Materials Science and Engineering B 224 (2017) 28–39

Contents lists available at ScienceDirect

Materials Science and Engineering B

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

Positron annihilation spectroscopy and photoluminescence investigation of LaOF:Tb^{3+} nanophosphor fabricated via ultrasound assisted sonochemical route

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ARTICLE INFO

Article history:
Received 5 April 2017
Received in revised form 4 June 2017
Accepted 4 July 2017

Keywords:
Positron annihilation spectroscopy
Doppler broadening spectroscopy
Sonochemical method
Photoluminescence
Light emitting diodes

ABSTRACT

LaOF:Tb^{3+} nanophosphors were synthesized by modified sonochemical route using extracted Epigallocatechin gallate (EGCG) from green tea powder as surfactant. Powder X-ray diffraction patterns confirm the tetragonal phase of samples. Morphology of the products was tuned by changing the influential experimental parameters. Positron annihilation spectroscopy (PAS) was used to investigate the defect chemistry of the prepared samples. PAS specified the presence of defects at crystallite boundaries, vacancy clusters and large voids in the prepared compounds. Photoluminescence emission spectra consists of characteristic green emissions owing to $^5D_4 \rightarrow {}^7F_J$ (J = 6, 5, 4, 3) transitions of Tb^{3+} ions. The estimated critical distance between dopant ions was found to be ~16.60 Å is majorly responsible for the dipole-dipole interaction and concentration quenching. The photometric study such as Commission Internationale de L'Eclairage, Correlated Color Temperature and Color purity indicates that the obtained phosphors could be a promising green component for optoelectronic applications in particular to white LEDs.

1. Introduction

In recent years, rare earth ions doped inorganic luminescent materials have fascinated due to their diverse potential applications namely white light-emitting diodes (WLEDs), sensors, biological imaging, field emission displays (FEDs), solar cells etc. [1–3]. The luminescent properties of Ln^{3+}-doped phosphors are host independent due to the transitions of inner f-shell electrons [4,5]. Therefore, the selection of appropriate inorganic phosphors with efficient luminescent performance creates numerous interests for research community. Until now, some inorganic hosts, namely molybdates, oxides, fluorides, and silicate, were extensively investigated towards display device applications and were listed in Table 1 [6–15]. Among, fluorides LaOF possess low cut-off phonon energy with decreasing the possibility of different non-radiative transition and thus leading to superior luminescent properties [16,17].

Further, during fabrication commonly occurred lattice defects such as voids or pores, clustered vacancies and mono vacancy greatly affected the luminescence. Positron annihilation spectroscopy (PAS) has been considered as new probe to illustrate surface defects and to understand the effect of size, quantum effects as well as surface defects of the nanomaterials, due to the better diffusion length of positrons as compared with crystallite size of the nanomaterial which makes restrictions on surface of the particles [18–21]. After thermal treatment, embedded positrons may diffuse in the medium followed by electron annihilation. High tendency of positrons induce defects in the material which results longer lifetime; therefore, longer positron life-times can be related with crystallite size and defect concentration [22–24].

Moreover, the Doppler broadening (DB) in the γ-spectrum was utilized to notice the particular type of defects, preserving and

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http://dx.doi.org/10.1016/j.mseb.2017.07.001
0921-5107/

Table 1
List of rare earth doped phosphors applicable to wLED's.

Phosphor	Excitation	Emission	CIE (X, Y)	CCT(K)	Refs.
Bi_2O_3:Eu^{3+}(1.5%):Tb^{3+}(0.5%)	374, 362, 322	590, 611, 623	(0.49, 0.34)	1830	Dimple et al. [6]
	322, 370, 380	486, 544, 584, 622	(0.31, 0.26)	7961	
			(0.27, 0.23)	32276	
LaF_3:Tm,Eu,Tb	378	541	(0.331, 0.332)	4991	Lorbeer et al. [7]
	355	449, 540	(0.317, 0.332)	6500	
		590	(0.312, 0.329)	3309	
ZnO:Eu^{3+}	394	590, 615, 648, 702	(0.501, 0.484)	–	Chandrashaker et al. [8]
Mg_2SiO_4:Sm^{3+}	315	576, 611, 656, 713	(0.588, 0.386)	1756	Naik et al. [9]
$Gd_{1.96-x}Y_xEu_{0.04}O_3$	305	611, 582, 641	(0.663, 0.328)	–	Shilpa et al. [10]
$Sr_3MgSi_2O_8$:Eu^{2+}	375	470, 570	(0.32, 0.33)	5892	Kim et al. [11]
$Sr_3Y_2(BO3)_4$:Dy^{3+}	370	488, 575, 665	(0.2997, 0.3142)	5896	Li et al. [12]
$GdAl_3(BO_3)_4$:Dy^+, Ce^{3+}	400	480, 575, 620	(0.31, 0.33)	6480	Zhang et al. [13]
$Sr_3B_2O_6$:Ce^{3+}, Eu^{2+}	351	434, 574	(0.31, 0.24)	–	Chang et al. [14]
	395	505, 625	(0.35, 0.41)	5088	
Sr_2SiO_4:Eu^{2+}	400	550	(0.39, 0.41)	–	Park et al. [15]

reflecting the energy momentum distribution of an electron in the material [25–27]. Energy momentum distribution of an electron in a defect was quite different from the electrons momentum in the bulk material, therefore DB considered as a probe to identify the specific defects [28–30]. The vacancy defects are playing a vital role in changing the properties of material at nanosized. Many in appropriate efforts have been done to identify the modifications of properties by altering experimental parameters. Thus, positron lifetime and Doppler broadening accurately identifies the vacancy-type defects [31,32].

Lanthanide oxyfluoride (LaOF) was considered to be a novel host and having a wide range of applications due to their high ionicity, low phonon energy (550 cm^{-1}) [33], chemical stability etc. compared with those of fluorides and oxides [34–37]. Since the La^{3+} ions has the largest ionic radius among the lanthanide series, it can be easy substituted by different Ln^{3+} ions in the structure [38].

Up to now, many efforts have been made to fabricate LaOF nanophosphor, by diverse routes namely hydrothermal, sol–gel, solution combustion method, Co-precipitation, etc., [39–43]. However, these methods have several disadvantages such as large crystallite size, harsh reaction conditions and require sophisticated instrumentation, which rigorously obstruct their possible applications. Therefore, eco-friendly and cost effective fabrication route which produce LaOF nanophosphor with reproducible shapes and dimensions is highly desired [44]. The importance of choosing a proper synthetic route in designing nanostructured materials has been a driving force for the development of new methodologies for several decades. Indeed, this has led scientist's interest to the development of versatile and generalized synthetic methods readily adaptable for the preparation of a variety of nanostructured materials. Among a variety of approaches, the utilization of ultrasound for materials synthesis has been extensively examined over many years and is now positioned as one of the most powerful tools in nanostructured materials synthesis.

Compared to traditional energy sources, ultrasonic irradiation provides rather unusual reaction conditions (in a short duration; there is a formation of extremely high temperatures and pressures in liquids) that cannot be realized by other methods. Interestingly, such extraordinary conditions are not derived directly from ultrasound itself: acoustic wavelengths are much larger than molecular dimensions. Thus, no direct, molecular level interaction between ultrasound and the chemical species takes place. Instead, acoustic cavitation (i.e., the formation, growth, and implosive collapse of bubbles in liquids (Fig. 1)) driven by high intensity ultrasound accounts for the chemical effects [45]. When liquids are irradiated with ultrasound, the alternating expansive and compressive acoustic waves creates bubbles (i.e., cavities) and makes the bubbles oscillate (Fig. 1). The oscillating bubbles can accumulate ultrasonic energy effectively while growing to a certain size (typically tens of mm). Under the right conditions, a bubble can overgrow and subsequently collapse, releasing the concentrated energy stored in the bubble within a very short time (with a heating and cooling rate of $>10^{10}$ K s^{-1}). This cavitational implosion is much localized and transient with a temperature of ~5000 K and a pressure of ~10^3 bar [46].

Surfactants have established to be the best shape modifying agents for the fabrication of nanostructures which is mainly associated to the surface adsorption of surface active molecules on diverse crystal planes of nucleating centers helps in engineering their morphology. Various types of modifying agents have been used for shape controlled production of nanostructures. Epigallocatechin gallate (EGCG) is found to be one of the key constituent found in green tea and contains 30–40% of water soluble polyphenols. Due to polyphenolic structure, it serves major contribution to hydrogen bonding. This hydrogen bonding enables the capacity of binding strongly to polyphenols present in EGCG and forms a micro/superstructures [47]. Further, EGCG is the most effective reactant when reacting with major reactive oxygen species (ROS) and free radicals through mechanisms namely electron delocalization, formation of intramolecular hydrogen bonds and molecular structure reorganization [48].

A many research has been carried out on the luminescence properties of RE^{3+} doped LaOF nanophosphor varying rare earth concentration to achieve a superior luminescent media. But as per our literature survey, till date no work has been reported on the synthesis of LaOF:Tb^{3+} (1–5 mol%) nanophosphor by eco-friendly ultrasound assisted sonochemical route using EGCG extract as a surfactant. The process of formation and the mechanism for the formation of morphologies were investigated on the basis of structural information provided by electron microscopy analysis. From Positron annihilation spectroscopic (PAS) analysis, the presence of defects at crystallite boundaries, vacancy clusters and large voids in the prepared samples was discussed. An attempt was made for the first time to estimate Judd-Ofelt parameters of the prepared samples from the emission spectra along with the structural information. The PL behavior and the spectroscopic investigation of LaOF:Tb^{3+} (1–5 mol%) nanophosphor are discussed.

2. Experimental and characterization

The precursors used for the preparation of LaOF:Tb^{3+} (1–5 mol %) nanophosphor were in analytical grade (AR) and without further purification. The chemicals used in the present work are