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Characteristics of large-sized ruby crystal grown by temperature gradient technique

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Abstract

Large ruby with the size of ∅75 × 45 mm was grown by temperature gradient technique for the first time. Absorption spectrum was carried out in the range of 190–800 nm by spectrophotometer, and the concentration spatial distribution of Cr^{3+} in ruby was calculated from the absorption coefficient that based on the Beer–Lambert's Law. Cr^{3+} ions gradually increase along both the growth axis and the radial direction. The shape and ingredient of the inclusions were measured by means of Leitz wide field microscopy and scanning electron microscopy. Laue photos and X-ray omega scan show the good quality of as grown ruby. The optimized growth conditions were pointed out based on the observation.

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1. Introduction

Ruby is a very important crystal not only for its applications in optics, but also for its nobleness in gemstones. It can act as a laser medium and make visible-light laser, which possesses many good properties such as narrow linewidth, long fluorescent lifetime, large quantum efficiency and very wide absorption band. Besides, the host crystal corundum makes its physical–chemical properties excellent. As a kind of gemstone, it has charming color that people are very fond of it. Thus, many techniques have been undertaken to artificially create ruby, such as flame fusion method [1,2], seeded solution growth and Czochralski method [3], floating zone method [4] and hydrothermal method [5]. In flame fusion method, the ruby "boule" usually splits to prevent cracking while cooling down, and they are often of undependable optical quality. In seeded solution growth, Czochralski and floating zone methods, the process is costly and takes considerable time to produce ruby large enough to cut crystals with good quality and the gas bubbles are inclined to be induced in ruby [4]. The hydrothermal methods cannot obtain large sized ruby. Previously our group have grown large sized Ti:Al_2O_3 [6], sapphire [7,8] and other crystals [9–12] successfully by temperature gradient technique (TGT). Currently, we have successfully grown large ruby with the size of ∅75 × 45 mm and with good quality. The regularity of Cr^{3+} distribution and the inclusions in the crystals have been investigated.

2. Experimental

2.1. Growth of ruby by TGT

The TGT method is a simple directional solidification technique that adapts for growing high temperature

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crystals. The setup with the proper thermal field for growing ruby is similar to that described elsewhere [7]. The stable thermal field with proper temperature is achieved by cylindrical graphite heating elements, the Mo crucible, the Mo shields in the furnace and the cooling water system. The typical dimensions of the tapered molybdenum crucible used here are OD = 80 mm, ID = 76 mm and cylindrical part height of 70 mm. The oxide powders of Al_2O_3 and Cr_2O_3 were ignited for several hours at 1300 °C to remove moisture, then the powders were mixed (Cr_2O_3) and pressed to the form of block with diameter closed to the inner diameter of the Mo crucible. The block was then sintered at ~1400 °C for 48 h in air and loaded into the crucible with the cylindrical [0001]-orientation $Cr{:}Al_2O_3$ (Cr_2O_3 = 0.05 wt%) seed in the bottom. Then the furnace was vacuumized to 10^{-5} Torr. After the materials totally melted and keeping the molten mixture for several hours, the crystallization of ruby was started and driven by slow cooling (~0.5–1 °C) with high precision temperature controller. The whole crystallization process was completed automatically. When the crystallization was complete, the crystal was then annealed in situ and cooled down to room temperature at the desired cooling rate (30–50 °C/h). The sanguine-colored ruby crystal boule with the diameter of 75 mm and the cylindrical part's height of 45 mm removed from the Mo crucible is shown in Fig. 1(a).

2.2. The absorption spectrum and distribution of Cr^{3+} in TGT-ruby

Several pieces of slabs were cut from as grown crystals that parallel to or perpendicular to the [0001] direction, then they were finely polished for observation. Absorption measurements were taken by V-570 UV/VIS/NIR spectrophotometer at RT on the slab with a spectral resolution of 0.5 nm in the 190–800 nm spectral region. From the absorption coefficient of the different part of the slab, which was cut from the center of as ruby that parallel to the [0001] direction, the concentration spatial distribution of Cr^{3+} in ruby was calculated based on the Beer–Lambert law.

2.3. Observation of macroscopic growth defects in TGT-ruby

Considering the symmetrical characteristic we observe different regions of the slab that cut from the center of as ruby that parallel to the [0001] direction (Fig. 1(b)) to find the regularity of the inclusion distribution. The shape of the inclusions was observed too, and the photos were selected and recorded on the PC via a CCD camera coupled with Leitz wide field microscopy, then analysis of the impurity elements was performed by energy dispersive X-ray (EDX) in JSM-6360LA scanning electron microscopy (SEM).

2.4. X-ray diffraction analysis

The crystallographic orientation was determined by using a homemade back-reflection Laue X-ray camera. An X-ray diffraction omega scan to the (0001) slab was taken by Philips X'pert MRD diffractometer.

3. Results and discussion

3.1. Absorption spectrum and spatial distribution of Cr^{3+} in TGT ruby

The absorption spectrums parallel to the [0001] direction is shown in Fig. 2. It shows the typical absorption peaks of Cr^{3+} in ruby near 410 nm and 550 nm. They are corresponding to the energy transition $^4A_2 \rightarrow {}^4F_1$ and $^4A_2 \rightarrow {}^4F_2$ of Cr^{3+}. The sharp and weak absorption peak R_1 and R_2 near 694 nm were detected too. Intense main absorption peak in the ultraviolet region at 206 nm and two small humps can be seen at the slightly low energy of 225 nm and 255 nm. They are related to the F-center in as grown crystal which is due to the oxygen vacancies during the growth process. This phenomenon is similar to Al_2O_3 single crystals that was described elsewhere [8,13], The formation of oxygen vacancies is caused by the reductive condition. The absorption spectrum indicate that there is no Cr^{2+}, that is because the fine vacuum impede the C transformed into CO during the growth process, and the solid–liquid

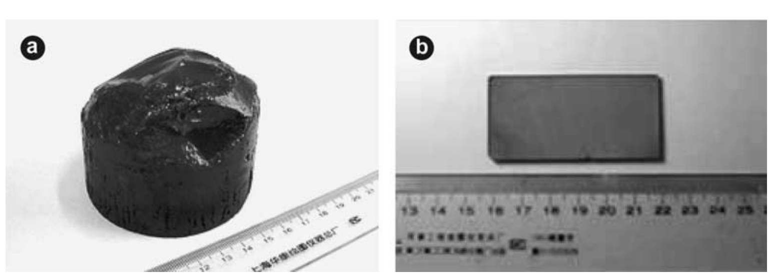

Fig. 1. Large ruby crystal grown by TGT. (a) 1075 g (∅75 × 45 mm) ruby as removed from TGT Crucible. (b) Slab cut from the crystal parallel to the [0001] direction.