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Original Paper

Preparation and luminescent properties of Cr^{3+}:Al_2O_3 nano-powders by low-temperature combustion synthesis

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ABSTRACT

Cr^{3+}:Al_2O_3 nano-powders were prepared through low-temperature combustion synthesis (LCS) method by using glucose as a dispersion agent for the first time. The Cr^{3+}:Al_2O_3 nano-powders samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and luminescence spectrometer. XRD results showed that pure α-Al_2O_3 phase was obtained for the sample fired at 1100 °C for 0.5 h. TEM results indicated that nano-powders were well dispersed. Luminescence spectrum analysis results indicated that the excitation spectrum of Cr^{3+}:Al_2O_3 nano-powders consisted of two bands peaking at 462 nm and 579 nm, respectively, and the emission spectrum consisted of two bands peaking at 692 nm and 668 nm, respectively.

1. Introduction

Transparent laser ceramic material has been paid much attention in the recent years for its excellent characteristics compared with laser crystals, such as shorter preparation period, high lasing ions doping concentration, high conversion efficiency and ease of fabrication of large dimension bulk materials. The emphasis has been mainly focused on Nd:YAG and Nd:Y_2O_3 ceramics, and laser output has been obtained [1–3]. Ruby (Cr^{3+}:Al_2O_3) crystal was the earliest laser material and has found many applications. However, research on Cr^{3+}:Al_2O_3 transparent laser ceramic is still limited up to now. Murotani [4] and Yang [5] reported the spectrum properties of the Cr^{3+}:Al_2O_3 ceramics. This work carries out the research work on the preparation of Cr^{3+}:Al_2O_3 nano-powders. Well-dispersed nano-powders with fine and even size are very important for the fabrication of transparent ceramics so that the pores in the microstructure of the ceramics can be eliminated easily and dense transparent body can be obtained. At present, several methods to prepare nano-powders for transparent ceramics have been studied, such as sol–gel method [6,7], co-precipitation method [8], and low-temperature combustion method (LCS) [9,10]. The low-temperature combustion synthesis method has been proved to be an effective method in the fabrication of multi-component nano-powders, such as Al_2O_3 and $SrTiO_3$ [9,10] with the features of simple route and ease of size control. However, the agglomeration of the nano-powders is still a problem encountered to ceramic fabrication. In order to alleviate the agglomeration of the nano-powders Cr^{3+}:Al_2O_3, nano-powders were prepared by the low-temperature combustion synthesis method with glucose as the dispersive agent for the first time in this paper. Influences of various synthesis conditions on the properties of the samples were systematically studied. Well-dispersed Cr^{3+}:Al_2O_3 nano-powders were fabricated and the luminescence properties of the samples were analyzed.

2. Experimental

2.1. Sample preparation

$Al(NO_3)_3 \cdot 9H_2O$(A.R), $Cr(NO_3)_3 \cdot 9H_2O$(A.R), urea(A.R), and glucose(A.R) were used as the starting materials. The amount of urea was according to the following chemical reaction formula and equaled to that of tri-valence metal ions

$$2M(NO_3)_3 \cdot 9H_2O + 5CO(NH_2)_2 \rightarrow M_2O_3 + 28H_2O\uparrow + 8N_2\uparrow + 5CO_2\uparrow \quad (M = Al^{3+}, Cr^{3+})$$

The amount of glucose was 20 wt% of the starting materials. $Cr(NO_3)_3 \cdot 9H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, urea and glucose were mixed together. The dosages of each reagent were 0.16 g, 14.49 g, 5.84 g and 0.2 g, respectively. The starting materials were thoroughly milled until a cream-like paste was formed and then the cream-like paste was fired at 600 °C, and brown powders were obtained. The

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brown powders were finally fired by using the SX_2-6-13 muffle furnace at 700 °C, 800 °C, 900 °C, 1000 °C, 1100 °C and 1200 °C, respectively, and the Cr^{3+}:Al_2O_3 nano-powders with light pink color were obtained.

2.2. Characterization

XRD pattern measurement was performed using a D/max-IIB Rotating Anode X-ray diffractometer with Cu Kα radiation (voltage = 40 KV, current = 20 mA, scanning speed = 4/min, step length = 0.02). A Hitachi F-4500 fluorescence spectrometer was used to measure the excitation and emission spectra of the products (power: 150 W Xenon lamp). A JEM-2010 transmission electron microscope was employed to examine the morphologies of the nano-powders. The particle size and particle size distribution analyses were carried out by ZETASIZER 3000HSA laser particle size analyzer. The element quantity analysis was tested by using OXFORD INCA X–Sight energy dispersive X-ray spectrometer allocated to the Hitachi S-520 scanning electronic microscope. All measurements were carried out at room temperature.

3. Results and discussion

3.1. XRD analysis of the samples

3.1.1. Influences of temperatures on phase composition

Fig. 1 shows the XRD patterns of the samples fired at 600 °C, 700 °C, 800 °C, 900 °C, 1000 °C, 1100 °C and 1200 °C for 0.5 h, respectively. The sample fired at 600 °C and 700 °C were black in color and showed amorphous structure without crystal phase. γ-Al_2O_3 phase was partially formed for the sample fired at 800 °C and the color of the products changed to brown indicating that amorphous C was gradually decreased. α-Al_2O_3 phase was observed for the sample fired above 1000 °C but there was still γ-Al_2O_3 phase existing. Pure α-Al_2O_3 phase with light pink in color (PDF Card No. 74-0323) was obtained for the sample fired at 1100 °C and 1200 °C. The particle sizes of the samples fired at 1100 °C were calculated according to Scherrer formula

$$d = \frac{K\lambda}{B\cos\theta}$$

where d is the particle size, λ is the wavelength of the X-ray, $\lambda = 0.154184$ nm, θ is Bragg angle, B is half height width of diffraction peak, $k = 0.89$. The crystallite diameters were calculated on each diffraction peak for the sample fired at 1100 °C and the average crystallite diameter was about 29 nm. No peak attributed to Cr^{3+} was found because of its small amount.

3.1.2. Influences of calcining time on phase composition

Fig. 2 shows the XRD patterns of the samples calcined at 1000 °C for different times. The patterns indicate that α-Al_2O_3 can be obtained at 1000 °C for 1 h.

3.2. Influence of glucose on dispersive property of the sample

Fig. 3 shows TEM images and the selected area electron diffraction patterns of Cr^{3+}:Al_2O_3 nano-powders fired at 1100 °C for 0.5 h.

Fig. 3a shows the TEM image of the sample without using glucose. From the image, we can see that the powders were heavily agglomerated together. The electron diffraction pattern showed a series of diffraction rings indicating polycrystal structure. Fig. 3b–d shows the TEM image of the sample with using glucose as dispersive agent. It can be found that the spherical particles are well dispersed with an average size of 20–35 nm, which was agreed with the results of XRD calculation. This result confirmed that the dispersive property of the samples was greatly enhanced by adding glucose as a dispersive agent. From electron diffraction image in Fig. 3b, both alternatively bright and dark rings and diffraction spots were observed. The alternatively bright and dark diffraction rings were originated from the long range ordered structure of the grain crystals. The temperature around the grains was increased due to glucose combustion, which caused the increase in the crystallization degree of the inner grain and produced the alternatively bright and dark diffraction rings. The diffraction spots were formed due to the overlapping of diffraction patterns from various tiny crystals with different orientations. The diffraction rings from inner to outer were attributed from different crys-

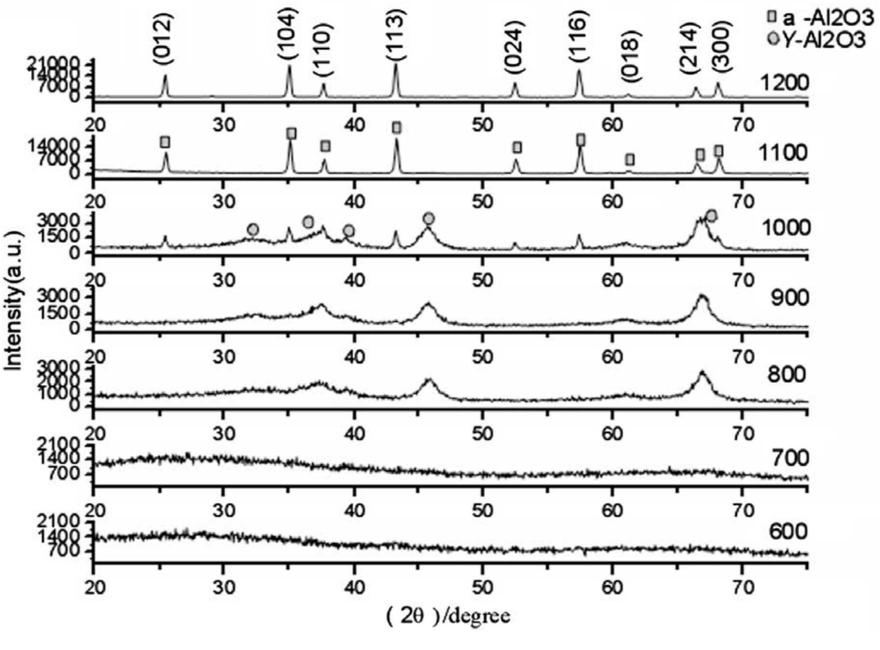

Fig. 1. XRD patterns of nano-powders synthesized at different.