Optical Materials 55 (2016) 68–72

Contents lists available at ScienceDirect

Optical Materials

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

Structure, photoluminescence and thermoluminescence study of a composite $ZnTa_2O_6/ZnGa_2O_4$ compound doped with Pr^{3+}

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ARTICLE INFO

Article history:
Received 2 December 2015
Received in revised form 19 February 2016
Accepted 15 March 2016
Available online 18 March 2016

Keywords:
$ZnTa_2O_6/ZnGa_2O_4:Pr^{3+}$
Photoluminescence
Thermoluminescence
Persistent luminescence

ABSTRACT

The study of persistent luminescence is interesting for applications related to biological imaging, self-lit roads and security signs. Composite Pr-doped samples were prepared in one pot by solid chemical reaction at 1200 °C for 4 h. The X-ray diffraction patterns of the samples showed mixed phases which correspond to $ZnGa_2O_4$ and $ZnTa_2O_6$ phases. Interestingly, the secondary electron microscopy images showed that the surface morphology is composed of particles with different shapes: irregular, rhombus and rod shapes. The X-ray maps obtained using field emission scanning electron microscopy, confirmed that the irregular particles correspond to $ZnTa_2O_6$, and the rods correspond to $ZnGa_2O_4$. Red emission was observed from $^1D_2 \rightarrow {}^3H_4$, $^3P_0 \rightarrow {}^3H_6$, $^3P_0 \rightarrow {}^3F_2$ and $^1D_2 \rightarrow {}^3H_5$ transitions of Pr^{3+}. The lifetime of the persistent luminescence was measured, and the corresponding trapping centres were investigated using thermoluminescence spectroscopy.

1. Introduction

Persistent luminescence is recently receiving attention because of the demand in applications in bio imaging for medical diagnostics and drug delivery, high energy radiation detection, thermal sensors, self-lit road lines and emergency signs [1–4]. Such luminescence continues after the removal of the excitation source, due to the stored energy from absorption that is gradually released as visible light [1,2,5]. Some persistent phosphors continue to glow for several hours in the absence of the excitation source [1,6]. Such phosphors include $Ca_2BO_3Cl:Eu^{2+},Ln^{3+}$ [6] and $Zn_3Ga_2Ge_2O_{10}:Cr^{3+}$ [1], with the persistent luminescence of the latter phosphor attributed to electron tunnelling back and forth between the electron trapping centres and the chromium luminescence centre. Persistent luminescence of $SrAl_2O_4:Eu^{2+},Dy^{3+}$ was reported to be attributed to the delay of emission by electron trapping centres associated with oxygen vacancies, before they reach the 5d state of Eu^{2+}, from where luminescence emanates [3]. One pot prepared composite phosphors have been prepared before, and they present properties which differ from those of the individually prepared compounds.

Some of our recent research was directed towards tantalite phosphors. Good chemical stability and persistent luminescence lasting more than ten minutes were reported for $YTaO_4$:Pr, $LaTaO_4$:Pr and $GdTaO_4$:Pr phosphors having multiple electron trapping centres [7,8]. The chemical stability was investigated by prolonged irradiation of the sample with an electron beam at 1×10^{-6} Torr O_2 pressure [7]. A red emitting phosphor $ZnTa_2O_6:Pr^{3+}$ was reported with a persistent emission lasting for 570 s after it was excited for five minutes using an ultraviolet lamp [9]. When 0.4 mol% doping of Pr^{3+} was used in the $ZnTa_2O_6$ host, emission resulted in a pure red colour coming from the $^1D_2 \rightarrow {}^3H_4$, $^3P_0 \rightarrow {}^3H_6$ and $^3P_0 \rightarrow {}^3F_2$ transitions at 608, 619 and 639 nm, respectively [10]. $CaTa_2O_6:Pr^{3+}$, with a greenish blue emission constituting of emission lines coming from the $^3P_0 \rightarrow {}^3H_4$ transition at 487 and 498 nm in the blue region of the electromagnetic spectrum, and at 530, 543 and 556 nm from $^3P_0 \rightarrow {}^3H_5$ transitions in the green region of the electromagnetic spectrum. Additionally, there were spectral lines in the red region of the electromagnetic spectrum at 597 and 610 nm from the $^1D_2 \rightarrow {}^3H_4$ transition, at 620 and 627 nm from $^3P_0 \rightarrow {}^3H_6$ transitions, and at 656 nm, attributed to the $^3P_0 \rightarrow {}^3F_2$ transition. The phosphor had a persistent luminescence lasting longer than 26 min [11]. The current paper presents a one pot prepared $ZnTa_2O_6/ZnGa_2O_4$:Pr composite phosphor. $ZnGa_2O_4$ is a spinel type compound, which crystallizes either into a normal spinel or mixed spinel [12]. In the normal spinel the Zn ion occupies the tetrahedral site and the Ga ion occupies the octahedral site, whereas in a mixed spinel the Zn and Ga ions are randomly distributed between in the tetrahedral and the octahedral

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http://dx.doi.org/10.1016/j.optmat.2016.03.029
0925-3467/

sites [12]. The compound exhibits strong blue emission attributed to the transition between the Ga and O defect levels, and has been reported to have applications in low voltage cathodoluminescence and liquid crystal displays [12]. A g-$C_3N_4/Y_2MoO_6:Eu^{3+}$ composite phosphor (where g-C_3N_4 stands for graphite-like carbon nitride) was prepared, which allowed a tuneable luminescence, in which white emission is obtainable [13]. A dual responsive composite phosphor $Sr_2SiO_4/Ba_3MgSi_2O_8:Eu^{2+},Mn^{2+}$ was prepared, and emitted blue–green–red tri-bands photoluminescence. Its dual-response characters was suitable for photosynthetic action spectrum of plant chlorophylls and photopic vision function of human eyes, for applications in both general lighting and plant lighting [14]. $ZnO/CaTiO_3:Er^{3+},Yb^{3+}$ nano composite was reported to have improved temperature sensing response [15]. $YVO_4/Y_2O_3:Eu^{3+}$, Bi^{3+} composites displayed tuneable emission, which could be tuned to display white emission by varying the ratio of the compounds [16]. A composite compound of $ZnO/ZnGa_2O_4$ was reported, which showed improved photocatalytic activities, compared to both ZnO and $ZnGa_2O_4$ prepared separately [17]. Porous nanospheres of Ag_2S/ZnS composite compound were prepared and showed enhanced visible-light photocatalytic activity [18]. A cerium doped $Y_2SiO_5/Y_3Al_5O_{12}$ composite phosphor was presented for field emission displays, which yielded tunable luminescence [19]. A Ni^{2+}-doped $ZnAl_2O_4/ZnO$ composite phosphor film was fabricated, which displayed a broadened and intense polychromatic emission covering the whole visible spectrum [20]. It is clear that unfamiliar luminescent characteristics were observed for a one pot synthesized composite in the past. The listed reports, show that one pot prepared composite compounds may reveal additional properties due to some synergistic effects, which are not present in individual compounds. In pursuit of tuning the properties of materials, preparation procedures of compounds are varied in order to prepare one compound with different properties. The motivation for preparing a one pot composite phosphor was therefor to investigate the possible optical differences between a one pot composite and the individual compounds. In the current paper we are introducing a composite phosphor based on both $ZnTa_2O_6$ and $ZnGa_2O_4$, doped with Pr. The luminescence properties and the energy distribution of the electron trapping centres was investigated.

2. Experimental details

A composite phosphor was prepared by doping 0.4 mol% of Pr^{3+} ions into $ZnTa_2O_6/ZnGa_2O_4$ composite compound. This was achieved via solid state chemical reaction by mixing ZnO, Ta_2O_5, Ga_2O_3 and $PrCl_3$ in stoichiometric amounts. The reagents were mixed into a slurry using ethanol. The slurry was preheated at 100 °C for 10 h and later sintered at 1200 °C for 4 h in air. The product was allowed to cool down to room temperature and then ground into a powder. The crystalline phase was identified by a Bruker AXS D8 Advance X-ray diffractometer (XRD) using CuKα radiation. The photoluminescence (PL) emission and excitation (PLE) properties of the phosphor were probed using an Edinburgh Instruments FS920 photoluminescence spectroscopy. The scanning electron microscopy (SEM) images were obtained using a Shimadzu SSX-550 SEM. The X-ray image along with the X-ray fluorescence maps were obtained with a field emission scanning electron microscope (Hitachi S3400N SEM), equipped with a Noran 7 from Thermo scientific for X-ray analysis. A PerkinElmer Lambda 950 UV/VIS/NIR spectrometer was used to record the diffuse reflectance spectra. The phosphorescence decay curves to determine the persistent emission lifetime were measured after exciting the phosphor with an ultraviolet source for 5 min, then monitoring the time it takes for the emission to decay using a photomultiplier tube (PMT). The glow curves were obtained using a 254 nm ultraviolet source for excitation, and measuring the thermoluminescence (TL) using a TL 10091, NUCLEONIX spectrometer.

3. Results and discussion

The composite samples were prepared and the phase purity was checked using XRD, and mixed phases were observed. The nature of the peaks confirms that crystalline particles were formed at 1200 °C. The XRD pattern (Fig. 1) matched with the patterns of $ZnTa_2O_6$ with a standard file indexed by ICSD 36289 and that of $ZnGa_2O_4$ with a standard file indexed by JCPDS 38-1240. Apparently, no solid solution of the zinc tantalite and zinc gallate is formed under these preparation conditions.

The SEM image in Fig. 2a is a representative of the surface morphology. The image shows that the particles crystallized into three different shapes: rod, rhombus and irregular shapes with different sizes. The irregular shaped particles are agglomerated to each other as a result of the high temperature used for the synthesis process [11,21]. The rhombus and rod shapes particles were not present in $ZnTa_2O_6:Pr^{3+}$ [9], and this may be an effect of the one pot synthesis of the composite phosphor. The X-ray image (Fig. 2b) and the fluorescent X-ray maps (Fig. 2c-f) were taken over a 10 × 7.1 μm^2 field of view. The X-ray maps clearly show a positive rod image on the Ga map, whilst showing a negative rod image on the Ta map. The Zn and O maps also show a positive image of the rod-shaped particles. The maps do clearly reveal that the rod shaped particles correspond to the gallium related phase, which, combined with the XRD patterns, is attributed to the $ZnGa_2O_4$ phase.

The PLE and PL spectra of the composite phosphor and the PLE and PL of $ZnTa_2O_6:Pr^{3+}$ (measured using a Varian Carry Eclipse [9]) are shown in Fig. 3. Upon exciting the materials with 274 nm ultraviolet source, there were emission lines that were observed from the different manifolds of the $^1D_2 \rightarrow {}^3H_4$ transitions at 600 and 608 nm, the $^3P_0 \rightarrow {}^3H_6$ transitions at 615 and 620 nm, and $^3P_0 \rightarrow {}^3F_2$ transitions at 628 and 635 nm, attributed to Pr^{3+} emission lines [9]. There are also emission lines attributed to different manifolds of $^1D_2 \rightarrow {}^3H_5$ transitions at 688 and 696 nm [9] and different manifolds of $^3P_0 \rightarrow {}^3F_3$ transitions at 709 and 715 nm [22]. The differences in excitation and emission of the pure $ZnTa_2O_6:Pr^{3+}$ are clear. The emission from the $^1D_2 \rightarrow {}^3H_5$ transitions ($ZnTa_2O_6:Pr^{3+}$ curve in Fig. 3) is also much more intense than usual as reported in our previous work [7–11]. The PLE spectra show a prominent excitation band at 274 nm, which corresponds to band to band (B–B) excitation and a charge transfer state at 330 nm as reported in our previous communication. The prominent excitation

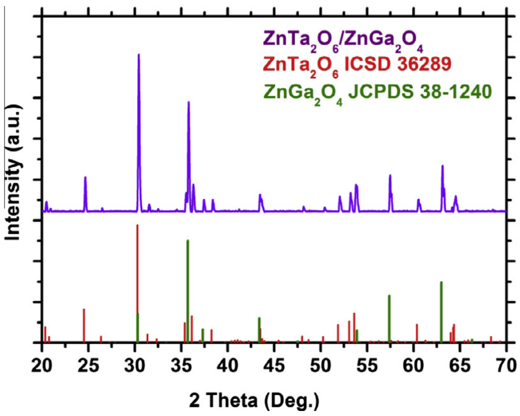

Fig. 1. The XRD patterns of the composite sample and the standard patterns of $ZnTa_2O_6/ZnGa_2O_4$.