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Synthesis and characterization of Sm^{3+}:$Bi_4Si_3O_{12}$ and dispersed into silica nanophosphor for sensing application

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ABSTRACT

Lanthanide doped bismuth silicate has been synthesized in micro scale domain and studied from structural, magnetic, thermal, as well as optical, and photoluminescent point of view. However, its preparation in nano-scale domain and applications in sensing field were still unexplored. In this study, we have applied different preparation conditions to prepare nano-phosphors based on samarium doped bismuth silicate (Sm^{3+}:$Bi_4Si_3O_{12}$) for sensing application. X mol Sm^{3+}:$Bi_4Si_3O_{12}$ (Sm^{3+}:BSO) (x = 0.01, 0.03, 0.05, 0.07 mol) were prepared using sol–gel method followed by heat treatment. The effect of different surfactants as well as dispersion into silica matrix on the crystal, morphological, optical, and photoluminescent properties of 0.03 mol Sm^{3+}:BSO Nano-phosphor were also studied. XRD and TEM results indicated that the capping agents (CTAB and TX100) and silica matrix can hinder BSO Nano-phosphor crystal growth, and, as a consequence, decrease their crystal size from micro to Nano-domain in case of sample dispersed into silica matrix (Sm^{3+}:BSO/SiO_2) (3 nm). Sm^{3+}:BSO/SiO_2 shows high PL properties. Optimized PL Nano-phosphor (Sm^{3+}:BSO/SiO_2) successfully developed latent fingerprint from various forensic relevant materials, including non-porous and porous surfaces. Moreover, the amino functionalized 0.03 mol Sm^{3+}:BSO/SiO_2 sensor was prepared for analytical determination of glucose.

1. Introduction

Photoluminescent lanthanide ion doped inorganic Nano-phosphors has much attracted the attention of scientists due to its unique properties, such as narrow emission bands, long lifetime and high quantum efficiency [1]. Lanthanide ions possess long lived excited states via energy transfer process from inorganic antenna to lanthanide ion. Then, the lanthanide ions emit visible and/or near infrared (NIR) light [2].

Inorganic antennas have photochemical and thermal stability advantages over organic-based ones [3]. Therefore, it has many applications in luminescence devices, luminescent sensors, optical transmission, forensic science, and medical diagnostics fields [4].

Bismuth silicate (BSO) is an example of inorganic host which has excellent photoluminescent, thermoluminscence, mechanical, optical, chemical, and photocatalytic properties [5–7]. Bismuth silicate (BSO) material is found in different crystalline structures with different phases, e.g., Bi_2SiO_5 and $Bi_4(SiO_4)_3$. This crystalline arrangement is dependent on working conditions; mainly on calcination temperatures [8]. BSO has an excellent scintillation material for nuclear and high-energy physics experiments. Also, it has a great use in medical imaging, geophysical exploration, and optics [9–11]. Good host is very important for efficient luminescence of lanthanide ions. $Bi_4Si_3O_{12}$ host provides advantage of wide band gap (3.5 eV) which makes host absorb in the UV region [12], as a consequence it acts as a good antenna for lanthanide ions. Bismuth silicate has been synthesized in micro scale domain and studied from structural, magnetic, thermal, and optical and photoluminescent point of view [13–19]. However, the reports about preparation and characterization of lanthanide doped bismuth silicate in Nano-scale domain and their applications as a photoluminescent sensor for latent fingerprint and glucose are still unexplored.

Therefore, this paper reports the effect of samarium doping and surfactant, as well as dispersion into silica matrix on the crystal, morphological, optical, and photoluminescent properties of Sm^{3+}:BSO nanophosphor. Also, the optimized nano-phosphor

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(0.03 mol Sm^{3+}:BSO dispersed into silica matrix) was applied as a latent fingerprint. Moreover, the amino functionalized 0.03 mol Sm^{3+}:BSO/SiO_2 sensor was prepared for analytical determination of glucose.

2. Experimental

2.1. Materials

$Bi(NO_3)_3 \cdot 5H_2O$ was obtained from Sigma. $Sm(NO_3)_3$ was prepared by reaction of samarium oxide (Aldrich) and nitric acid. Tetraethyl orthosilicate $Si(OC_2H_5)_4$ (TEOS) was obtained from Aldrich. Cetyl trimethyl ammonium bromide (CTAB), Triton X-100, sodium dodecyl sulfate (SDS), and ammonium hydroxide were purchased from BDH. Ethanol, glucose, 3-aminopropyl triethoxysilane (APTS), and glacial acetic acid (Sigma-Aldrich) were used as received. Distilled water was used.

2.2. Phosphor preparation

The typical process [5]; 0.8 ml water, 1.0 ml absolute ethyl alcohol, and 1.0 ml TEOS were put into a round bottom flask with a plug at room temperature under the magnetic stirring. Complete hydrolysis was considered until a transparent solution was obtained. Then, stoichiometric 2.887 g $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in the 5.0 ml glacial acetic acid to prevent hydrolysis of Bi^{3+} while stirring. Bi^{3+} solution was slowly dropped to the pre-hydrolyzed TEOS solution with stirring. Then 0.01, 0.03, 0.05, and 0.07 mol of samarium salt were added to the above mixture as dopant under stirring for 2 h at room temperature. After 12 h gelling at room temperature, the transparent solution changed into a nearly transparent gel. The gel was then dried in a vacuum oven at 70 °C for 3 days. The dried gel was calcined at 900 °C for 2 h and the obtained powders were used for further analyses.

The effect of different surfactants and dispersion into silica matrix were studied for pure 0.03 mol Sm^{3+}: BSO phosphor. So the 0.03 mol Sm^{3+}: BSO phosphor was prepared with the same method in presence of various surfactants at different concentrations above their critical micelle concentration; CTAB, Triton X-100, and SDS. Also, 0.03 mol Sm^{3+}:BSO dispersed into silica matrix was prepared with the previous method using excess TEOS to obtain 1:5 S m^{3+}:BSO to SiO_2 mole ratio.

2.3. Characterization of the prepared phosphors

The prepared samples are characterized with transmission electron microscopy (TEM, JEM-2100(JEOL)), operating at 200 kV accelerating voltage. XRD patterns were recorded using 'PHILIPS' diffractometer with CuKα1 radiation (kα = 1.54056 Å). An accelerating voltage of 40 kV and an emission current of 30 mA were applied. The UV–Vis. diffuse reflectance (DR) spectra of the prepared samples were recorded using 'JASCO V-530' spectrometer (Japan) equipped with an integrating sphere accessory to diffuse reflectance spectra. $BaSO_4$ was used as a reference. The photoluminescence emission and lifetime data of the prepared samples were obtained using a 'Perkin Elmer LS55' Luminescence Spectrometer (USA).

2.4. Application in fingerprint development

Fresh fingerprints from healthy donor were deposited on different non-porous substrates (aluminum foil, and plastic bag) and porous surfaces (Papers and green leaf). Prepared fluorescent powder was brushed carefully and uniformly on the latent fingerprint samples. Then the prepared samples were illuminated with UV lamp (4 W, 254 nm) and images of the fingerprint were photographed using a digital camera (Sony D80).

2.5. Amino-functionalized Sm^{3+}:BSO/SiO_2 for analytical determination of glucose

Sm^{3+}:BSO/SiO_2 was dispersed into mixed solution of anhydrous ethanol (8.0 ml) and distilled water (0.6 ml). Thereafter, 0.6 ml of NH_4OH and 0.2 ml of APTS were added to the above mixture. The mixture was stirred overnight. The amino-functionalized Sm^{3+}:BSO/SiO_2 was obtained by centrifugation. The amino-functionalized Sm^{3+}:BSO/SiO_2 powder was washed with water and ethanol for at least three cycles using ultra-sonic cleaner to remove any physically adsorbed molecules from the surface of nano-particles [20]. 0.1 gm of the as-prepared amino-functionalized Sm^{3+}:BSO/SiO_2 was dispersed in 4 ml of glucose solution of different concentrations with stirring for 1 h. It was then centrifuged, decanted and dried in oven 80 °C. After 20 min, the fluorescence intensity was measured with excitation at 265 nm.

3. Results and discussion

3.1. Crystal structure and morphology

Fig. 1 shows XRD patterns of x mol Sm^{3+} doped BSO as a function of Sm^{3+} doping concentrations. Pure and doped samples show several sharp peaks at 2θ = 21.2, 27.5, 32.6, 43.0, 44.9, 51.8, 55.0, 56.6, and 58.1°. These peaks originate from reflections of (211), (310), (321), (422), (431), (530), (532), (620), and (541) planes of $Bi_4Si_3O_{12}$ (BSO) (JCPDS No. 35–1007). Small percentage of another minor phase (Bi_2SiO_5) was observed at 2θ = 29.44 and 34.7° (JCPDS No. 36–0287) [17]. No peaks corresponding to Sm_2O_3 phase were detected in XRD patterns even at high Sm^{3+} ion concentration.

Crystal data of prepared phosphors was collected in Table 1. The main diffraction peak of BSO phase (2θ = 32.60°) was slightly shifted to low angle as an influence of Sm^{3+} ion doping. By comparison, it can be found that the crystal size of Sm^{3+}:BSO phosphor increased than that of pure BSO (Table 1). This means that Sm^{3+} doping to BSO enhances the crystal growth. It is well known that the ionic radius of Bi^{3+} (1.17 Å) is slightly larger than Sm^{3+} ion dopant (1.09 Å) [21].This means that Sm^{3+} ion enters into BSO lattice via substitution mode. Therefore, no big difference was observed in lattice parameters in case of doped sample relative to pure one. But a significant change in lattice parameter at high Sm

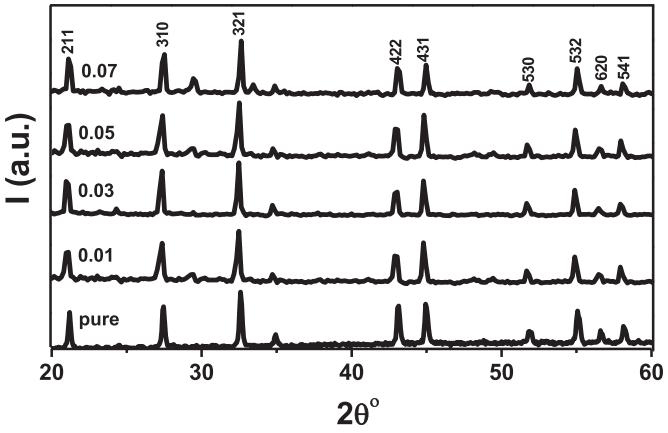

Fig. 1. XRD patterns of Sm^{3+}:BSO prepared by sol-gel method followed by annealing at 900 °C for 2 h in air at different Sm^{3+} concentrations.