Divalent europium-activated alkaline-earth-metal chlorophosphate luminophores [$M_5(PO_4)_3Cl:Eu^{2+}$; M = Ca, Sr, Ba] by self-propagating high-temperature synthesis

M. Kottaisamy, M. Mohan Rao and D. Jeyakumar*

Central Electrochemical Research Institute, Karaikudi, 630 006, India

Divalent europium-activated alkaline-earth-metal chlorophosphate luminophores (MCAP : Eu^{2+}; M = Ca, Sr, Ba) have been prepared by self-propagating high-temperature (SPHT) synthesis in one pot employing the corresponding nitrates/chlorides, urea and diammonium hydrogen phosphate. The synthesized materials have been characterized by X-ray diffraction, photoluminescent emission spectroscopy, thermogravimetry, scanning electron microscopy and particle size analysis. The formation of chloroapatite depends on the nature of acid used in the combustion mixture. The photoluminescent emission efficiency and particle size distribution are found to depend on the amount of metal chloride used and on the sintering temperature. The results obtained are discussed with respect to the processing method employed.

Alkaline-earth-metal halophosphates, also known as apatites, have the generic molecular formula $M_5(PO_4)_3X$ (M = Ca, Sr, Ba; X = F, Cl, Br, OH) and are well known for their applications as phosphor materials,[1,2] laser hosts[3] and biocompatible materials.[4] Among these, divalent europium-activated strontium chlorophosphate (SCAP : Eu^{2+}) is an efficient photoluminescent material, used as the blue component in high-efficiency compact fluorescent lamps.[2] Barium chlorophosphate (BCAP : Eu^{2+}) is a promising material for X-ray imaging.[5] Hence, the luminescence properties of Eu^{2+} in chloroapatite matrices have been studied extensively.[6–8]

Various routes have been reported for the preparation of MCAP employing different phosphate sources.[1,6,9] The commercial method is based on the conventional ceramic route, involving high temperatures, employing $MHPO_4$ as the phosphate source, along with MCO_3, Eu_2O_3 and MCl_2 in suitable proportions. Eqn. (1) depicts the formation of MCAP : Eu^{2+}.

$$6MHPO_4 + (3-x)MCO_3 + xEu_2O_3 + MCl_2 \rightarrow M_{10-x}(PO_4)_6Cl_2 : xEu^{2+} \quad (1)$$

The reaction pathways for the formation of apatite can be given as follows:

$$6MHPO_4 \rightarrow 3M_2P_2O_7 \quad (2)$$

$$3M_2P_2O_7 + (3-x)MCO_3 + x/2Eu_2O_3 \rightarrow 3M_{3-x}(PO_4)_2 : xEu \quad (3)$$

$$3M_{3-x}(PO_4)_2 : xEu + MCl_2 \rightarrow M_{10-x}(PO_4)_6Cl_2 : xEu \quad (4)$$

As can be seen from eqn. (2)–(4), the formation of apatites involves the formation of various intermediates. Hence, the homogeneous mixing of raw materials must be ensured and intermittent grinding is also essential. Further, the preparation of luminescent-grade raw materials like $MHPO_4$ and MCO_3 is cumbersome, time consuming and critically dependent on various parameters such as pH, concentration of the metal and phosphate ions, precipitation temperature, rate of addition, digestion.[1]

Recently, a novel technique, self-propagating high-temperature (SPHT) synthesis, has been reported for the preparation of oxygen-rich ceramic materials[10–13] through solution processing. Recently, we have exploited the SPHT synthetic route for the preparation of $Y_2O_3 : Eu^{3+}$ red phosphor.[14] In continuation of this, an attempt has been made to synthesis an SCAP : Eu^{2+} phosphor in one pot and the results obtained are presented in this paper. For completion and comparison, results obtained on its analogues, namely CCAP : Eu^{2+} and BCAP : Eu^{2+}, are also discussed briefly.

Experimental

The stoichiometric compositions of the redox mixtures for the combustion reaction were calculated, using the total oxidizing (O) and reducing (R) valences of the individual components, which serve as the numerical coefficients for the stoichiometric balance, so that the equivalent ratio, R_e is unity (*i.e.* O : R = 1) and the energy released by the combustion is maximum.[15] Based on the concept used in propellant chemistry, the elements H, C, M (Ca, Sr, Ba and Eu) are considered as reducing species with valencies of +1, +4, +2, +3 (for Eu). The oxygen is considered as an oxidizing species with a valency of −2 and the valency of nitrogen is considered as zero. According to this concept, the oxidizing valences of $M(NO_3)_2$, $Eu(NO_3)_3$ and NH_4NO_3 become −10, −15 and −2, respectively, and the reducing valences of urea and DAP become +6 and +6, respectively.

The required amounts of Analar-grade metal nitrate, ammonium nitrate, europium nitrate and urea were dissolved in deionised water. Then the appropriate quantity of diammonium hydrogen phosphate (DAP) was added after adjusting the pH of the solution to 1–2 by the addition of either dil. HNO_3 or HCl. Note that at higher pH, precipitation was observed which lead to inhomogeneity in the solution. The activator, europium (1.4 mol% with respect to metal), was added as europium nitrate, after dissolving corresponding Eu_2O_3 in nitric acid (the excess nitric acid was evaporated off). According to the MCAP formula [$M_5(PO_4)_3Cl$], the theoretical M : P ratio should be 5 : 3, but in practice the best results are obtained (in terms of luminous intensity) wherein the metal (including Eu) : P ratio is in the range 4.9–4.95 : 3, and accordingly due consideration was given in calculating the composition of the combustion mixture.

In a typical experiment $Sr(NO_3)_2$ (18.53 g), urea (9.6096 g), NH_4NO_3 (14.4036 g), $SrCl_2$ (5.332 g) and europium nitrate (corresponding to 0.2463 g Eu_2O_3) were dissolved in 200 ml of acidic (HCl) solution at pH 1–2 and then DAP (7.9236 g) was added. This solution in a 1000 ml beaker was inserted into the resistance heating furnace at 400 °C. After a few minutes the solution evaporated off, igniting to yield a less voluminous white powder than usual combustion synthesis products.[14]

The material obtained was removed and transferred to an alumina crucible (covered with AR-grade activated charcoal to create a CO atmosphere to reduce any unreduced Eu^{3+}

present in the combustion product) and placed inside a silica crucible with a lid. The sample was heated from 900 to 1100 °C for 2 h. The material was then washed thoroughly with hot water to remove the excess of chloride and dried in an air oven at 120 °C for further characterisation.

The powder diffraction patterns of the products were recorded with a JEOL (JDX-8030) X-ray powder diffractometer and Cu-Kα = 1.5418 Å radiation using a nickel filter. The powder morphology was studied by SEM (JEOL JSM CF-35). Thermogravimetry of the combustion products was carried out in the air with a heating rate of 20 °C min^{-1} using an STA-500 thermal analyser supplied by Polymer Laboratory, UK. Photoluminescent (PL) measurements were made with a Hitachi 650-10S fluorescence spectrophotometer equipped with a 150 xenon lamp as the excitation source. The relative PL emission intensities of the samples were measured by fixing the excitation at 254 nm and comparing the blue emission at 445 nm with an internal standard, Eu^{2+}-doped SCAP blue phosphor. The percentage of reflectance at 254 nm [R(%)] was also measured with the above instrument using an alumina disc (99.9%) as the reference. The powder density was determined using a pycnometer employing xylene as the medium.

Results and Discussion

Eu^{2+}-doped MCAP is obtained by heating rapidly an aqueous concentrated solution containing stoichiometric amounts of metal nitrates, chlorides, urea and DAP as given in the following equation.

$$\begin{aligned}&(9-x)\mathrm{M(NO_3)_2}+x\mathrm{Eu(NO_3)_3}+15\mathrm{NH_2CONH_2}\\&+18\mathrm{NH_4NO_3}+6\mathrm{(NH_4)_2HPO_4}+\mathrm{MCl_2}\\&\rightarrow 2\mathrm{M}_{5-x}\mathrm{Eu}_{x/2}\mathrm{(PO_4)_3Cl}+49\mathrm{N_2}+93\mathrm{H_2O}+15\mathrm{CO_2}\end{aligned} \qquad (5)$$

The solution boils initially, undergoes rapid dehydration and foaming followed by decomposition, generating combustible gases such as nitrogen oxides, HNCO and NH_3. The volatile combustible gases ignite with a white flame, resulting in the formation of MCAP, which was confirmed by its powder pattern (*vide infra*).

It is known that the emission maximum of Eu^{2+} depends on the cohesive energy exerted by the host matrix.[16] The luminescent emission spectrum of SCAP : Eu^{2+} (combustion product wherein HCl was used as one of the ingredients with 2 mol equiv. of $SrCl_2$) is shown in Fig. 1. It can be seen from the emission spectrum that there is a band emission of Eu^{2+} (due to $4f^65d$–$^8S_{7/2}$) with a maximum at 445 nm. In addition to this dominant emission band, a weak emission at 610–620 nm (due to $^5D_0$–^7F_j) can also be seen, which indicates the trace amount of unreduced Eu^{3+} present in the as-formed product. Similar observations have been made in the case of CCAP. However, in the case of BCAP no characteristic emission of Eu^{2+} was observed in the as-formed product (not shown). This observation can be rationalised as follows. Since the ionic radii of Sr^{2+}, Ca^{2+} and Eu^{2+} are nearly equal (1.13, 0.99 and 1.12 Å, respectively), Eu^{3+} shows a tendency to be reduced to the divalent state even in open air during combustion, and substitutes for Sr^{2+} and Ca^{2+} during the formation of apatite. The ionic radius of Ba^{2+} (1.35 Å) is higher than that of Eu^{2+} (1.12 Å). Hence, during combustion synthesis Eu^{3+} is preferred to Eu^{2+} in the BCAP matrix.[6] When the combustion products were heated at 1100 °C in a reducing atmosphere, the trivalent europium present in the MCAP matrix in trace amounts is completely reduced. The PL spectra of the reduced products are shown in Fig. 2. It can be seen that all the materials after reduction gave rise to the characteristic band emission with maxima at 453, 445 and 438 nm corresponding to CCAP, SCAP and BCAP, respectively. This observation supports the formation of the MCAP matrix during combustion synthesis.

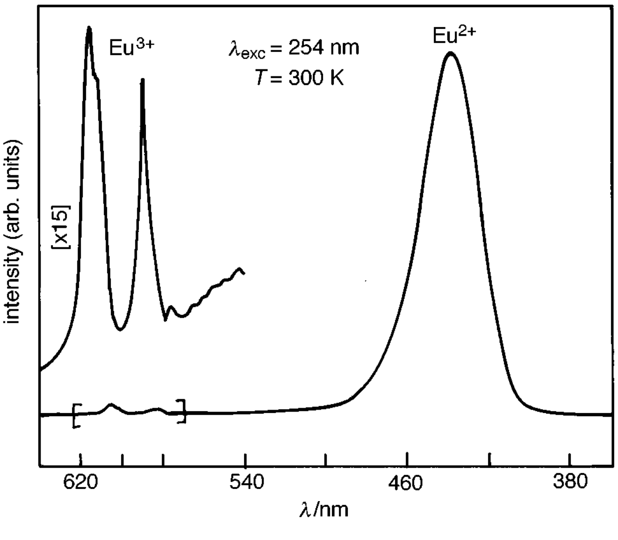

Fig. 1 Photoluminescent emission spectrum of Eu^{2+} (0.14 mol) in the as formed combustion product (inset: emission spectrum of Eu^{3+}) employing HCl as the medium with 2 mol equiv. of $SrCl_2$ in the combustion mixture

The XRD patterns of SCAP as formed and after heating in a reducing atmosphere are given in Fig. 3. The pattern of the as-formed product [Fig. 3(a)] suggests the formation of a crystalline SCAP matrix. The pattern was matched with the JCPDS file for SCAP and the lines were indexed. Fig. 3(b) gives the powder pattern of the sintered product at 1100 °C. It can be seen that there was no marked change in the pattern or in the FWHM values. This suggests that SCAP phase formation is complete within the short duration of SPHT synthesis. The XRD patterns of CCAP and BCAP after heat treatment are given in Fig. 4, and the lines were indexed and compared with the JCPDS files. All these patterns seem to

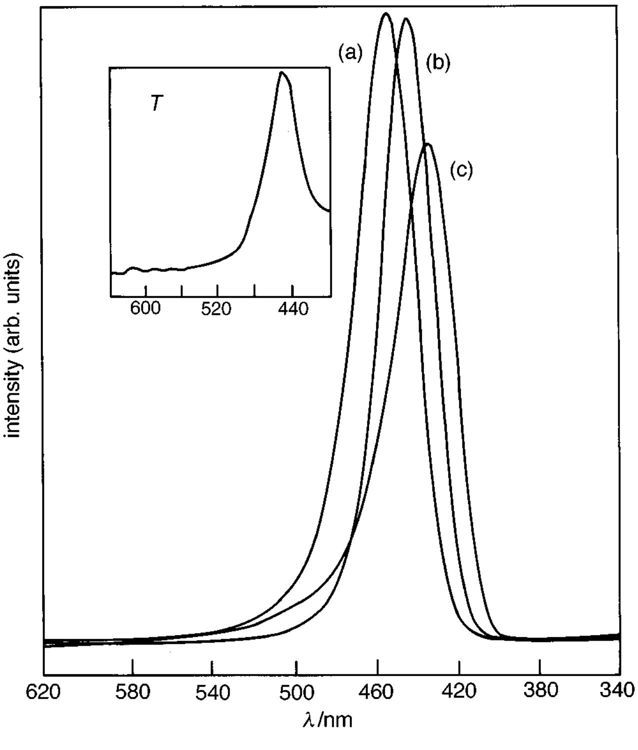

Fig. 2 PL emission spectrum (λ_{exc} = 360 nm) of Eu^{2+} in CCAP (a), SCAP (b) and BCAP (c), after heating at 1100 °C for 2 h under a reducing atmosphere (inset: emission spectrum of Eu^{2+} in the as-formed CCAP at 300 K)

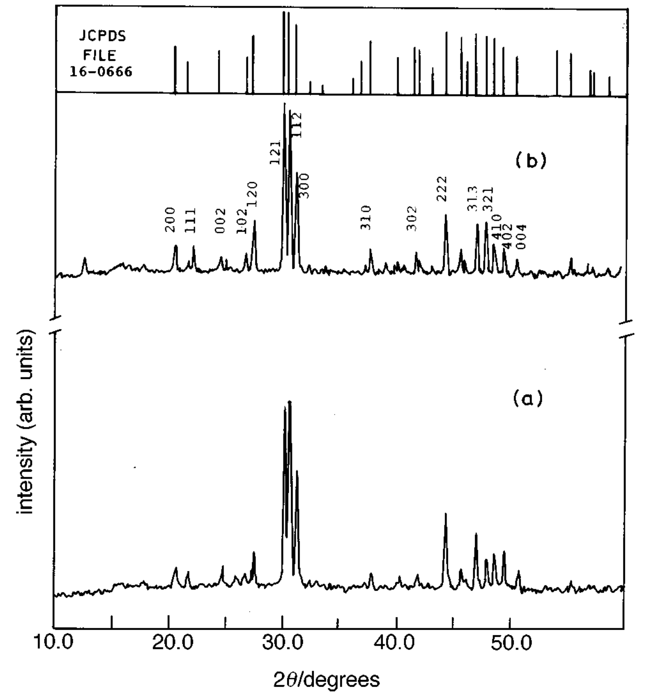

Fig. 3 Powder XRD pattern of strontium chloroapatite: Eu^{2+} (1.4 mol%) prepared by employing HCl with 2 mol $SrCl_2$ in the ingredients in the combustion mixture: (a) as-formed; (b) sintered at 1100 °C

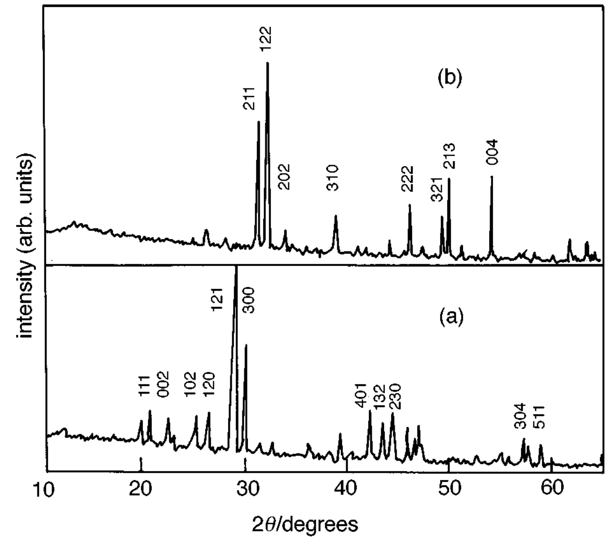

Fig. 4 Powder XRD pattern of combustion products of (a) CCAP (from HCl and $CaCl_2$), (b) BCAP (from HCl and $BaCl_2$)

suggest the formation of a crystalline MCAP matrix considering the reaction time and conditions.

Further, the thermogravimetry results (Fig. 5) shows the overall mass loss in the range of 2–3% for SCAP and BCAP. In the case of CCAP it goes up to 8%, owing to the crystallized water of excess chloride. These results indicate that the combustion products are only thermally stable apatite, with no decomposable intermediates.

Effect of acid on the preparation of SCAP : Eu^{2+}

For an effective combustion synthesis, all the ingredients should be in homogeneous solution. In the preparation of MCAPs alkaline-earth-metal phosphate tends to precipitate out, leading to inhomogeneity at elevated solution pHs. Hence, the pH of the solution must be adjusted to 1.0 before the addition of DAP to avoid the precipitation of alkaline-earth-metal phosphates. Experiments were carried out using either HCl or HNO_3 for adjusting the pH with 1 mol equiv. $SrCl_2$ (theoretical requirement) along with the other ingredients for the preparation of SCAP. The materials obtained were characterised using PL emission spectroscopy (Fig. 6). The emission maxima of these materials are distinctly different from one another. The PL emission spectra of the product obtained when HCl is used shows an emission maximum at 445 nm that corresponds to the Eu^{2+} emission from the SCAP host matrix. The material obtained using HNO_3 to adjust the pH has its emission maximum at 405 nm. This value was compared with the values reported in the literature and we believe that a strontium orthophosphate (SOP) host has formed during the process.[1,6] The formation of SOP when nitric acid was used in the reaction medium, may be due to the expulsion of chloride as HCl from the strontium chloride (source of chloride for the formation of SCAP). Hence, during the reaction there will be a deficiency of chloride, resulting in the formation of SOP. When HCl is used, the loss of chloride is not possible and the product obtained is SCAP. This fact is further substantiated by the XRD patterns of these materials. Fig. 7 gives the powder pattern of these materials and the data agree with the

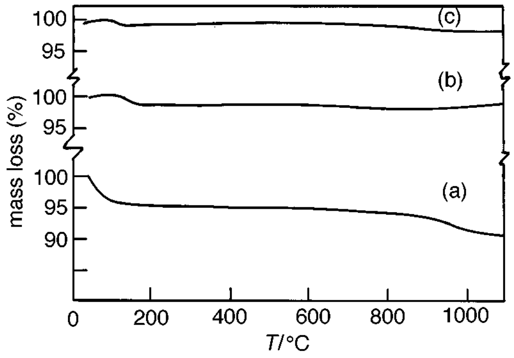

Fig. 5 TG curves of as-formed products of (a) CCAP, (b) SCAP and (c) BCAP where HCl and 2 mol of the corresponding chloride were used in the mixture

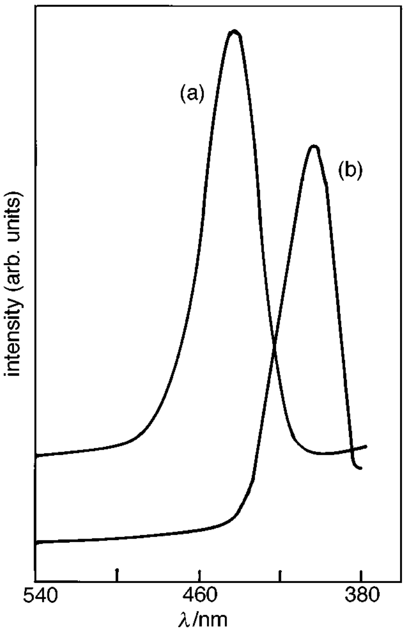

Fig. 6 PL emission spectra ($\lambda_{exc}=360$ nm, $T=300$ K) of Eu^{2+} activated combustion products, after sintering at 1100 °C under a reducing atmosphere, using 1 mol $SrCl_2$ in the reaction mixture with acids for adjusting pH: (a) HCl and (b) HNO_3

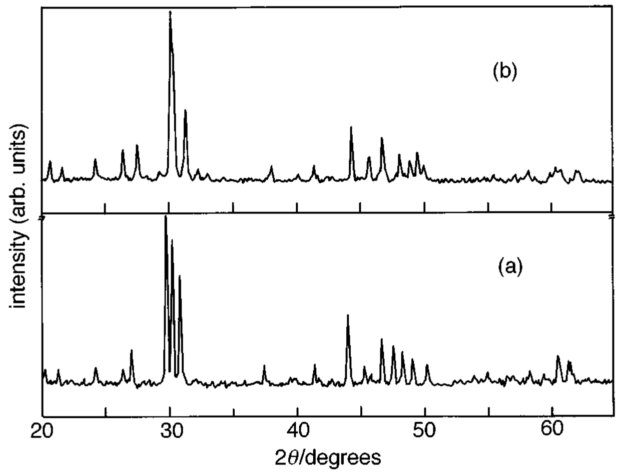

Fig. 7 Powder XRD pattern of combustion products (as in Fig. 6): (a) HCl, (b) HNO_3

JCPDS files corresponding to SOP and SCAP. Hence, wherever the preparation of MCAP is mentioned HCl is used.

Mechanism of MCAP formation

Combustion synthesis is a dynamic process, wherein the raw materials undergo a thermal decomposition and form new phases that are themselves later consumed in forming the MCAP:Eu^{2+} phosphors. The tentative reaction pathway for the formation of apatite is proposed based on the studies carried out using either HCl or HNO_3 for adjusting the pH of the precursor solution. During combustion, the metal nitrates decompose with urea giving europium-doped SrO. Simultaneously NH_4NO_3, a known explosive, decomposes in the presence of DAP without explosion and generates phosphoric acid in the reaction mixture.[17] SrO and H_3PO_4 may react immediately to yield the corresponding orthophosphate (MOP). The tentative reaction scheme is given in eqn. (6)–(8).

$$(9-x)M(NO_3)_2 + xEu(NO_3)_3 + 15NH_2CONH_2 \rightarrow (9-x)MO:xEu + 15CO_2 + 24N_2 + 30H_2O \quad (6)$$

$$18NH_4NO_3 + 6(NH_4)_2HPO_4 \rightarrow 6H_3PO_4 + 63H_2O + 51N_2 \quad (7)$$

$$(9-x)MO:xEu + 6H_3PO_4 \rightarrow 3M_{3-x}(PO_4)_2:xEu^{2+} + 9H_2O \quad (8)$$

The orthophosphate formed during combustion *in situ* reacts with the molten MCl_2 (by the heat evolved during combustion) to yield MCAP [eqn. (9)].

$$3M_{3-x}(PO_4)_2:xEu^{2+} + MCl_2 \rightarrow M_{10-x}(PO_4)_6Cl_2:xEu^{2+} \quad (9)$$

Note again that if MCl_2 is not available then the reaction stops with the formation of MOP:Eu^{2+}, as discussed in the case of SCAP.

Effect of sintering on PL efficiency and microstructure of SCAP:Eu^{2+}

Effect of temperature. In general, during combustion synthesis the products are foamy, fluffy, porous, low density materials with nanometre-sized crystallites, owing to the simultaneous evolution of a large volume of gases. However, in the present case the SCAP obtained shows remarkable crystallinity when compared to the products obtained by SPHT synthesis, especially considering the reaction conditions and time.[14] Note that the density and crystallite size of the materials prepared by combustion synthesis depend critically on the chemical characteristics of the fuels. In the present case, urea is used as the fuel, during SPHT synthesis it forms polymeric imide, preventing effective heat dissipation.[18] $SrCl_2$, one of the nonvolatile ingredients used for the preparation of SCAP, utilises this excess heat for melting, thereby forming SCAP. Hence, the relatively dense, crystalline, phase-pure formation of SCAP during SPHT synthesis. However, the product does not possess a well defined grain boundary and size, owing to the spontaneous reaction between the oxidizer and fuel, and the evolution of large volume of gaseous products. It should be noted that the PL efficiency of a phosphor depends critically on the activator concentration, density and morphology of powder particles such as size, shape, crystallinity and grain boundaries.

Even though the material obtained is single-phase, crystalline SCAP with divalent Eu^{2+}, the luminescent yield is very low because of the high reflectance at 254 nm (which is important in Hg discharge lamps; Table 1). Hence, in order to improve the density and morphology of the products, a heat treatment was applied to the material with 2 mol $SrCl_2$ added, at 900, 1000 and 1100 °C for 2 h in a reducing atmosphere. Table 1 shows that the material sintered at 1100 °C has 90% emission intensity (relative) and low UV reflection loss compared to that sintered at low temperature. This may be due to the recrystallization that leads to the regrowth of the particles with high density and better morphology.

Effect of $SrCl_2$. It is well known[6] that the solid-state preparation of SCAP:Eu^{2+} with high luminescent yield requires an excess of $SrCl_2$ (1.5–2.0 mol equiv.). Hence, for the combustion synthesis of SCAP:Eu^{2+}, the concentration of $SrCl_2$ is varied from 1–2 mol equiv. Table 2 lists some important properties of SCAP:Eu^{2+}, using different amounts of $SrCl_2$ in the combustion mixture after heat treatment at 1100 °C. Interestingly, for all the $SrCl_2$ concentrations used for the combustion synthesis, phase-pure SCAP was the only product. It can be seen, however, that the PL emission intensity increases with increasing concentration of the $SrCl_2$ in the mixture. The optimum particle sizes with maximum density and PL intensity, are achieved only for the product with 2 mol $SrCl_2$ added. At the same time, for the products with 1.5 mol $SrCl_2$ added, there seems to be a narrow particle size distribution of the phosphor material with lower PL emission intensity, because of the reduced UV absorbance and decreased visible transmittance.

The microstructure of the SCAP:Eu powders prepared with varying amounts of $SrCl_2$, after heat treatment in reducing atmosphere at 1100 °C are shown in Fig. 8. It can be seen that the as-formed product obtained using 2 mol equiv. $SrCl_2$ has an ill-defined grain boundary [Fig. 8(a)]. The SEM images

Table 1 Effect of sintering temperature on the PL yield and density of SCAP:Eu^{2+} (0.14 mol) combustion product (2 mol $SrCl_2$ employed)

sintering temperature/°C	density/ g cm^{-3}	relative intensity at 445 nm (%)	reflectance at 254 nm (%)
as formed	2.08	10	88
900	3.54	58	44
1000	3.81	71	26
1100	4.01	90	18

Table 2 Effect of $SrCl_2$ on the photoluminescent yield and PSD of SCAP:Eu^{2+}, after heat treatment at 1100 °C for 2 h

$SrCl_2$ in the combustion mixture/mol	relative luminescent yield at 445 nm (%)[a]	reflectance at 254 nm (%)	particle size distribution[b]/μm
1.0	17	27	4–5
1.5	60	35	0.5–3
2.0	90	18	3–4

[a] λ_{exc} = 254 nm. [b] By SEM.

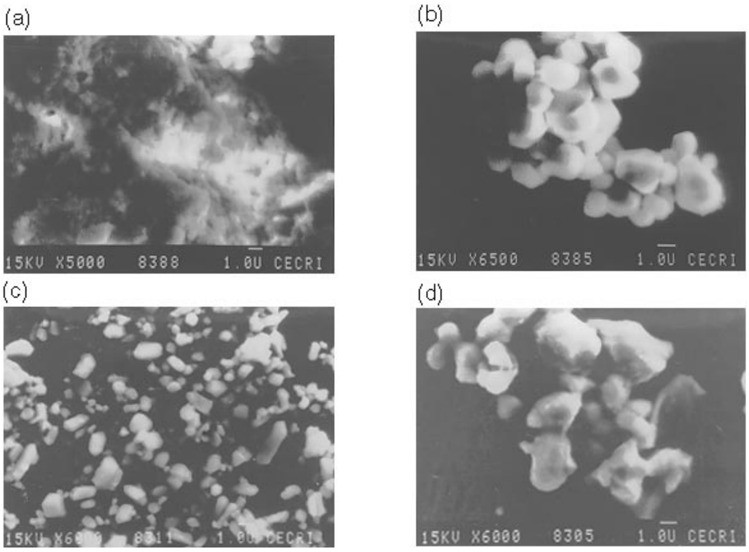

Fig. 8 Microstructure of SCAP:Eu^{2+} with different amounts of $SrCl_2$ sintered at 1100 °C for 2 h: (a) 2 mol (as-formed); (b) 2 mol; (c) 1.5 mol and (d) 1 mol

[Fig. 8(b)–(d)] show that the shape and sizes of the particles are dependent on the amount of $SrCl_2$ employed in the combustion mixture. This may be due to the fact that, after consuming the stoichiometric requirements of chloride, the excess chloride present in the products acts as a flux and plays an important role in controlling the morphology during post-heat treatment. In the presence of a flux melt, the particles are brought together and reprecipitate with bigger crystallite sizes and a pore-free structure. The flux melt also helps to lubricate the particles, allowing them to slip into a closer packing arrangement. When the theoretical amount of $SrCl_2$ was used for the combustion synthesis, particles with irregular shapes were formed during sintering due to the non-availability of the flux [see Fig. 8(d)]. However, when an excess of $SrCl_2$ was used for the SPHT synthesis the particle sizes and grain boundaries were well defined. The product obtained employing 1.5 mol% $SrCl_2$ gave rise to fine particles (0.5–3.0 μm), while the product obtained using 2.0 mol% $SrCl_2$ is well defined particles in the size range 2–5 μm. This observation is in concurrence with the observed PL emission intensity of the products and the higher UV reflectance of the phosphor materials.

Conclusions

A novel combustion synthesis method has been employed for the first time to prepare alkaline-earth-metal chlorophosphate:Eu^{2+} luminophore within a few minutes at 400 °C from its nitrates and chlorides. The synthesised materials were subjected to heat treatment at 1100 °C in a reducing atmosphere in order to achieve the optimum brightness and better morphology. The sintered products (SCAP:Eu^{2+}) have high final densities with 90% photoluminescent intensity compared with the internal standard phosphor. Based on the medium employed for the combustion synthesis a tentative mechanism is proposed for the formation of MCAP matrix by the SPHT route.

The authors thank the Director, Central Electrochemical Research Institute, Karaikudi for his kind permission to publish this work and Dr. R. Jagannathan for helpful discussions. M.K. thanks CSIR, India for the award of a Senior Research Fellowship. Mr. A. Mani, Mr. K. Athinarayanasamy and Mr. P. Kamaraj are acknowledged for their help in taking XRD and SEM.

References

1 K. H. Butler, *Fluorescent Lamp Phosphors*, University Press, 1986.
2 T. Welker, *J. Luminesc.*, 1991, **48 & 49**, 49.
3 J. B. Budin, J. C. Michael and F. Auzel, *J. Appl. Phys.*, 1979, **50**, 641.
4 K. Kaniya, M. Tanakasi, T. Suzuki and T. Tanaka, *Mater. Res. Bull.*, 1990, **25**, 63.
5 M. Sato, T. Tanaka and M. Ohta, *J. Electrochem. Soc.*, 1994, **141**, 1851.
6 F. C. Pallila and B. E. O'Reilly, *J. Electrochem. Soc.*, 1968, **115**, 1076.
7 E. Yu, H. Hartl, H. J. Schulz and M. Thiede, *Z. Anorg. Allg. Chem.*, 1988, **567**, 60.
8 M. Kottaisamy, R. Jagannathan, P. Jeyagopal, R. P. Rao and R. L. Narayanan, *J. Phys. D: Appl. Phys.*, 1994, **27**, 2210.
9 A. H. Hoekstra, W. L. Wanmaker and J. G. Verriet, *J. Inorg. Nucl. Chem.*, 1970, 32.
10 S. Ekambaram and K. C. Patil, *J. Mater. Chem.*, 1995, **5**, 905.
11 N. Aruldhas and K. C. Patil, *J. Alloys Comp.*, 1993, **202**, 137.
12 S. S. Manoharan and K. C. Patil, *J. Am. Ceram. Soc.*, 1992, **75**, 1012.
13 K. Suresh, N. R. S. Kumar and K. C. Patil, *Adv. Mater.*, 1991, **3**, 148.
14 M. Kottaisamy, D. Jeyakumar, R. Jagannathan and M. Mohan Rao, *Mater. Res. Bull.*, 1996, **31**, 1013.
15 S. R. Jain, K. C. Adiga and V. R. Pai Verneker, *Combust. Flame*, 1981, **40**, 71.
16 G. Blasse and A. Bril, *J Electrochem. Soc.*, 1968, **115**, 1067.
17 A. M. Rouchi, *Chem. Eng. News*, July 24, 1995.
18 A. M. Wynne, *J. Chem. Educ.*, 1987, **64**, 180.

Paper 6/03885I; *Received* 4*th June*, 1996