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Effect of Li^+ codoping on structural and luminescent properties of $Mg_2SiO_4:RE^{3+}$ (RE = Eu, Tb) nanophosphors for displays and eccrine latent fingerprint detection

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ABSTRACT

Luminescent nanophosphors find wide range of applications for the fabrication of WLEDs as well as in fingerprint detection techniques. Lithium co-doped $Mg_2SiO_4:Tb^{3+}$ and $Mg_2SiO_4:Eu^{3+}$ nanophosphors were prepared by low temperature solution combustion method. The effect of Li^+ co-doping in Mg_2SiO_4 was systematically studied by Powder X-ray Diffraction (PXRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), UV–Vis- Diffuse reflectance spectroscopy (DRS) and Photoluminescence (PL) spectroscopy. Further, the optimized powders were used to analyze the eccrine latent fingerprint. The DRS analysis show red shift of the absorption edges in Li^+ co-doped nanophosphors. PL studies revealed that a small quantity of Li^+ (1 mol %) ions was effective for charge compensation as well as creation of lattice defects to enhance the luminescence emission. The high quantum efficiency and color purity projects it to be a new material for commercial application in white light emitting diodes.

1. Introduction

Recently, the development of nanophosphors for WLEDs [1–3] and fingerprint detection applications has widened the implications in a variety of areas with enhancing contrast and increasing selectivity [4]. The detection of latent fingerprints using nanophosphors with a wide range of articles of evidence represents a new model in criminalistics that had its beginning in 1976 [5]. In forensic investigations, chemical substances are often used to make latent fingerprints visible using conventional powdering technique. The powder dusting technique involves superior adherence of particles to fingerprint ridges to provide contrast between the fingerprint profile and the background surface [6]. To detect latent fingerprints, physical property such as adhesion is very important, because selective adsorption of nanophosphors to the fingerprint ridges is vital. Also, optical property of the prepared nanophosphors plays important role in exhibiting its emission color when they are excited under UV light [7].

From an application point of view, it is obvious that size reduction of nanoparticles can significantly enhance the surface phenomena. Due to this reason, study of optical properties of rare earth doped nanophosphors synthesized at low temperature as compared to their bulk counterparts encouraged this research more intensely. The main aim of this study was to prepare highly-luminescent nanophosphors with greater brightness with the addition of alkali metal ions like Li^+ as co-dopants. Alkali metal ions removes charge unbalance problem, increases the crystallanity and enhances the emission intensity of nanophosphors due to having low oxidation states and distinct ionic radii [8,9]. This technique was employed on several systems, like $ZnB_2O_4:Eu^{3+}$, $CaWO_4:Eu^{3+}$, $YBO_3:Eu^{3+}$, $YVO_4:Eu^{3+}$, $GdVO_4$:Yb,HO, $GdVO_4$:Yb,Er etc. to achieve impressive luminescence properties [8–14].

Judd-Ofelt theory introduced by B.R. Judd and G.S. Ofelt in 1962 to study the quantum efficiency of the nanophosphors based on the intensities of 4f-4f transitions has become a focus in optical spectroscopy. The theory proves and supports applications of rare earth doped materials in solid-state lasers, optical amplifiers, phosphors for displays, solid-state lighting, upconversion, quantum cutting materials and fluorescent markers [15]. In this paper, we report on

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Table 1
The stoichiometric quantities required for the synthesis.

Li^{+} (mol %)	$Mg(NO_3)_2$ gm	SiO_2 gm	ODH gm	Eu_2O_3/Tb_2O_3 gm	$LiNO_3$ gm
0.5	5.1025	0.608	2.362	0.1925/0.0545	0.0069
1	5.0769				0.014
2	5.0256				0.0275

low temperature synthesized, as formed Li^{+} co-doped $Mg_2SiO_4:Eu^{3+}$ and $Mg_2SiO_4:Tb^{3+}$ nanophosphors in continuation of our previous work [16,17]. The photoluminescence properties, Judd-Ofelt radiative analysis and fingerprint detection technique were studied in detail.

2. Experimental

2.1. Materials

The starting materials used in the present study are analytical grade magnesium nitrate [Mg $(NO_3)_2\cdot 6H_2O$] as oxidizer (O), fumed silica [SiO_2], oxalyl dihydrazide (ODH; $C_2H_6N_4O_2$) fuel (F) was prepared in our laboratory, Eu_2O_3, Tb_2O_3 and $LiNO_3$:99.99% Sigma Aldrich Ltd. Eu_2O_3 and Tb_2O_3 were made water soluble by converting it to europium nitrate and terbium nitrate respectively using 1:1 HNO_3.

2.2. Preparation of nanophosphors

Nanophosphors of undoped, Li^{+} codoped $Mg_2SiO_4:RE^{3+}$ (RE = Eu (11 mol%) or Tb(3 mol %)) were prepared by the low temperature (350 °C) solution combustion method. Stoichiometric compositions were calculated based on propulsion chemistry keeping the O/F ratio unity. The quantities required for the synthesis were shown in Table 1. The aqueous solution of the redox mixture containing oxidizer, fumed silica, fuel and dopants were taken in a petridish and mixed clearly on a magnetic stirrer and introduced in a preheated muffle furnace maintained at ~350 °C. The reaction mixture underwent dehydration and smoldering. Further, iginition took place which resulted in flame type combustion. The energy required for the synthesis was provided by the exothermic combustion process itself, without further requirement of calcination [16,17]. The flow chart of the combustion method is shown in Scheme 1. After combustion, foam type product obtained was collected and grinded using pestle and mortar. The balanced chemical equation used for the synthesis is as follows.

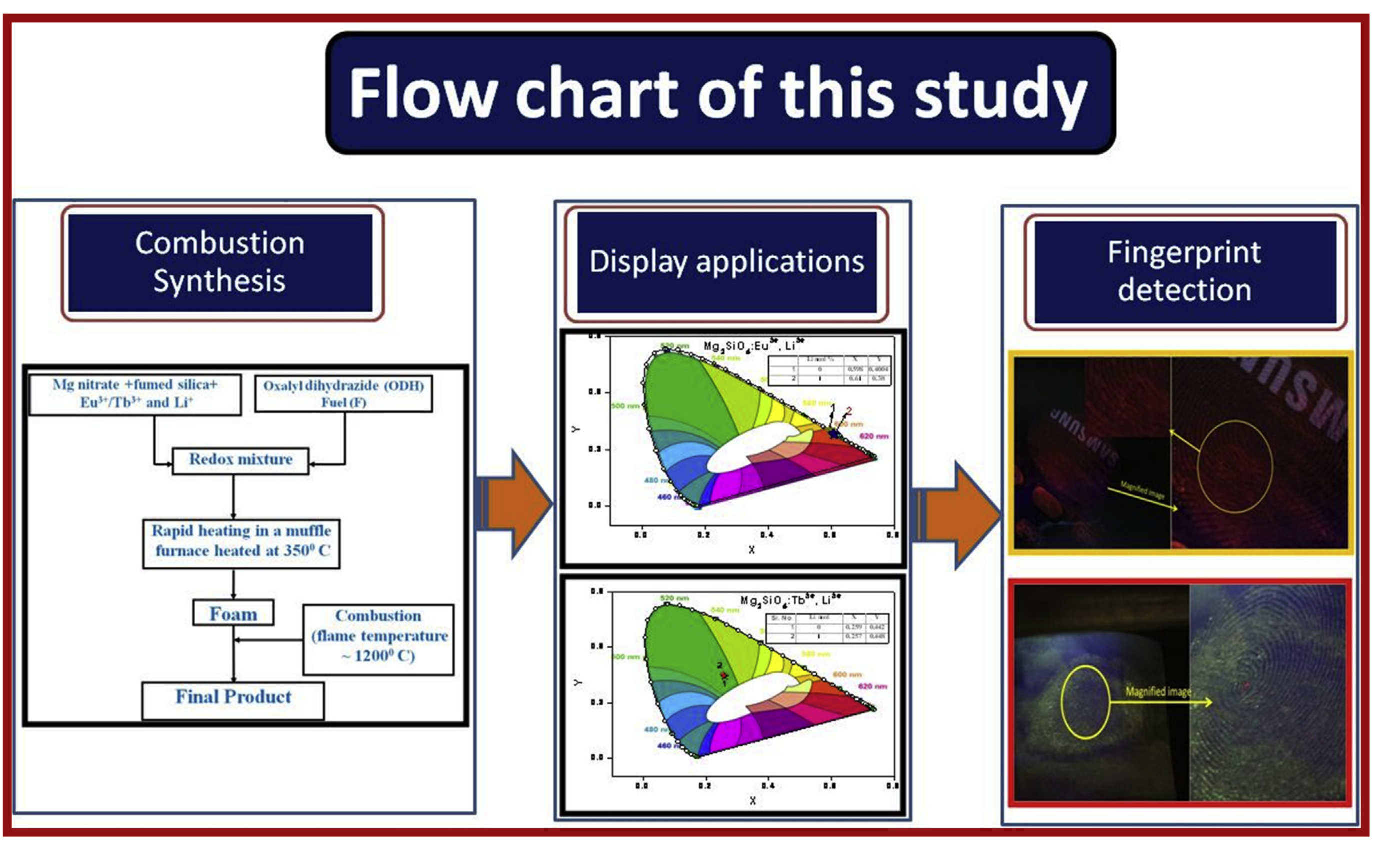
$$2\,Mg(NO_3)_2 + SiO_2 + 2\,Eu(NO_3)_3 + 2\,Li(NO_3) + 6\,C_2H_6N_4O_2 = Mg_2SiO_4Eu_2O_3Li_2O + 12\,CO_2 + 18\,N_2 + 18\,H_2O$$

and

$$2\,Mg(NO_3)_2 + SiO_2 + 2\,Tb(NO_3)_3 + 2\,Li(NO_3) + 6\,C_2H_6N_4O_2 = Mg_2SiO_4Tb_2O_3Li_2O + 12\,CO_2 + 18\,N_2 + 18\,H_2O$$

2.3. Characterization of nanophosphors

The phase formation of the powder sample was characterized by PXRD using X-ray diffractometer (Shimadzu) (operating at 50 kV and 20 mA by means of CuKα (1.541 Å) radiation with a nickel filter at a scan rate of 2° min^{-1}). The surface morphology of the product



Scheme 1. General idea of the present study.