Arc discharge synthesis and up-conversion emissions of Er$^{3+}$ doped Al$_2$O$_3$ nanoparticles

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Abstract

The Er$^{3+}$ doped Al$_2$O$_3$ nanoparticles with an average particle size of about 50 nm have been synthesized by an arc discharge synthesis method. The strong up-conversion emissions centered at about 526, 547, and 668 nm were detected by a 978 nm laser diode (LD) excitation. The evident effect of annealing on the up-conversion emissions of the samples was studied. Before annealing, the red up-conversion emission was noticeable because of a high transition probability of the $^4$I$_{13/2} + \alpha$ photon $\rightarrow ^4$F$_{5/2}$. However, the green up-conversion emission became predominant due to an enhancement of the $^4$I$_{11/2} + \alpha$ photon $\rightarrow ^4$F$_{7/2}$ and $^4$I$_{11/2} + ^4$I$_{11/2} \rightarrow ^4$F$_{7/2}$ processes after annealing. The results proved that arc discharge synthesis is a new promising preparation technology for optical materials.

Keywords: Optical materials and properties; Er$^{3+}$ doped Al$_2$O$_3$; Arc discharge synthesis

1. Introduction

Recently, the infrared-to-visible up-conversion emissions from trivalent-rare-earth ions doped materials have been investigated for a wide range of potential applications, such as color display, optical data storage, biomedical diagnostics, and sensor technology [1–4]. In particular, the Er$^{3+}$ is the most attractive element because its favorable energy level structure with $^4$I$_{15/2} \rightarrow ^4$I$_{11/2}$ transition, which can be excited easily using a 978 nm laser diode [5,6]. Al$_2$O$_3$ is a remarkable matrix material for Er$^{3+}$ because it can increase the dispersion of Er$^{3+}$ and then fluorescence efficiency and radiative transition rate [7,8]. Furthermore, Al$_2$O$_3$ has high chemical durability, thermal stability, and mechanical strength besides a high transparency window from ultraviolet to infrared [9]. Up to date, the up-conversion emissions have been obtained from the Er$^{3+}$ doped Al$_2$O$_3$ particles prepared by the sol–gel method and the low temperature direct combustion synthesis method. Unfortunately, however, the OH$^-$ was introduced inevitably in the two methods [9,10]. The OH$^-$ acts as a fluorescence quenching center because two OH$^-$ vibrational quanta can bridge the energy gap between the $^4$I$_{13/2}$ and $^4$I$_{15/2}$ levels, leading to a decrease of fluorescence efficiency [11]. Compared with the two methods, the arc discharge synthesis method is more favorable to prepare the oxide particles under a non-aqueous environment [12,13]. Though extensive researches proved that the arc discharge synthesis method is one of the most promising technologies to prepare metallic nanoparticles with excellent magnetic properties and large specific surface area under the absence of OH$^-$, little was reported about preparation about the optical materials. In this paper, we present the preliminary experiment results of Er$^{3+}$ doped Al$_2$O$_3$ nanoparticles prepared by the arc discharge synthesis method, in order to explore a new
synthesis technology of optical materials and investigate the corresponding up-conversion emission characteristics.

2. Experimental

Using the same arc discharge synthesis method as described in the previous work [12]. \( \text{Er}_2\text{O}_3 \) (0.14 g) and Al powders (20 g) to be evaporated served as the cathode. After the chamber was evacuated, a mixture of hydrogen (50%) and argon (50%) was introduced to reach 0.8 MPa as a source of hydrogen plasma and a condensing atmosphere. The 0.6 wt.% \( \text{Er}^{3+} \) doped \( \text{Al}_2\text{O}_3 \) nanoparticles were heated up to the annealing temperature of 1000 °C with a heating rate of 5 °C min\(^{-1}\), maintained for 1 h, and cooled down to room temperature in the furnace.

The size distribution and shape of the \( \text{Er}^{3+} \) doped \( \text{Al}_2\text{O}_3 \) nanoparticles were observed by a Tecnai F20 transmission electron microscopy (TEM). The phase structure of the samples was analyzed by a SHIMADZU XRD-6000 X-ray diffractometer (XRD) with Cu K\( \alpha \) radiation. The up-conversion emissions in the wavelength range of 500–740 nm were obtained respectively from the samples by a 978 nm semiconductor laser diode (LD) excitation. The up-conversion emissions from the samples were focused onto a single-monochromator, detected with a CR131 photomultiplier tube, associated with a lock-in amplifier. The spectral resolution of the experimental set-up was 0.1 nm. All spectroscopic measurements were carried out at room temperature.

3. Results and discussion

Fig. 1 shows the TEM micrograph of the \( \text{Er}^{3+} \) doped \( \text{Al}_2\text{O}_3 \) nanoparticles annealed at 1000 °C. It can be seen that the \( \text{Er}^{3+} \) doped \( \text{Al}_2\text{O}_3 \) nanoparticles were obtained with an average particle size of about 50 nm, ranging from 40 to 80 nm.

Fig. 2 shows the XRD patterns of the unannealed and annealed \( \text{Er}^{3+} \) doped \( \text{Al}_2\text{O}_3 \) nanoparticles. Before annealing, the mixture of pure Al phase (JCPDS No. 89-2837) and \( \alpha-(\text{Al,Er})_2\text{O}_3 \) phase (JCPDS No. 43-1484) was detected. After annealing at 1000 °C, the peaks of \( \alpha-(\text{Al,Er})_2\text{O}_3 \) phase became more obvious, indicating that the good crystallization was obtained by annealing. In addition, the precipitation of two stoichiometric compounds composed of Al, Er, and O, \( \text{ErAlO}_3 \) phase (JCPDS No. 24-0396) and \( \text{Al}_{10}\text{Er}_6\text{O}_{24} \) phase (JCPDS No. 32-0012) were also observed.

Fig. 3 shows the up-conversion emissions spectra in the wavelength range of 500–740 nm for the unannealed and annealed \( \text{Er}^{3+} \) doped \( \text{Al}_2\text{O}_3 \) nanoparticles. The green and red up-conversion emissions bands centered at about 526, 547, and 668 nm were attributed to the \( ^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}, ^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}, \) and \( ^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2} \) transitions, respectively.

Fig. 4 shows the logarithmic dependence of intensity of the up-conversion emissions at 526, 547, and 668 nm on the pump power for the unannealed and annealed \( \text{Er}^{3+} \) doped \( \text{Al}_2\text{O}_3 \) nanoparticles.
transitions of Er³⁺, respectively. The annealing has no evident effect on the peak positions, but strongly affected the intensity of the green and red up-conversion emissions of the samples. A much stronger intensity of the red relative to green up-conversion emission was observed before annealing. It is worthwhile to point out that the Er³⁺ doped Al₂O₃ nanoparticles with 0.1–1.0 wt.% Er³⁺ doping concentration were prepared, and all samples showed the similar up-conversion emission properties. Compared with other samples, the 0.6 wt.% Er³⁺ doped Al₂O₃ nanoparticles has the strongest up-conversion emissions, indicating that 0.6 wt.% Er³⁺ is a proper doping concentration for Er³⁺ doped Al₂O₃ nanoparticles.

Fig. 4 shows the logarithmic dependence of peak intensity of the up-conversion emissions centered at about 526, 547, and 668 nm on the pump power for the unannealed and annealed Er³⁺ doped Al₂O₃ nanoparticles. The up-conversion emission intensity (I_{up}) depends on the incident pump power (P_{pump}) according to the relation of I_{up} \propto P_{pump}^n, where n = 2, 3, ... is the number of photons required to populate the up-conversion emissions states [14]. The slope in Fig. 4 were approximately equal to 2 for the green and red up-conversion emissions centered at about 526, 547, and 668 nm, indicating that the two-photon process was responsible for the up-conversion emissions of the Er³⁺ doped Al₂O₃ nanoparticles.

Based on the energy matching conditions and quadratic dependence on pump power, as well as the up-conversion emissions spectra, it was proposed that the excited state absorption (ESA) \(^4\text{I}_{13/2}\) + a photon \(\rightarrow \ ^4\text{F}_{9/2}\) is the main process in the unannealed Er³⁺ doped Al₂O₃ nanoparticles. For the annealed nanoparticles, green up-conversion emission became predominant mainly due to an enhancement of the ESA \(^4\text{I}_{11/2}\) + a photon \(\rightarrow \ ^4\text{F}_{7/2}\) and the cooperative up-conversion (CU) \(^4\text{I}_{11/2} + ^4\text{I}_{11/2} \rightarrow ^4\text{F}_{7/2}\) processes. It should be noted here that an intense green up-conversion emission was also observed in the ceramic powders consisting of Er₃Al₅O₁₂ and a smaller amount of α-(Al,Er)₂O₃ phases [9], suggesting that Er₃Al₅O₁₂ phase is more favorable for green up-conversion emission though it has a higher cutoff phonon energy about 700 cm⁻¹. It was found that the nanoparticles shape and dispersion can affect the shape of the emission peaks [15], and the corresponding investigations will be explored in the further work.

4. Conclusions

The Er³⁺ doped Al₂O₃ nanoparticles were prepared by the arc discharge synthesis method. The green and red up-conversion emissions centered at about 526, 547, and 668 nm were detected by a 978 nm LD excitation. The annealing has evident effect on the up-conversion emissions of the samples. A much stronger intensity of the red relative to green up-conversion emission was caused by the ESA \(^4\text{I}_{11/2} + \text{a photon} \rightarrow ^4\text{F}_{9/2}\) process before annealing. After annealing, the green up-conversion emission became predominant mainly due to an enhancement of the ESA \(^4\text{I}_{11/2} + \text{a photon} \rightarrow ^4\text{F}_{7/2}\) and CU \(^4\text{I}_{11/2} + ^4\text{I}_{11/2} \rightarrow ^4\text{F}_{7/2}\) processes. The results proved that arc discharge synthesis is a new promising preparation technology for optical materials.

References