Effects of Cr3+ concentration on the crystallinity and optical properties of Cr-doped Al2O3 powders by solid-state reaction method

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Abstract. The Al2O3 crystal contains a little of amount of Cr3+, which name is ruby, is applied to ruby laser. In our research, Al2O3: Cr3+ powder material is prepared via solid state reaction. Effects of different Cr3+ concentration on the crystallinity and optical properties of the material were investigated. The experimental results indicate that the material shows good crystallinity at 1200°C. The α crystal of Al2O3: Cr3+ powder is improved its optical properties. Moreover, the optical of Al2O3: Cr3+ increases by the Cr3+ concentration’s increasing until 0.3 wt%. Then, the optical of Al2O3: Cr3+ decreases by the Cr3+ concentration’s increasing until 0.3 wt%. So the 0.3 wt% of Cr3+ is the best results. This kind of luminescence material has a very obvious emission peak under the incident light of 694nm.

1. Introduction
The pure aluminum oxide crystal is colorless [1]. The luminescence of Al2O3 is mainly divided into the self defect luminescence of the material and the doping of different ions, such as chromium, iron, titanium or vanadium, in the Al2O3 matrix [2] [3]. At present, the research on the luminescent properties of Al2O3 materials are concentrated in two aspects: first, the Al2O3 material photoluminescence spectrum (PL spectrum) mechanism research, in order to adjust the preparation process parameters for high quality, high purity, high brightness, violet blue emission; the two is the study of doped ion luminescence effects on the properties of Al2O3 materials. [4][5]

Al2O3 has a variety of homogeneous crystals. There have been dozens of reports of α-Al2O3, β-Al2O3, γ-Al2O3 and so on. After annealing over 1200°C, the Al2O3 of different structures will eventually turn to α-Al2O3. α-Al2O3 belongs to the hexagonal crystal system [6]. It has many excellent properties, such as high melting point, high mechanical strength, good thermal stability, high thermal conductivity and corrosion resistance [7]. It is widely used in many industrial and medical fields, such as powder ceramics, optical devices, electronic engineering materials and so on. As a laser medium, Al2O3: Cr3+ is the first laser material to be used [8]. It has become the foundation of modern laser technology, and is still one of the main materials of solid state lasers for manufacturing high-power lasers. The luminescence wavelength is 694nm, which is a emission peak caused by the transition from the 2A level to the 4A2 level of the Cr3+ ions doped in the α-Al2O3 crystal. However, the Al2O3 single crystal has the disadvantages of high melting point, low doping concentration and uneven doping and so on, which limits its application in production [9] [10].

In 1962, L.Coble made α-Al2O3 transparent ceramics for the first time [11]. The research on the manufacturing technology and application of transparent ceramics has developed rapidly. As a laser
medium, the transparent ceramics can not only replace the single crystal, but also produce some single crystal characteristics. It has a low sintering temperature, a high knowing rate, and can achieve a large concentration of doping and other points.

In this article, we used high energy ball milling and annealing to prepare $\alpha$-Al$_2$O$_3$: Cr$^{3+}$ powder. Compared with the traditional solid phase sintering and sol-gel method, the high energy ball milling method has high efficiency and can accurately control the doping content. The samples of $\alpha$-Al$_2$O$_3$: Cr$^{3+}$ powder with mass fraction of 0.1 wt%, 0.3 wt%, 0.3 wt%, 0.3 wt% and 0.3 wt% were prepared respectively, and their luminescence properties were studied.

2. Experiment

2.1. The preparation of Al$_2$O$_3$: Cr$^{3+}$

The chromium-doped alumina fluorescent material was prepared by the mechanical ball grinding and sintering of the planetary ball mill. First, the initial mixture solution employed in this study were Cr$_2$O$_3$ (99.95%, Arkema,), Al$_2$O$_3$ (99.99%, Arkema,) at a Cr/Al mass ratio of 0.001/1, 0.003/1, 0.005/1, 0.007/1, 0.009/1, and mixed in ball mill jar with absolute ethanol(99.9%, Arkema), and followed by grounding in a planetary ball mill (QM-3SP2) for 6 hours to obtain the powder. Second, the mixture prepared after ball milling was dried in a water bath at 80°C. Third, the obtained sample was sintered in a thermostat box resistance furnace (SX-G13135, China) at 1200°C for 10h. And finally, to obtain the chromium-drop alumina fluorescent material, the sintered sample was cool slowly to room temperature.

2.2 X-ray diffraction patterns

X-ray diffraction patterns of the chromium-doped alumina fluorescent material were obtained using an X-ray diffractometer (Rigaku Ultima IV, Japan) with CuKa radiation. The X-ray diffraction data was collected in a 0.02° step width over the 2θ range of 20° to 80°.

2.3 Scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX)

Scanning electron microscope (SEM) images and energy-dispersive X-ray spectroscopy (EDX) of the chromium-doped alumina fluorescent material were obtained using a scanning electron microscope (Nava Nano SEM450, America) to characterize the surface morphology of the powder and the element composition and proportion of the chromium-doped alumina fluorescent material.

2.4 Ultraviolet–visible spectroscopy (UV-Vis)

The absorption spectrum and emission spectrum of the chromium-doped alumina fluorescent material were measured using a spectrophotometer (Cary 5000 UV-Vis-NIR, Agilent).

3. Analysis and discussion

Al$_2$O$_3$: Cr$^{3+}$ powders with different doping concentration were cooled naturally at 1200 °C for 10 hours under air conditions, and $\alpha$- Al$_2$O$_3$: Cr$^{3+}$ was obtained. The doping concentration is 0.1 wt%, 0.3 wt%, 0.7 wt% and 0.9 wt%. As shown in Figure 1, the diffraction peaks of other substances are not found in the doped samples, and there are $\beta$ phase in some samples. The results show that the in situ substitution of the Cr$^{3+}$ ions and the Al$^{3+}$ ions in the Al$_2$O$_3$ powder has not resulted in the destruction of the original crystal structure of the Al$_2$O$_3$. When the amount of doping is 0.9 wt%, the lower intensity of the $\gamma$ phase diffraction peak is found in the sample except the main phase of the $\alpha$- Al$_2$O$_3$. 
Figure 1 X-ray diffraction patterns of Al₂O₃:Cr³⁺ in different Cr³⁺ concentration

Comparison of X-ray diffraction (XRD) peak position in (113) and (116) diffraction peaks as an example, with the increase of Cr³⁺ doped, the sample diffraction peaks gradually to the high angle offset, in the 0.5 wt% doped reaches the maximum at saturation, formation, continue to increase the doping concentration of diffraction peak angle without big offset.

As shown in the scanning electron microscope (SEM) image of Figure 2, the size distribution of Al₂O₃: Cr³⁺ powders particles are concentrated and distributed evenly.

Figure 2 Photographs of Al₂O₃ powders with Cr³⁺ concentration of (a)0.1 wt%, (b) 0.3 wt%, (c) 0.5 wt%, (d) 0.7 wt%, and (e) 0.9 wt%, respectively.

As shown in Figure 3, the grain size of the Al₂O₃:Cr³⁺ powder is 100-200nm. Compared with the Al₂O₃ powder, the lattice constant of the doped sample increases. When the doping concentration of Cr³⁺ is 0.3wt%, the lattice constant reaches the maximum. With the increase of the amount of doping, the lattice constant of the sample decreases. This shows that with the further increase of the doping content, the Cr³⁺ ion in the sample can not be completely replaced by the Al³⁺ ion in the Al₂O₃ powders.
Agilent Cary 5000 UV-Vis-NIR fluorescence spectrometer uses 579 nm light as excitation light source, detection of the emission spectra of samples. As shown in Figure 4. After annealing at 0.1 wt% doped sample, strong luminescence peaks appear at 469-492 nm, but only 0.3 wt% doped with strong luminescence peaks near 694 nm. Oxygen vacancies exist inside Al₂O₃, and oxygen vacancies can form the heart of F⁺ and F after capturing 1 or 2 electrons. The F⁺ heart and F heart provide transition energy levels for the transition between the O²⁻ ions and the central ions in the eight - hedron and the defective eight - hedron. Thus, Al₂O₃ appears to be fluorescence in the vicinity of 470 nm. The 3 continuous luminescence peaks of the sample at 469-492 nm should be taken as the oxygen vacancies in the sample to capture the fluorescence produced by an electron to form a F⁺ heart. The luminescence strength of 0.3 wt%-0.9 wt% doped samples is found to be increased with the increase of doping amount, and the maximum value is reached at the concentration of 0.9 wt%. When the doping concentration is increased, the fluorescence intensity will decrease. It is indicated that the doping of low concentration Cr³⁺ ion promotes the formation of F⁺ heart in Al₂O₃, while excessive Cr³⁺ ions can inhibit the formation of F⁺ heart in Al₂O₃.

Chromium as a transition element, the outer layer of electronic distribution is 3d⁵4s¹, lost two 3d electrons and one 4s electrons to form the 3d⁴ structure of the Cr³⁺. Electrons of Cr³⁺ transition from ground state ⁴A₂ to ⁴F₁, ⁴F₂, and rapidly without radiation to ⁴E level under the excitation of light. When the electrons transition from the 2A level to the E level to ⁴A₂ level, the light of 694.3 nm and 692.9 nm is sent out respectively. After annealing at 1200 °C, samples at 469-492 nm and 694 nm showed different intensity of fluorescence peaks as shown by the excitation wavelength of 579 nm. In Figure 5, Al₂O₃ has the highest luminescence intensity at 469 nm, 482 nm, and 492 nm. With the
increase of the amount of Cr\textsuperscript{3+}, the luminescence intensity of the sample at this band has been weakened to varying degrees. It is indicated that under this experimental condition, Cr\textsuperscript{3+} ions can inhibit the production of oxygen vacancy in the sample.

| Table 1. temperature | Element | Ratio(%) |
|----------------------|---------|----------|
|                      | O       | 48.5     |
|                      | Al      | 0.15     |
|                      | Cr      | 51.35    |

The luminescence intensity of each sample near 694nm is shown in Figure 4. The maximum luminescence intensity of Cr\textsuperscript{3+} Al\textsubscript{2}O\textsubscript{3} powder prepared by ball milling in the 694 nm wavelength range is 0.3wt\%, which is the best doping concentration in this experiment. The analysis of the EDX components of the 0.3wt\% sample is shown in Table 1. With the increase of doping concentration, the luminescence intensity gradually weakened. According to the results of XRD, we found that when the doping concentration is greater than 0.3wt\%, the Cr\textsuperscript{3+} ion in the sample can not effectively replace the Al\textsuperscript{3+} ion in the Al\textsubscript{2}O\textsubscript{3}, forming an effective luminescent center. On the contrary, due to the increase of the amount of doping, the Cr\textsuperscript{3+} distance in the Al\textsubscript{2}O\textsubscript{3} lattice is too close, and the coupling of the lotus root occurs.

4. Conclusion
In this study, high purity Al\textsubscript{2}O\textsubscript{3}: Cr\textsuperscript{3+} powders were prepared by high energy ball milling and annealing. The crystal structure analysis shows that after annealing at 1200 °C, the structure of the sample is α-Al\textsubscript{2}O\textsubscript{3}: Cr\textsuperscript{3+}. When the Cr\textsuperscript{3+} doping concentration is lower and higher, the sample appears lower intensity of γ phase. Via using the 579nm wavelength light source, the sample has the defect luminescence caused by the Al\textsubscript{2}O\textsubscript{3} in the 469-492 nm wavelength, and the luminescence intensity is the strongest when the doping concentration is low. At the 694 nm, the strongest fluorescence peak was found in the sample with a concentration of 0.3 wt\%. The fluorescence peak is caused by the transition from the 2A level to the 4A\textsubscript{2} level in the Cr\textsuperscript{3+} ion. It is found that 0.3 wt\% is the best doping concentration. When the doping concentration is 0.1 wt\%, Cr\textsuperscript{3+} can not fully replace Al\textsuperscript{3+} ions in Al\textsubscript{2}O\textsubscript{3}, and the luminescence is mainly caused by the defect luminescence of alumina. When the doping concentration is 0.5 wt\%, 0.7 wt\% and 0.9 wt\%, Cr\textsuperscript{3+} fails to enter the crystal structure completely. From the crystal structure analysis and fluorescence spectrum analysis, we can see that too many Cr\textsuperscript{3+} appear coupling, resulting in the concentration quenching phenomenon, and weaken the 694 excited luminescence caused by the transition from 2A level to 4A\textsubscript{2} level transition. Further, we will use high throughput experiments to screen for more accurate and optimal material formulations.

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