



Al₂O₃:Cr³⁺ microfibers by hydrothermal route: Luminescence properties

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ABSTRACT

Uniform Al₂O₃:Cr³⁺ microfibers were synthesized by using a hydrothermal route and thermal decomposition of a precursor of Cr³⁺ doped ammonium aluminum hydroxide carbonate (denoted as AAHC), and characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), photoluminescence (PL) spectra and decay curves. XRD indicated that Cr³⁺ doped samples calcined at 1473 K were the most of α-Al₂O₃ phase. SEM showed that the length and diameter of these Cr³⁺ doped alumina microfibers were about 3–9 μm and 300 nm, respectively. PL spectra showed that the Al₂O₃:Cr³⁺ microfibers presented a broad R band at 696 nm. It is shown that the 0.07 mol% of doping concentration of Cr³⁺ ions in α-Al₂O₃:Cr³⁺ was optimum. According to Dexter's theory, the critical distance between Cr³⁺ ions for energy transfer was determined to be 38 Å. It is found that the curve followed the single-exponential decay.

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1. Introduction

Recently, much more attention has been paid to explore transition metal (TM) ions doped materials' uses in photonic applications [1–5]. Among the TM ions, Cr³⁺ and Ti³⁺ doped α-Al₂O₃ materials are the most important laser materials, possessing excellent luminescent properties [6–9].

There are various methods of preparing Cr³⁺ doped Al₂O₃. Fahlman et al. have developed a chemical vapor deposition synthetic strategy for preparing chromium-doped alumina “ruby” thin films [10]. Pan et al. have successfully synthesized dense Al₂O₃:Cr³⁺ condensates by laser-ablation route on clamped Al/Cr targets in oxygen [11]. Li et al. described a flame spray pyrolysis method for doped nano-alumina [12]. Cheng et al. reported the preparation of Al₂O₃:Cr³⁺ nanotubes via homogenization precipitation followed by heat treatment [13]. Although many investigations have been carried out to study optical properties of Al₂O₃:Cr³⁺ system, there are a few investigations on the effect of dopant concentration in Al₂O₃:Cr³⁺ materials [14].

In this paper, we report the synthesis of α-Al₂O₃:Cr³⁺ microfibers using a hydrothermal method followed by heat treatment. The luminescence properties are probed in detail and PL spectra indicate that the Al₂O₃:Cr³⁺ microfibers present excellent red emission at 696 nm excited at 400 nm. The optimum

concentration and critical distance of Cr³⁺ ions in the Al₂O₃ have been systematically discussed.

2. Experimental

2.1. Synthesis of Al₂O₃:Cr³⁺ microfibers

All the reagents used are the analytical grade without further purification. In a typical synthesis, 8 g poly-glycol (PEG) (Kermel, 99%) with relative molecular mass $M = 20,000$, was dissolved in deionized water to form a clear solution, to which 7.5 g Al(NO₃)₃·9H₂O, different amounts of Cr(NO₃)₃·9H₂O (0.01, 0.04, 0.07, 0.10 mol%) were added. After the salts were totally dissolved, 20 g urea was added. The mixed solution was further magnetically stirred for 3 h. Then the final mixture was transferred to three Teflon-lined autoclaves of 40-mL capacity and placed in an oven at 393 K for 24 h. After that, the autoclave cooled to the room temperature, the precipitation were collected by washing several times with deionized water and ethanol to remove the impurities, and then dried at 353 K in a vacuum oven for 24 h. The surfactant was removed by calcination in air at 1473 K for 2 h with the heating rate of 2 K/min.

2.2. Characterization

The XRD patterns of the samples were recorded on a high resolution X-ray diffractometer (XRD, D/MAX 2200pc, Japan). Their diffraction patterns were obtained by using Cu Kα radiation of wavelength $\lambda = 0.15418$ nm. The morphology of the powder was

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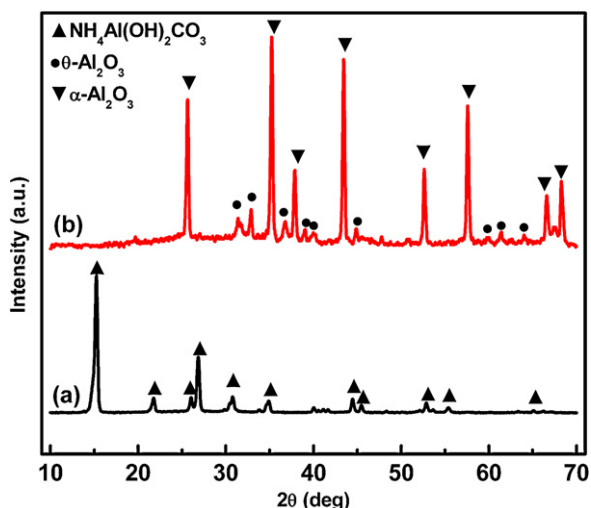


Fig. 1. XRD patterns of the Cr^{3+} doped samples: (a) as-grown from solution and (b) postannealed at 1473 K for 2 h.

recorded by using a field-emission scanning electron microscope (JSM-6700F, JEOL, Japan) operated at 5 kV. The room temperature PL, photoluminescence excitation (PLE) spectra and decay curves of the products were measured by a fluorescence spectrophotometer (Hitachi F-4600) with a 450 W xenon lamp. In all experiments, both excitation and emission slits were 2.5 nm.

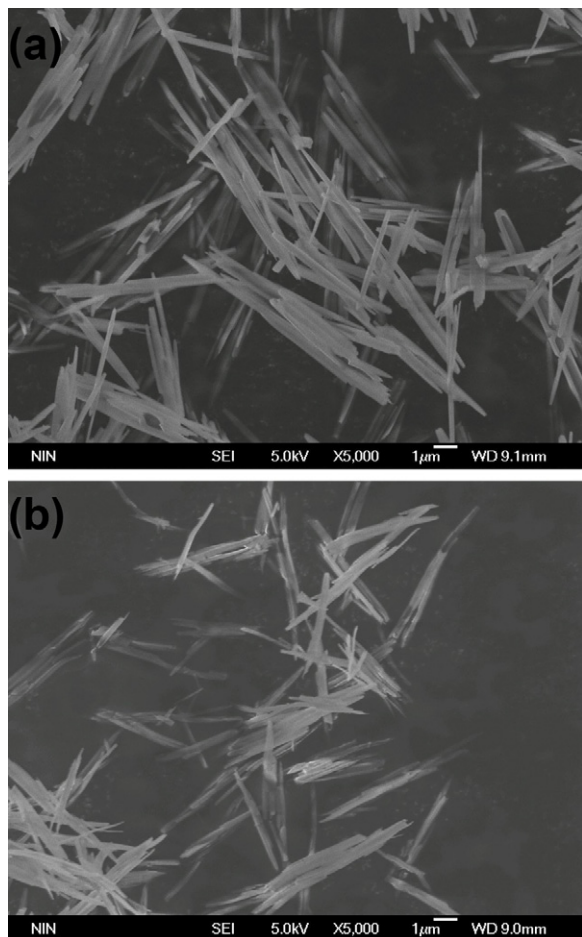


Fig. 2. SEM micrographs for AAHC: Cr^{3+} (0.07 mol%) precursor (a), and Al_2O_3 : Cr^{3+} (0.07 mol%) powder (b) calcined at 1473 K.

3. Results and discussion

3.1. Crystallization behavior and morphology

The loose powders, obtained from aqueous solution, were heated at 1473 K for 2 h in the static air atmosphere. The structural analysis by XRD for the samples, obtained from solution and postannealed at 1473 K, is presented in Fig. 1. As can be seen from Fig. 1, curve a, the clearly distinguishable sharp peaks of the product, prepared by the soft chemical method, are indicative of high crystallinity. All of the diffraction peaks can be neatly indexed to end-centered orthorhombic ammonium aluminum hydroxide carbonate $[\text{NH}_4\text{Al}(\text{OH})_2\text{CO}_3]$ (denoted as AAHC) phase (JCPDS No. 76-1923). No extra diffraction peaks were detected, indicating that no impurity exists in the AAHC: Cr^{3+} precursor. Under the assistance of PEG-20000 surfactant, the well-crystallized AAHC phase was formed during the hydrothermal treatment process. After thermal decomposition of AAHC at 1473 K, Fig. 1, curve b shows the most of $\alpha\text{-Al}_2\text{O}_3$ (JCPDS No. 78-2427) phase, and the $\theta\text{-Al}_2\text{O}_3$ (JCPDS No. 23-1009) phase still existed. Using the Scherrer equation, the calculated crystal size of AAHC, $\alpha\text{-Al}_2\text{O}_3$ microfibers is about 22, 32 nm, respectively. No extra phases are found, because the foreign element, such as carbon and hydrogen from the surfactant, can be oxidized easily at high temperature. Additionally, the concentration of Cr^{3+} is low, furthermore, Cr^{3+} ions can incorporate into Al_2O_3 lattice and might form substituted solid solution.

Fig. 2 shows selected SEM micrographs of the AAHC: Cr^{3+} (0.07 mol%) precursor and the Al_2O_3 : Cr^{3+} (0.07 mol%) powder calcined at 1473 K for 2 h. As it can be seen from the SEM images, the length and diameter of all the samples are about 3–9 μm and 300 nm, respectively. A slight average decrease in diameter is noticeable. The shrinkage of the diameter is attributed to the pyrolysis of the precursor and the increase of the crystallinity. Moreover, from the SEM investigation, we can see that both the morphology and size of the Al_2O_3 : Cr^{3+} microfibers are almost the same as that of the AAHC: Cr^{3+} microfibers, implying that the heat treatment has little influence on the morphology of the final products. Thermal treatment only induces AAHC: Cr^{3+} into Al_2O_3 : Cr^{3+} .

3.2. Luminescence properties of Al_2O_3 : Cr^{3+}

Due to the similarities in PLE and PL spectra of the samples with different Cr^{3+} concentrations, typical spectra of Al_2O_3 with

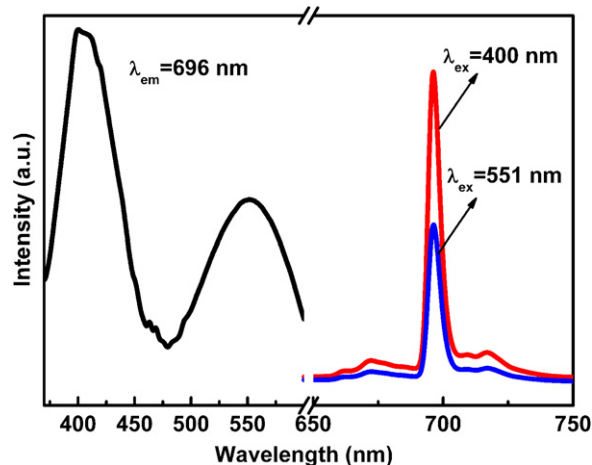


Fig. 3. Room temperature excitation (left) and emission (right) spectra for the Al_2O_3 : Cr^{3+} (0.07 mol%) microfibers calcined at 1473 K, measured with a xenon lamp as a light source.

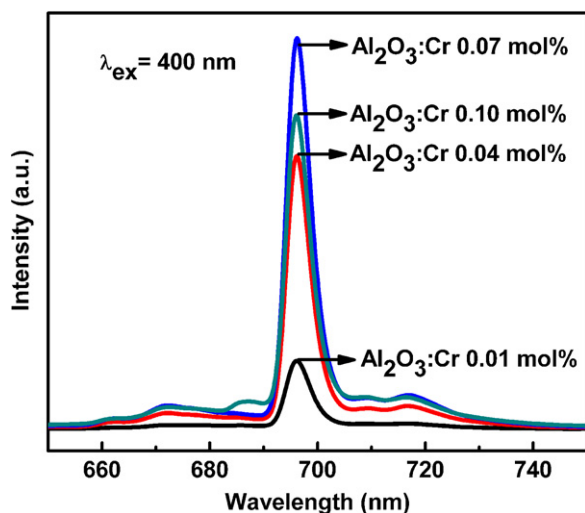


Fig. 4. Emission spectra of $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ synthesized at 1473 K for 2 h with different doping concentrations of Cr^{3+} (0.01, 0.04, 0.07, and 0.10 mol%).

0.07 mol% Cr^{3+} content are shown in Fig. 3. As seen from the PLE spectrum monitored at 696 nm, two strong broad absorption bands are observed. Their peak positions are at around 400 and 551 nm, which are corresponding to spin-allowed $^4\text{A}_2(^4\text{F}) \rightarrow ^4\text{T}_1(^4\text{P})$ and $^4\text{A}_2(^4\text{F}) \rightarrow ^4\text{T}_2(^4\text{F})$ transitions of Cr^{3+} ions on the octahedral sites of $\alpha\text{-Al}_2\text{O}_3$. From the PL spectrum, well-known narrow R lines at 696 nm, ascribed to the $^2\text{E} \rightarrow ^4\text{A}_2$ transition of isolated single Cr^{3+} ions which substitute for Al^{3+} ions on the octahedral sites of the alumina block, are observed. Furthermore, the intensity is excited more with use of the 400 nm ultraviolet light than with use of the 551 nm yellow light.

Fig. 4 shows the PL spectra of $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ synthesized at 1473 K for 2 h with different doping concentrations of Cr^{3+} (0.01, 0.04, 0.07, and 0.10 mol%). Upon excitation at 400 nm, the red emission band at the wavelength 696 nm is from the $^2\text{E} \rightarrow ^4\text{A}_2$ transition. The almost alike bands of PL spectra indicate that the symmetry of emitting centers of Cr^{3+} is the same. It is evident that the emission intensity strongly depends on the doping concentration. At low Cr^{3+} concentrations ($\chi < 0.07$ mol%), the emission intensity is

weak because there are not sufficient luminescence centers. However, under the condition of increasing Cr^{3+} concentration, the emission intensity increases, and reaches the maximal value at 0.07 mol%. When the Cr^{3+} doping ratio is greater than 0.07 mol%, the luminescence intensity starts to reduce as concentration quenching occurs due to the decrease in Cr–Cr distance. Based on Dexter's theory [15], the critical distance between Cr^{3+} ions for energy transfer can be calculated by the following relation:

$$R_c \approx 2 \left[\frac{3V}{4\pi x_c Z} \right]^{1/3} \quad (1)$$

where V is the volume of the unit cell, x_c the critical concentration of the doping ions and Z the number of host cation in the unit cell. For $\alpha\text{-Al}_2\text{O}_3$, $V = 254.7 \text{ \AA}^3$, $Z = 12$ and the critical concentration of Cr^{3+} in the Al_2O_3 host is 0.0007. Therefore, the R_c of Cr^{3+} ions is determined to be 38 Å.

PL decay curves of $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ with different concentrations of Cr^{3+} (0.01, 0.04, 0.07, and 0.10 mol%), shown in Fig. 5, were used to calculate the lifetime and investigate the luminescence dynamics of the samples. The samples are excited at 400 nm and monitored at 696 nm, and the curves are obtained with an F-4600 fluorescence spectrophotometer (Hitachi Corp., Tokyo, Japan) under Time Scan mode, and the lifetime values are calculated by the software of the spectrophotometer (FL Solutions for F-4600). It is found that the curves followed the single-exponential decay

$$I_t = I_0 \exp\left(-\frac{t}{\tau}\right) \quad (2)$$

where I_t is the intensity at time t , I_0 is the intensity at $t = 0$, and τ is the decay lifetime. The fitted fluorescence lifetime values of $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ are 5.34, 5.39, 5.30, and 5.26 ms corresponding to the Cr^{3+} concentration 0.01, 0.04, 0.07, and 0.10 mol%, respectively.

4. Conclusions

AAHC: Cr^{3+} microfibers were prepared via a hydrothermal method and then were calcined to produce $\alpha\text{-Al}_2\text{O}_3:\text{Cr}^{3+}$ microfibers. The average diameter of $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ microfibers was about 300 nm, and the length was around 3–9 μm. As seen from the PLE spectrum monitored at 696 nm, two strong broad absorption bands are observed. Their peak positions are at around 400 and 551 nm, which are corresponding to spin-allowed $^4\text{A}_2(^4\text{F}) \rightarrow ^4\text{T}_1(^4\text{P})$ and $^4\text{A}_2(^4\text{F}) \rightarrow ^4\text{T}_2(^4\text{F})$ transitions of Cr^{3+} ions. From the PL spectrum, well-known narrow R lines at 696 nm, ascribed to the $^2\text{E} \rightarrow ^4\text{A}_2$ transition of isolated single Cr^{3+} ions, were observed. From the luminescence study the optimum concentration of luminescence was found to be 0.07 mol%. The critical energy transfer distance of Cr^{3+} in Al_2O_3 host is calculated to be 38 Å. In conclusion, we consider that the luminescence properties of Cr^{3+} ions are strongly dependent on concentration of the microfibers. These studies also indicate that hydrothermal method is a facile route for the synthesis of luminescent nanomaterials.

Acknowledgments

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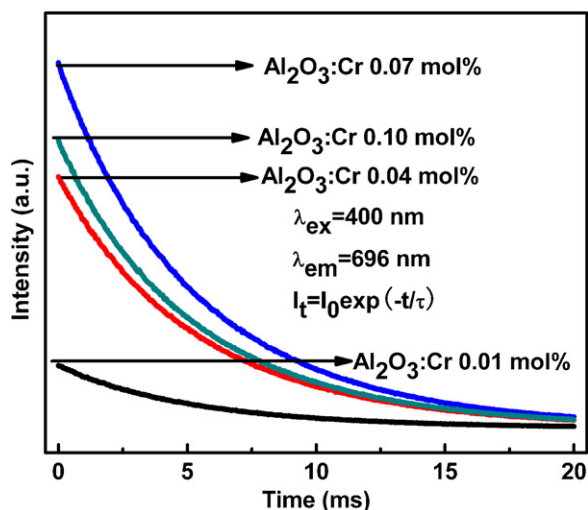


Fig. 5. The decay curves of $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ microfibers synthesized at 1473 K for 2 h with different concentrations of Cr^{3+} (0.01, 0.04, 0.07, and 0.10 mol%).

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