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Blue light emitting ceramic nano-pigments of Tm^{3+} doped $YAlO_3$: Applications in latent finger print, anti-counterfeiting and porcelain stoneware

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ABSTRACT

A new class of ceramic pigments based on orthorhombic Thulium (Tm^{3+}) doped $YAlO_3$ nanophosphors are synthesized by a simple and efficient low temperature solution combustion method using oxalyl dihydrazide (ODH) as fuel. The phosphors exhibit bright blue emission upon 359 nm excitation. Judd–Ofelt (*J–O*) theory is applied to a series of Tm^{3+} doped phosphors based on their emission spectra. CIE chromaticity co-ordinates confirm blue emission of the phosphor. The prepared nano-phosphor was successful in developing latent fingerprint from various forensic relevant materials. A preliminary investigation of their anti-counterfeiting performance has been made, and the results indicate that the color emitting capability and high concealment makes this nanophosphor can provide a strengthened and more reliable anti-counterfeiting effect. As a result the optimized $YAlO_3$:Tm^{3+} (3 mol%) phosphor is quite useful for potential application of pigments of desired color, solid state lighting, latent fingerprint, display and anti-counterfeiting applications.

1. Introduction

Phosphors are efficient luminescent materials and indispensable components in generating white light in WLED devices; phosphors typically possess good thermal stability, high conversion efficiency and strong absorption in the UV to blue region (380–460 nm) [1–4]. Now a days rare earths (REs) are widely used as luminescence activators in photonic, opto-electronic materials and are very much useful in the technological fields such as solid state lighting and optical communications because their electronic transitions can generate intense emissions of light. The factors that motivated the researchers on RE^{3+} doped materials are their successful application as optical fiber amplifiers (EDFAs, TDFAs, YDFAs) used as boosters, repeaters, lasers, light sources and pre-amplifiers in the optical networks [5–11]. Moreover, the solid state lighting technology utilizes rare earth doped phosphors in the fabrication of white light emitting diodes (W-LEDs) with high luminescence efficiency, low power consumption, energy efficiency, durability, reliability, and environmental friendliness [12–17]. Currently, W-LEDs are fabricated by the combination of UV/blue LED chips with suitable luminescent phosphors.

Phosphors are also used as luminescent pigments and can be used in many transparent or translucent media, such as plastic, paint, glaze, ink, rubbers, glasses and printing slurry, to produce luminous products. These materials can be widely used in emergency signs, passageway signs, switches, enamel nameplates, road signs, toys, handicrafts, clock meter panels and textiles. In addition, luminescent pigments with a short-afterglow are applied to security offset printing ink that is suitable for fluorescent crack

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detection. The use of pigments is not only due to their coloristic properties. They also protect the coating from the effects of solar light (UV, VIS and IC light).

The ceramic pigments with a particle size on the nanoscale have a massive potential market due to their high surface area, which assures higher surface coverage. In paint formulations, the small particle size allows for uniform dispersion by homogeneous mixing with binders, which enhances the mechanical strength of the paint after drying [18].

An enormous number of host/activator combinations have been studied for luminescence with a fair degree of success. However, the development of new materials will most likely require an improved understanding of the relationship between the host crystal structure and the energy levels of the dopant ions. The properties of these materials arise from complex interactions among the host structure, activators, and defects, which are strongly dependent on the composition [19].

In recent years, the Tm^{3+} ions continue to attract more attention because of their spectroscopic advantages. Among them, Tm^{3+} ion acts as both donor and acceptor in the cross-relaxation energy transfer (CRET) [20] that makes one avoid the introduction of a second type of dopant ions leading to additional unwanted relaxation channels. The choice of this kind of RE ions is motivated by its well-known blue emissions and the relative simplicity of its energy-level diagram. These emissions are characterized by the following transitions: $^1D_2 \rightarrow {}^3F_4$, $^3P_0$, $^1I_6 \rightarrow {}^3H_4$ and $^1G_4 \rightarrow {}^3H_6$. Among the trivalent RE ions, Tm^{3+} seems to be the most interesting ion leading to a blue phosphor material [21].

Yttrium Orthoaluminate ($YAlO_3$: YAP), is a host material exhibiting good optical, thermal and mechanical properties similar to YAG crystals [22]. The YAP crystals belong to a group of materials serving as the basic materials for laser technique, scintillators, optical recording media and substrate materials for thin films of high temperature superconductors [23]. YAP has a comparatively high effective atomic number ($Z_{eff} = 31.4$) that specifies the possible application of the material where a tissue equivalence is not needed. It offers several advantages when doping with some of the active transition elements which will significantly alter the laser emissions [24]. Here considerable attention has been paid to orthorhombic phase $YAlO_3$ (YAP) host due to its wide applications in laser materials, phosphors, scintillators, thermoluminescent (TL) dosimetry of ionizing radiation and as pigments [25]. Here we report for the photoluminescence properties and Judd Ofelt analysis of Tm^{3+} doped nanocrystalline $YAlO_3$ phosphor. Besides the synthesis, this paper also provides a detailed analysis of this phosphor using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), UV–Vis spectroscopy, photoluminescence (PL), Judd Ofelt analysis, CIE chromaticity, Correlated color temperature, mechanism of latent fingerprint development and anti-counterfeiting applications.

2. Experimental

2.1. Synthesis

Solution combustion technique is employed for the preparation of $YAlO_3$:Tm^{3+} (1–11 mol%) nanophosphor. The starting materials used for the preparation are of analytical grade Yttrium nitrate [$Y(NO_3)_3 \cdot 4H_2O$ (99.9%)], Aluminum nitrate [Al $(NO_3)_3 \cdot 9H_2O$ (99.9%)] and Thulium nitrate [Tm $(NO_3)_3$ (99.9%)]. The fuel oxalyl dihydrazide [ODH: $C_2H_6N_4O_2$] is prepared in our laboratory and discussed elsewhere [26]. The stoichiometric composition of the redox mixture is calculated by taking the ratio of total oxidizing (O) to the reducing (F) valences as equal to unity i.e., (O/F = 1), so that maximum energy is released during combustion. The stoichiometric ratio of nitrates and ODH are taken into the cylindrical petri dish of ~300 ml capacity and well dissolved in double distilled water. The aqueous redox mixture is dispersed uniformly by stirring the mixture using a magnetic stirrer for ~10 min. Then the resulting mixture is placed into a muffle furnace maintained at (350 ± 10 °C). At the beginning, the solution is thermally dehydrated and ignited with the liberation of large amount of gases (N_2, O_2, etc.). The entire process took place within 5 min. After completion of the process, the product obtained is grinded well using mortar and pestle. In addition, the final product is heat treated at 1000 °C for ~3 h and then used for structural characterization and luminescence studies.

2.2. Characterization

The phase purity and the crystallinity of the nanophosphor were examined by powder x-ray diffractometer (Shimadzu) using Cuk_α (1.541 Å) radiation with a nickel filter in the 2θ range 10–80°. The surface morphology of the product was examined by Scanning Electron Microscopy (SEM) Hitachi table top (SEM) (Model TM 3000). TEM analysis was performed on a Hitachi H-8100 (accelerating voltage up to 200 KV, LaB_6 filament) equipped with EDS (KEVEX sigma TM Quasar, USA). The FT-IR studies were performed on a Perkin Elmer Spectrometer (Spectrum 1000) with KBr pellets. The diffuse reflectance spectra of the samples were recorded on Perkin Elmer spectrometer (Lambda 35). The photoluminescence (PL) measurements of excitation and emission were performed on a JobinYvon Spectroflourimeter Fluorolog-3 equipped with 450 W Xenon lamp as an excitation source. All the luminescence properties of the phosphors were studied at room temperature.

2.3. Application in fingerprint development

A multitude of surface substrates were chosen for the fingermark experiments. These include non-porous surfaces, such as glass, transparent plastic sheet, stainless steel, aluminum foil and a porous surface like freshly cut leaf. Natural fingermarks were collected from donor, known to produce good natural and charged marks, ensuring that the hands had not been washed with soap within the previous 4 h. The fingers were then gently wiped across the forehead. Finally, the fingers were pressed on the surfaces of different substrates at room temperature to obtain latent fingermarks. To develop the resultant latent fingermarks, the dry $YAlO_3$:Tm^{3+} (3 mol%) was carefully applied to the surface of the substrates with a light brushing action. The excess powder was removed by dusting the substrate surfaces with a gentle, smooth motion until a fingermark image was developed. The fingermark images were photographed *in situ* with a Canon 700D digital camera equipped with an Tamron 90 mm VC lens and a 365 nm UV light for exciting the $YAlO_3$:Tm^{3+} nanophosphor.

3. Results and discussion

The crystallinity and phase formation of $YAlO_3$:Tm^{3+} (1–11 mol %) nanophosphors were studied by powder X-ray diffraction patterns (Fig. 1). All the PXRD peaks of the samples at (1 0 1), (1 1 1), (2 0 0), (1 2 1), (2 2 0) are well indexed to orthorhombic phase (JCPDS card No. 87-1290) of $YAlO_3$ with small traces of impurity peaks at $2\theta = 29.50°$ and 30.82° corresponds to $Y_3Al_5O_{12}$ phase [27]. Further, no diffraction peaks from Tm^{3+} ions detected up to 11 mol% indicating that Tm^{3+} ions were homogeneously mixed and effectively doped in the host lattice in Y^{2+} sites ($R^{3+}_{Tm} = 1.052$ and $R^{3+}_{Y} = 1.075$ nm). From PXRD, it is evident that the introduction of an activator (Tm^{3+}) did not influence the crystal structure of the phosphor matrix but certainly modified the lattice parameters due