Electronic Supplementary Information

Chemistry of extracting high contrast invisible fingerprints from transparent and colored substrates using novel phosphorescent label

G. Swati, Swati Bishnoi, Paramjeet Singh, Naina Lohia, Vishnu V. Jaiswal, M. K. Dalai and D. Haranath*

Preparation of long afterglow (LA) phosphor:

Auto-combustion is a self-proliferating exothermic reaction between oxidizing metal nitrate and reducing organic water soluble fuels like urea, glycine and citric acid. It is a highly exothermic reaction and enormous heat is produced resulting into highly sintered product. To sum up, the overall reaction taking place is as following

$$Sr(NO_3)_2.6H_2O + Al(NO_3)_3.6H_2O + CO(NH_2)_2 \rightarrow SrAl_2O_4 + H_2O + NO_x$$
 (1)

In typical experiment, in order prepare water soluble homogenous solution, the rare earth oxides of europium and dysprosium were dissolved in stoichiometric amount of concentrated nitric acid to make $Eu_2(NO_3)_3$ and $Dy_2(NO_3)_3$, respectively according to the reaction no. 2,3. All the nitrate precursor chemicals and urea as fuel were dissolved in minimum quantity water and stirred for 30 minutes. Concentration of fluxing agent, boric acid was fixed at 15 mole%. The solution was kept overnight in oven maintained at a temperature of 80°C. As formed thick viscous gel was later fired in a pre-heated muffle furnace at 600°C, to obtain voluminous and highly sintered SrAl₂O₄:Eu²⁺,Dy³⁺ phosphor powder.

$$Eu_2O_3 + 6HNO_3 \rightarrow 2Eu(NO_3)_3$$
⁽²⁾

 $Dy_2O_3 + 6HNO_3 \rightarrow 2Dy(NO_3)_3$

(3)

Morphological analysis

Effectiveness of the phosphor powder in adhering to latent fingerprints is primarily governed by size and shape of particles of powder being used [1]. Auto-combustion process results into highly exothermic reaction between oxidizing metal nitrate ions and reducing organic fuel, as a consequence there is evolution of large volume of gases during reaction resulting into ultrafine and voluminous mass with cotton like appearance.

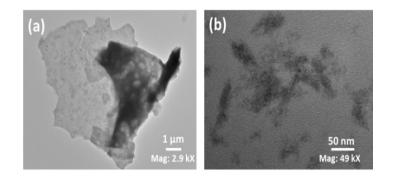


Figure 1(a-b) shows Transmission Electron Microscopy (TEM) images of the as-prepared $SrAl_2O_4$:Eu²⁺,Dy³⁺ phosphor at different magnifications.

As seen from fig. 2(a), phosphor powder synthesized using auto-combustion process results into particles with fine flake-like morphology with the diameter of ~10 μ m. During the course of reaction urea gets decomposed into variety of precipitating ions like OH⁻, NH⁴⁺ and CO₃²⁻. These precipitating ions complexes with the metal ions in the ionic solution which play an crucial role in the development of the final morphology of the as prepared nanostructures [2]. Such fine flake-like morphology adheres more firmly with ridges, with only a few particles present in the furrows of the developed fingerprints [3]. The increased surface area of the flake relative to the weight of the particle contributes to this powder's adhesion. Flake powder with a mean diameter of 10 μ m and an average thickness of 0.5 μ m is optimum for latent print development [4,5]. Thus overall visual contrast of ridge pattern upsurges to a large extent. Upon further magnification, the tendency of smaller particles accretion of smaller particles into large flake-like structures has been observed.

Florescence confocal microscopic analysis

The confocal fluorescence images of $SrAl_2O_4:Eu^{2+},Dy^{3+}$, excited by 375 nm laser are shown in figure 2. Confocal images clearly show the uniform distribution of the dopants within the host lattice and high CCD counts shows the bright luminescence intensity from the sample. In order to visualize the dopant distribution, artificial colors have been assigned intentionally to the confocal fluorescent image for host lattice and rare earth dopants.

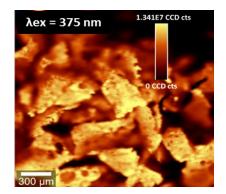


Figure 2: Confocal fluorescent images of SrAl₂O₄:Eu²⁺,Dy³⁺ phosphor recorded under excitation of 375 nm.

Photoluminescence excitation analysis

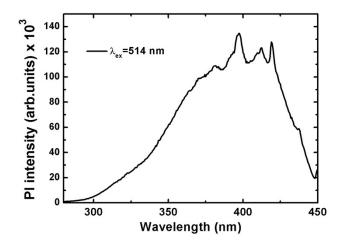


Figure 3: Photoluminescence excitation spectra of as-synthesised phosphor at an emission of 514 nm

References

- 1 G. S. Sodhi and J. Kaur, *Forensic Sci. Int.*, 2001, **120**, 172.
- 2 Anna M. Kaczmarek, Kristof Van Heckeb and Rik Van Deun Chem. Soc. Rev., 2015, 44, 2032.
- 3
- 4 5
- B. Wilshire, *Endeavour.*, 1996, **20**, 12. G L Thomas, *J. Phys. E: Sci. Instrum.*, 1978, **11**, 713. Brian Yamashita and Mike French, Latent print development In: National Institute of Justice, US Department of Justice (ed) The Fingerprint Sourcebook. Washington D.C. USA, pp 7.1-7.67.