Journal of Luminescence 199 (2018) 240–244

Contents lists available at ScienceDirect

Journal of Luminescence

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

# $Eu^{2+}$ photoluminescence in $Al_2O_3$ coatings obtained by plasma electrolytic oxidation

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ARTICLE INFO

*Keywords:*
Plasma electrolytic oxidation
$Eu^{2+}$
Photoluminescence
$Al_2O_3$

ABSTRACT

$Al_2O_3$ coatings doped with Eu ions were prepared by plasma electrolytic oxidation (PEO) process in electrolyte containing $Eu_2O_3$ particles. The analysis of the photoluminescence (PL) spectra showed that $Eu^{3+}$ ions were reduced to $Eu^{2+}$ during PEO in $Al_2O_3$ host. The most intense PL was obtained under excitation of 260 nm. PL emission spectra consist of two distinct broad bands with corresponding maxima at around 410 nm and 500 nm related to $4f^65d^1 \rightarrow 4f^7$ electronic transitions of $Eu^{2+}$ ions. Sharp emission band in orange-red region of $Eu^{3+}$ ions attributed to f-f transitions $5D_0 \rightarrow 7F_J$ were not observed in PL emission spectra. Two PL bands in emission spectra indicate existence of two different $Eu^{2+}$ sites in $Al_2O_3$ host. Relative ratio of these two broad bands depends on excitation wavelength as well as concentration of $Eu^{2+}$ ions incorporated into $Al_2O_3$ coatings.

## 1. Introduction

Over recent years, europium ion has received increasing attention due to its outstanding spectroscopic properties. It can exist in two stable oxidation states, divalent ($Eu^{2+}$) and trivalent ($Eu^{3+}$) states. Both of these Eu states show many different characteristics as emitting centers. In the case of $Eu^{3+}$ ions, orange-red photoluminescence (PL) typically originates from the $4f^6 \rightarrow 4f^6$ electronic transitions, usually from the excited $^5D_0$ state to lower levels $^7F_J$ ($J = 1,2,3,4$, and 5) [1]. On the other hand, $Eu^{2+}$ ions show intense excitation and strong emission band due to the parity allowed (Laporte's selection rule is obeyed) 5d→4f electronic transitions [2]. The positions of excitation and emission PL bands of $Eu^{2+}$ ions are strongly dependent on the crystal field splitting of the 5d excited level. The 5d electrons are located in the outermost orbitals unshielded by outer orbital electrons, hence the electrons in the 5d orbitals are significantly affected by the crystal fields of the host lattice [3]. As a result, $Eu^{2+}$ ions emit light in a large wavelength region ranging from ultraviolet to red.

It is well known that there is no natural material containing $Eu^{2+}$ ions. Raw materials of europium compounds are usually $Eu_2O_3$ or $EuCl_3$ where europium ions exist in trivalent oxidation state. For synthesis of $Eu^{2+}$ doped luminescent materials $Eu^{3+}$ ions must be reduced to $Eu^{2+}$. Mostly, the reduction of $Eu^{3+}$ to $Eu^{2+}$ in matrix could be realized if preparation is carried out in reducing atmospheres, such as $H_2$, $H_2/N_2$, or CO [4]. Also, in some cases this reduction occurs during the preparation in air at high temperatures [5]. Extreme PEO processing conditions (locally high temperature and pressure) [6], may be beneficial for the reduction of $Eu^{3+}$ to $Eu^{2+}$ in $Al_2O_3$:Eu coatings. In this work, we have shown that $Eu^{2+}$ doped $Al_2O_3$ coatings can be formed by plasma electrolytic oxidation (PEO) process of aluminum in electrolyte containing $Eu_2O_3$ particles. It is also worth mentioning that $Al_2O_3$ is an attractive host for rare-earth ions because it presents a high transparency window from ultraviolet to near infrared wavelength range, it has excellent mechanical strength, and good chemical and photochemical properties, high melting point, etc. [7–9]. Up to now, only a few papers have been devoted to the study of the PL of the $Eu^{2+}$ ions in the $Al_2O_3$ host [10–12].

## 2. Experimental details

Aluminum samples with active surface of 15 mm × 10 mm were obtained from 99.9% purity aluminum sheet of 0.25 mm thickness. The samples were cleaned with acetone and distilled water in an ultrasonic bath, and finally dried in a warm air stream. Water solution of 0.1 M $H_3BO_3$ + 0.05 M $Na_2B_4O_7{\cdot}10H_2O$ with addition of $Eu_2O_3$ powder in concentrations up to 4 g/L was used as electrolyte. For PEO process, electrolyte was placed into a 500 mL Pyrex beaker. Aluminum samples were used as anode while two platinum plates (40 mm × 20 mm) were used as cathodes in the experiment. The PEO process was performed by using DC power supply Consort EV 261 (0–600 V, 0–1A) under constant current density of 150 mA/cm$^2$, while duration of PEO process was varied up to 10 min. During the PEO, the electrolyte was stirred with a magnetic stirrer and circulated through the chamber-reservoir system [13] and the temperature of the electrolyte was maintained at

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https://doi.org/10.1016/j.jlumin.2018.03.062
Received 9 February 2018; Received in revised form 20 March 2018; Accepted 21 March 2018

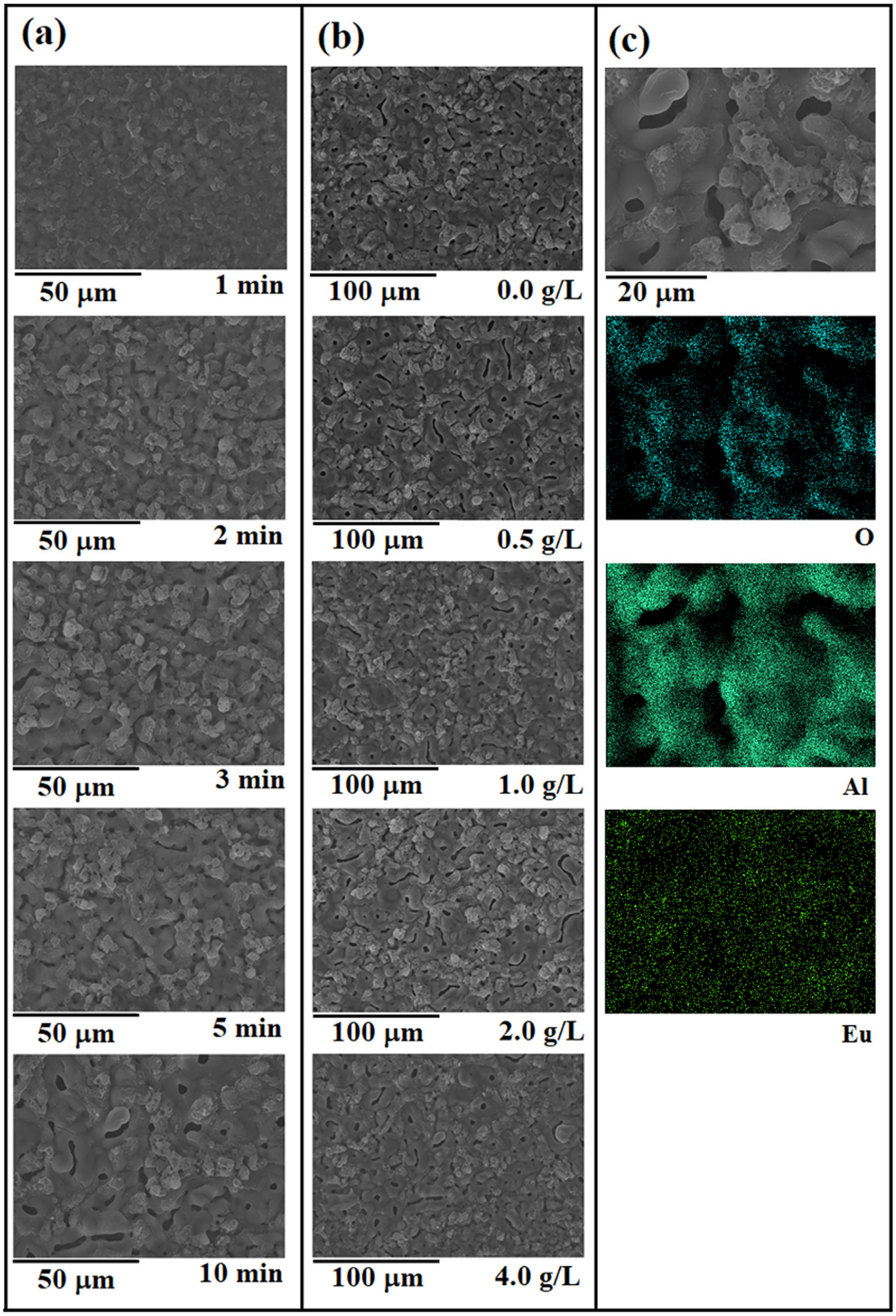

**Fig. 1.** (a) SEM micrographs of coatings formed at various stages of PEO process in 0.1 M $H_3BO_3$ + 0.05 M $Na_2B_4O_7{\cdot}10H_2O$ + 4.0 g/L $Eu_2O_3$; (b) SEM micrographs of coatings formed by PEO for 10 min in 0.1 M $H_3BO_3$ + 0.05 M $Na_2B_4O_7{\cdot}10H_2O$ with addition of $Eu_2O_3$ powder in various concentrations; (c) EDS maps of coating formed by PEO for 10 min in 0.1 M $H_3BO_3$ + 0.05 M $Na_2B_4O_7{\cdot}10H_2O$ + 4.0 g/L $Eu_2O_3$.

(18 ± 1) °C. After the PEO process, the coated samples were rinsed with distilled water and dried.

A scanning electron microscope (SEM, JEOL 840A) combined with energy dispersive spectrometer (EDS) system was used to examine the microstructure and chemical composition of the PEO coatings. PEO coatings phase composition was analyzed by X-ray diffraction (XRD), using a Rigaku Ultima IV diffractometer in Bragg-Brentano geometry, with Ni-filtered Cu Kα radiation ($\lambda = 1.54178$ Å). The X-ray photoelectron spectra (XPS) were acquired on a Kratos AXIS Supra photoelectron spectrometer using a monochromatic Al Kα source with energy of 1486.6 eV. The base pressure in the analysis chamber was $5 \times 10^{-8}$ Pa. PL spectral measurements at room temperature were obtained using a Horiba Jobin Yvon Fluorolog FL3–22 spectrofluorometer. The excitation light source was a xenon lamp (450 W) coupled to a double grating monochromator in a wavelength range from 220 nm to 600 nm. Emission spectra were measured using a double grating monochromator in a wavelength range from 290 nm to 850 nm and side-on photomultiplier (Hamamatsu, model 928 P). The obtained spectra were corrected for the spectral response of the measuring system and spectral distribution of the xenon lamp.