Journal of Alloys and Compounds 576 (2013) 195–200

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

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

Synthesis of $Y_3Al_5O_{12}:Ce^{3+}$ colloidal nanocrystals by pulsed laser ablation and their luminescent properties

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ARTICLE INFO

Article history:
Received 25 March 2013
Accepted 19 April 2013
Available online 29 April 2013

Keywords:
$YAG:Ce^{3+}$ nanocrystal
Pulsed laser ablation
LDA
Luminescence
Blue-shift

ABSTRACT

Cerium-doped $Y_3Al_5O_{12}$ ($YAG:Ce^{3+}$) colloidal nanocrystals were synthesized by pulsed laser ablation (PLA) in de-ionized water and lauryl dimethylaminoacetic acid betain (LDA) aqueous solution for luminescent bio-labeling application. The influence of LDA molecules on the crystallinity, crystal morphology, crystallite size and luminescent properties of the prepared $YAG:Ce^{3+}$ colloidal nanocrystals was investigated in detail. When the LDA solution was used, smaller average crystallite size, narrower size distribution and enhanced luminescence were observed. These characteristics were explained by the effective role of occupying the oxygen defects on the surface of $YAG:Ce^{3+}$ colloidal nanocrystal because the amphoteric LDA molecules were attached by positively charged $YAG:Ce^{3+}$ colloidal nanocrystals. The blue-shifted phenomena found in luminescent spectra of the $YAG:Ce^{3+}$ colloidal nanocrystals could not be explained by previous crystal field theory. We discuss the 5d energy level of Ce^{3+} with decreased crystal size with a phenomenological model that explains the relationship between bond distance with 5d energy level of Ce^{3+} based on the concept of crystal field theory modified by covalency contribution.

1. Introduction

Integrated sensors for biological application and a variety of molecular-sensing schemes characterized by electrochemistry, refractive index, UV absorption and luminescence have been devised in an effort to understand the spatio-temporal interplay of biomolecules in biology [1–4]. In particular, luminescent labeling for cellular imaging and assay detection is a standard technique used to understand the interaction of biomolecules in biology [5–7]. However, organic dyes, luminescent proteins or lanthanide chelates as bio-labeling agents may cause problems such as broad spectrum profiles, low photo-bleaching thresholds and poor photochemical stability.

Ce^{3+}-doped yttrium aluminum garnet ($Y_3Al_5O_{12}:Ce^{3+}$, $YAG:Ce^{3+}$), which has been widely used as a white solid-state light emitting device, may be an alternative label to overcome these problems because of its chemical and thermal stability [8]. We believe that $YAG:Ce^{3+}$ nanocrystal can be substituted for chalcogenide phosphor as a bio-label for several reasons. Not only does $YAG:Ce^{3+}$ have the potential to obtain luminescent quantum efficiency up to 40% by the allowed $4f \rightarrow 5d$ transition of Ce^{3+}, but it is also considered as a non-toxic material [9]. In addition, in the *in vivo* experiment, the cells are not degraded by blue light, the excitation source for emission from $YAG:Ce^{3+}$.

Generally, the conventional solid-state reaction method has been used to fabricate $YAG:Ce^{3+}$ crystal. However, this method requires a relatively long processing time and temperature over 1500 °C to obtain single-phase product. Moreover, there have been few reports on the preparation of nano-sized $YAG:Ce^{3+}$ crystals [10]. Under these circumstances, a novel preparation method for $YAG:Ce^{3+}$ nanocrystal would be greatly valuable. One novel technique for synthesizing $YAG:Ce^{3+}$ nanocrystals is pulsed laser ablation (PLA) in liquid media. This technique provides remarkable advantages: simplicity in the synthesis process, the availability of various liquid media, and the absence of chemical reagents in solution [11–13]. Moreover, pulsed laser ablation is a convenient technology for synthesize nanostructured materials, and some researchers have made achievements on this research field [14–16].

In general, luminescence efficiency of phosphor materials goes down with diminution of cryatallite size into nanometer range, because an increase in surface-to-volume ratio seriously induces non-radiative processes related to surface defects [17]. Therefore, it is necessary to cap such defects by an appropriate surfactant to enhance luminescence efficiency. In this work, we report a new synthetic approach to directly produce highly dispersed and strongly luminescent $YAG:Ce^{3+}$ colloidal nanocrystals for application to luminescent bio-labeling by PLA in aqueous solution. Moreover,

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http://dx.doi.org/10.1016/j.jallcom.2013.04.134

the change of 5d electron energy level of Ce^{3+} in nanoscaled YAG crystal, which has attracted much discussion in recent years [18,19], was investigated in detail.

2. Experimental

A cerium 3 mol% doped YAG:Ce^{3+} target ($(Y_{1-x}Ce_x)_3Al_5O_{12}$, $x = 0.03$) was fabricated by spark plasma sintering (SPS) method at 1400 °C for 5 min. The fabricated YAG:Ce^{3+} target was fixed in the bottom of a glass vessel containing 5 ml high-purity de-ionized water and solution of lauryl dimethylaminoacetic acid betaine (LDA, 10^{-2} mol/l) as an amphoteric surfactant. Although a number of surfactants are widely used in laser ablation process, the LDA have been reported to lead to smaller average size and narrow distribution, as well as enhanced emission intensity [20]. The fixed target was irradiated by a Nd:YAG pulse laser (repetition rate of 30 Hz, pulse width of 5–7 ns, maximum output of 60 mW) with the third harmonic wavelength (355 nm). The laser was focused on a spot 1 mm in diameter on the YAG:Ce^{3+} target with a focal length of 250 mm. The target was rotated during laser ablation to avoid deep ablation traces by continuous irradiation of the laser beam. Laser ablation of the YAG:Ce^{3+} target was carried out for 1 h at room temperature. Fig. 1 illustrates the laser ablation process in liquid medium for preparation of YAG:Ce^{3+} nanocrystals.

The colloidal suspension was dropped on a copper mesh coated with amorphous carbon film to observe the microstructure and shape of nanocrystals by a transmission electron microscope (JEOL JEM-2010). The size of the nanocrystals was statistically analyzed using a TEM image. The precipitates of colloidal suspension were repeatedly centrifuged at 30,000 rpm by an ultracentrifuge (Hitachi CS100GXL) for the X-ray diffraction (XRD, Rigaku RAD-C, Cu Kα radiation). Luminescence spectra of the YAG:Ce^{3+} nanocrystal-dispersed suspensions were measured using a fluorescence spectrometer (PerkinElmer LS-45) at room temperature. The excitation wavelength used for measuring emission spectra was 460 nm, and the excitation spectra were measured at emission maxima.

3. Results and discussion

3.1. Synthesis of YAG:Ce^{3+} colloidal nanocrystals

Fig. 2 shows XRD patterns of the YAG:Ce^{3+} nanocrystals collected from colloidal suspensions prepared by PLA in (a) de-ionized water and (b) LDA solution. Bragg reflection peaks of the nanocrystals corresponded to the cubic structured YAG:Ce^{3+} without any peaks assigned to Y_2O_3, Al_2O_3, $YAlO_3$ or $Y_2Al_4O_9$ phases. The YAG:Ce^{3+} nanocrystals formed in de-ionized water had some amorphous phase. However, in the case of LDA solution, the broad amorphous component was diminished and crystallinity was improved compared to the case of de-ionized water.

The crystal morphology, crystal size and crystallinity were observed more closely by TEM. Fig. 3 represents typical TEM micrographs of YAG:Ce^{3+} colloidal nanocrystal prepared by PLA in (a) de-ionized water and (b) LDA solution with corresponding electron diffraction patterns. The morphology of the nanocrystals prepared

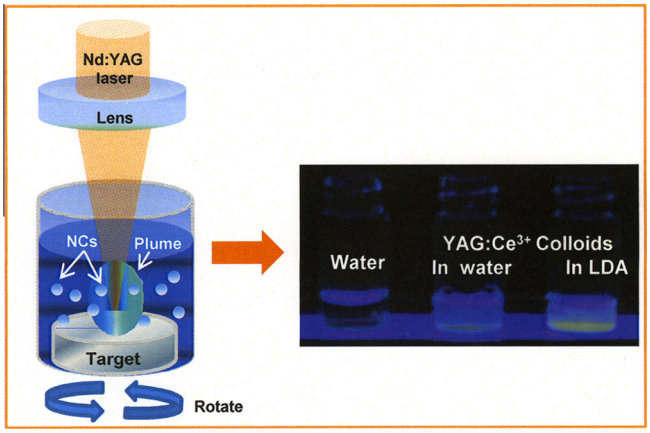

Fig. 1. Schematic diagrams representing pulsed laser ablation of target in liquid medium. The insets illustrate YAG:Ce^{3+} colloidal suspensions prepared by PLA in de-ionized water and LDA solution for 1 h excited by an UV lamp.

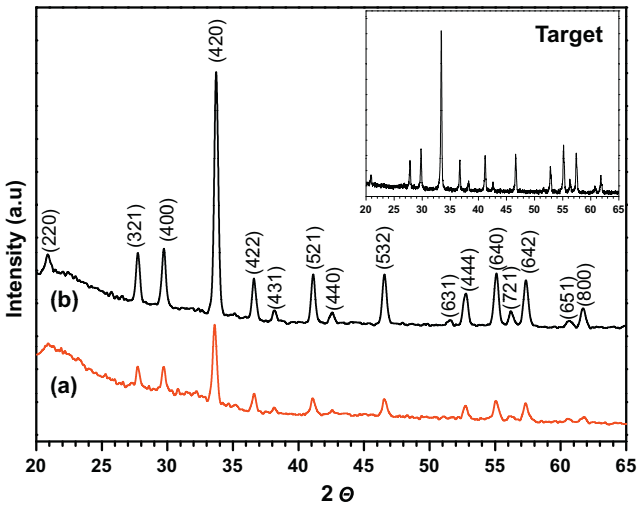

Fig. 2. XRD patterns of the YAG:Ce^{3+} nanocrystals prepared by PLA in (a) de-ionized water and (b) LDA solution. The inset depicts the XRD pattern of YAG:Ce^{3+} bulk target fabricated by SPS.

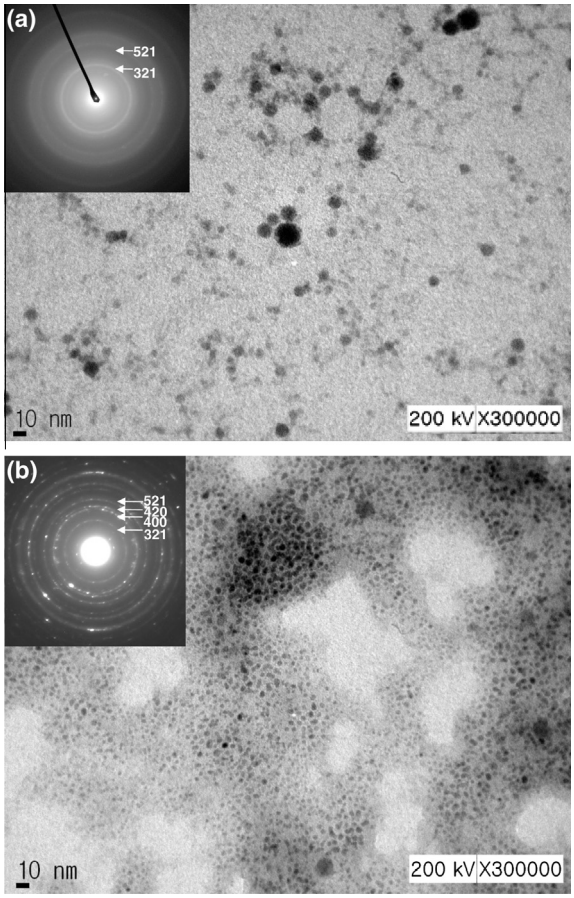

Fig. 3. Typical TEM micrographs of YAG:Ce^{3+} colloidal nanocrystal prepared by PLA in (a) de-ionized water and (b) LDA solution with corresponding electron diffraction patterns.

in de-ionized water (a) indicated that spherical aggregates coexisted with dispersed spherical nanocrystals. Corresponding selected area electron diffraction (SAED) patterns revealed diffused characteristic ring patterns, which confirmed the presence of an amorphous phase. Compared to the case of de-ionized water, smal-