the Ce activator in Li_2SiO_4. In the case of Li_2SiO_4;Ce, the glow curve is simple and the peak of the glow curve is at 523 K. The glow curve for Li_2SiO_4:Mg, Ce shows peak at 575 K.

Thus, several types of silicates were successfully prepared using the combustion synthesis. The well known phosphors Zn\(_2\)SiO\(_4\):Mn and Ba\(_2\)Si\(_2\)O\(_5\):Pb could
be reproduced using this synthesis. Characteristic emission of activators such as \( \text{Ce}^{3+} \), \( \text{Eu}^{2+} \) and \( \text{Pb}^{2+} \) could be observed in the silicates prepared by this method. The combustion synthesis thus furnishes a fast and simple method for preparing silicate phosphors.

The synthesis of \( \text{YVO}_4: \text{Eu}^{3+} \) and \( \text{YVO}_4: \text{Dy}^{3+} \) phosphors using novel synthesis methods was undertaken to compare suitability of various methods. The phosphors \( \text{YVO}_4: \text{Eu}^{3+} \), \( \text{YVO}_4: \text{Dy}^{3+} \), \( \text{YV}_{0.4}\text{P}_{0.6}\text{O}_4: \text{Eu}^{3+} \), and \( \text{YV}_{0.4}\text{P}_{0.6}\text{O}_4: \text{Dy}^{3+} \) were prepared by solid-state reaction, precipitation, and combustion synthesis using different fuels, with \( \text{Eu} \) concentration of 0.05 per mole of \( \text{Y} \) (5 mole %) and \( \text{Dy} \) concentration of 0.005 per mole of \( \text{Y} \) (0.5 mole %). The X-ray diffraction investigations on all the samples proved them to be single phase and crystalline.

Intense emission was observed in the samples prepared by Solid State synthesis as well as the combustion synthesis using 3MP5O (3-methylpyrazole-5-one), Glycine, Citric acid or Urea as fuels. Similar results were obtained for \( \text{YVO}_4: \text{Dy} \) phosphor also. Efficient, rare earth doped \( \text{YVO}_4 \) phosphors can thus be obtained by various syntheses including the conventional solid-state synthesis.

Efficient red emission was obtained in \( \text{YV}_{0.4}\text{P}_{0.6}\text{O}_4: \text{Eu} \). Addition of phosphorus modifies the excitation spectrum resulting in better overlap with mercury emission. The emission spectrum remains more or less the same. In case of \( \text{YV}_{0.4}\text{P}_{0.6}\text{O}_4: \text{Dy} \) addition of \( \text{Dy} \) modifies the excitation as well as the emission. The emission in \( \text{YV}_{0.4}\text{P}_{0.6}\text{O}_4: \text{Dy} \) is white while that in \( \text{YVO}_4: \text{Dy} \) is yellow.

The \( \text{Li}_{10}\text{La}_{10-x}\text{VO}_4: \text{Eu}^{3+} \) (\( x = 0.3 \)) phosphor was prepared by citrate sol-gel method and combustion method using urea as fuel, and ammonium nitrate as oxidizer. \( \text{Li}_{10}\text{La}_{10-x}\text{VO}_4: \text{Eu}^{3+} \) cannot be efficiently excited by 254 nm excitation. The emission spectra for \( \text{Li}_{0.9}\text{La}_{0.7}\text{VO}_4: \text{Eu}^{3+} \) resembles that of \( \text{YVO}_4: \text{Eu}^{3+} \) for the transition corresponding to \( ^5D_0 \rightarrow ^7F_2 \) (around 610 nm). The synthesis of \( \text{Li}_3\text{VO}_4 \) was also attempted. The materials prepared by solution process were found to be hygroscopic, which may presumably be due to the unreacted lithium nitrate in the product. The samples prepared by solid-state reaction, using \( \text{Li}_2\text{CO}_3 \), \( \text{V}_2\text{O}_5 \), and the dopant salts gives crystalline single phase product which is seen from the XRD pattern. It was found that slow heating rate is essential for the formation of the appropriate phase. It seems that the solution method is not appropriate for the preparation of \( \text{Li}_3\text{VO}_4 \). The solid-state reaction with slow heating appears to be most
suitable. The characteristic emission of Eu$^{3+}$ could be observed in Li$_{0.6}$La$_{0.7}$VO$_4$:Eu$^{3+}$ and Li$_3$VO$_4$:Eu.

Thus, vanadate based phosphors were prepared by various methods. Efficient phosphors can be prepared by the conventional solid-state synthesis; however, slow heating is essential for obtaining phosphors without body colour.

5.2 Suggestions for the Future Study

The combustion synthesis using urea and ammonium nitrate has provided very encouraging results during the course of this study. Many silicates could be successfully synthesised using this method. The silicates are the promising candidates in many technological applications. Due to the time-bound nature of the work, only few of them were studied. The synthesis of other silicates with the combustion method can be undertaken. The silicates find use in not only the photoluminescence applications, but also in many other applications such as CL, El, PSL, etc. In this study only the photoluminescence and to some extent the thermoluminescence properties were studied. It will be of immense interest to study other luminescence applications in the silicates. The silicates also have applications in the fields other than the luminescence. The synthesis of such materials and their study can be a promising task.

The combustion synthesis is the quick, efficient and cost effective method for the synthesis of oxide based materials. The extension of this method to large scale processing with batch homogeneity and reproducibility is a demanding field. Further characterization of the synthesised materials for the particle morphology using the SEM and TEM facilities will be much useful.

The investigations on the TL properties of Lithium orthosilicate suggest that extension of this study with the proper choice and control over the co-dopants, may yield high TL intensity and the peak of the glow curve at appropriate temperature. The further study of these systems with respect to dose linearity, fading characteristics, reuse treatment, batch processing to decide their usefulness in the TL dosimetry is again a new avenue.

During the course of study it was observed that the efficient phosphors could be reproduced using the readily available materials. Therefore, the synthesis of other oxide based host materials may be undertaken using the urea-ammonium nitrate combustion synthesis.