Dyes and Pigments 134 (2016) 227–233

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Neodymium doped yttrium aluminate synthesis and optical properties – A blue light emitting nanophosphor and its use in advanced forensic analysis

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ARTICLE INFO

Article history:
Received 12 March 2016
Received in revised form
12 June 2016
Accepted 20 June 2016
Available online 21 June 2016

Keywords:
Nanoparticles
Photoluminescence
Fingerprint
Forensic science
Solution combustion

ABSTRACT

A series of neodymium ions activated yttrium aluminate nanophosphors of various concentrations were synthesized by solution combustion method using oxalyl dihydrazide as a fuel. The crystal structure, optical energy gap, luminescent properties and Judd-Ofelt analysis were carried out. The use of the phosphor in revealing/enhancing the fingerprints quality was investigated in detail. The powder X-ray diffraction results confirmed the orthorhombic phase for the prepared samples. From diffuse reflectance spectra, estimated energy gap was found to be in range of 5.38–5.80 eV. The photoemission profile of $YAlO_3$: Nd^{3+} exhibit a blue emission upon 364 nm excitation. Further, the prepared materials were used for enhancing the quality of latent fingerprint technique. The present method was facile and robust for visualization of fingerprint with enhanced sensitivity, low glare light and high efficiency on various surfaces. The demonstrated results on facile detection of fingerprints virtually on any surfaces using $YAlO_3$:Nd^{3+} nanophosphors are versatile tool which hold great promise for practical applications on forensic sciences.

1. Introduction

Recently inorganic nanophosphors doped with various trivalent rare-earth (RE) ions have been an active area of research due to wide range of applications namely medical diagnostics, solid state lighting, display, optoelectronic devices, sensors, etc., [1–4]. It is well known that the aluminate based nanopowders (NPs) have been deployed in a variety of technologies such as plasma, field emission, and surface conduction electron displays [5–7]. Among aluminate based NPs, yttrium aluminate ($YAlO_3$) is most extensively produced laser gain host and also a substrate material for optical components. The Al_2O_3–Y_2O_3 system has three crystalline phases: $Y_3Al_5O_{12}$, $Y_4Al_2O_9$ and $YAlO_3$ of which the first two are stable and the latter is metastable. Among all the phases orthorhombic phase of $YAlO_3$ exhibit interesting properties such as high refractive index, better optical transparency, inert to toxic chemicals, fast scintillators, and ceramic pigments, etc., [8].

Aluminates are prepared by various techniques namely solid state method, sol-gel, etc., among them solution combustion synthesis (SCS) is a versatile method due to its simple experimental set-up, molecular level of mixing, high degree of homogeneity, fast, cost effective, ultra-pure, large surface area etc. For the preparation of aluminates generally high temperature is required to obtain the desired phase as result the product is highly agglomerated and produce large surface defects. Due to this reasons, the product is unfavorable to use in industry applications. However in SCS

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http://dx.doi.org/10.1016/j.dyepig.2016.06.029
0143-7208/

method, the product obtained is highly homogenous with less impurity and higher surface area to volume ratio [8,9]. Further several experimental parameters can be set in SCS method, namely F/O ratio, furnace temperature, etc to achieve the desired type of nanoparticles. However to the best of our knowledge use of ODH fuel for the synthesis of $YAlO_3$ is limited.

DNA profiling is a characteristics used in forensic labs to identify individuals. All unrelated individuals likely to be different with small set of DNA variations thereby being as unique to individuals as fingerprints. Even though the DNA profiling is most advanced, fingerprint (FP) recognition tool plays a major role in the recognition of individuals persons. Normally to recognize latent FPs at crime scenes requires an enhancement for picturing and recognition. The practice of recognition to be used in each case depends on the characteristics of the FPs and the type of the surface on which they are found. Finding an easy and sensitive method to detect latent FPs effectively in forensic applications is essential [10].

Generally for FP revelation based on chemical categories can be classified into two types: (1) revelation technique that relies on non-covalent interactions such as dusting, gentian violet staining and small particle reagent. (2) revelation technique that involve chemical reactions such as ninhydrin, DFO (1, 8-diazafluoren-9-one), and silver nitrate. FP dusting is a simple technique that can be performed with almost any age group as it does not require specialized equipment except focused UV light, brush and uniform dusting powder.

Normally powdering method (PM) is preferred as a primary evidence for the FP detection at a crime scene. Generally, the PM method is categorized into regular, metallic and luminescent. PM method consists of a resinous polymer for adhesion and a colorant for contrast. Networked metals such as lead, gold and silver are used as powders for the detection of finger prints. This method is performed in proper ventilation and requires safety equipment's because of usage of toxic chemicals and their vapors. Some of the toxic chemical reagents used in this method of detection are listed in Table 1.

To overcome all the above limitations recently, luminescent based nano powders are used in latent FP detection. The size and shape of the NPs play an important role in strong bonding efficiency to the FP and these NPs adhere better than macro and micro particles [11]. Therefore, RE doped luminescent NPs have been explored as a potential technique in FP development has provoked the research community.

In the present work, synthesis, morphology and photoluminescence studies of Nd^{3+}:$YAlO_3$ NPs prepared via low temperature solution combustion route. The compounds were well characterized by PXRD, SEM, TEM, UV-Vis, PL, etc. Further an attempt has been made to apply the prepared nanopowders of $YAlO_3$:Nd^{3+} on various smooth surfaces namely aluminum foil, chocolate wrapping foil, mobile phone display screen and surface of a PET bottle. The prepared samples showed better usability in both latent fingermark detection and display device applications.

2. Experimental

2.1. Synthesis

All the chemicals used are of analytical grade and used without further purification. The stoichiometric ratios of yttrium nitrate [$Y(NO_3)_3 \cdot 4H_2O$ (99.9%)], aluminum nitrate [$Al\ (NO_3)_3 \cdot 9H_2O$ (99.9%)] and neodymium nitrate [$Nd\ (NO_3)_3 \cdot 9H_2O$ (99.9%] are used as oxidizers and dopant to get a desired product of chemical formula $Y_xNd_{1-x}AlO_3$. The preparation process for ODH [$C_2H_6N_4O_2$], a fuel is explained elsewhere [9]. The oxidizer to fuel ratio is calculated based on oxidizers (O) and reducer (F) valences of the reactants, keeping O/F ratio as unity [12]. Aqueous solution containing all the above reactants are taken in 300 ml cylindrical petri dish and is placed in a preheated muffle furnace maintained at 400 ± 5 °C. The reaction mixture undergoes thermal dehydration and auto-ignites with the liberation of large gases [9]. The flame propagates throughout the reaction mixture causing decomposition of the reactants and subsequent formation of the desired product. The obtained product is calcined at 1000 °C for 3 h and used for further studies.

2.2. Characterization

Powder X-ray diffractometer (XRD, Shimadzu 7000) is used to measure phase purity and crystallinity of NPs using a Cuk$_\alpha$ (1.541 Å) radiation. Scanning electron microscopy (SEM) (Hitachi table top, Model TM 3000) is used to analyze the surface morphology. Transmission electron microscopy (TEM) analysis is performed on a Hitachi H-8100 accelerating voltage up to 200 KV. Diffuse reflectance spectroscopy of the samples is analyzed by Perkin Elmer (35λ). The photoluminescence (PL) measurements are performed on a Jobin Yvon Spectroflourimeter Fluorolog-3 equipped with 450 W Xenon lamp as an excitation source.

2.3. Relevance in FP development

Various smooth surface were chosen for the Latent FP experimental studies, includes non-porous surfaces such as aluminum foil, glass, and plastic etc. Before applying the FPs on few distinct surfaces, the donor hands were adequately washed and then pressed using medium pressure. The synthesized $YAlO_3$:Nd^{3+}NPs were used to develop ensuing latent FPs by cautiously applying powder on various surfaces and excess powder was removed by smooth brushing via a typical powder brush method. By using *in situ* with a Nikon D3100/AF-S Nikkor 50 mm f/1.8G ED lens digital camera and a 365 nm UV light, images of developed FPs were photographed.

3. Results and discussion

The powder X-ray diffraction patterns (PXRD) of $YAlO_3$:Nd^{3+}

Table 1
Hazards reagents used for the chemical revelation of FP residues.

Sl.No	Chemicals	Hazards
1	Ninhydrin solution	Flammable. Harmful vapors. Skin and eye irritant.
2	DFO (1,8-diazafluoren-9-one) solution	Flammable. If inhaled it may be quit dangerous. May be absorbed through the skin. Respiratory and digestive region irritant. May cause skin andeye irritation.
3	Silver nitrate solution	Oxidizer. May be harmful if inhaled. Respiratory and digestive tract irritant. May cause skin and eye burns, argyria, a blue-gray discoloration of the skin, eyes, and mucous membranes.
4	Cyanoacrylate glue	Respiratory tract, eye and skin irritant. Bonds skin rapidly and strongly. May cause skin burns.
5	Iodine crystals	Oxidizer. May be harmful if inhaled, ingested, or contacted by skin or eyes. Respiratory irritation. May be corrosive to skin and eyes.
6	Gentian violet solution	May be absorbed through the skin. Respiratory, digestive, skin and eye area will getaggravation.