



Luminescence and coloration of undoped and Ti-doped sapphire crystals grown by Czochralski technique

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ARTICLE INFO

Article history:

Received 14 November 2014

Received in revised form

14 January 2015

Accepted 1 February 2015

Keywords:

Sapphire

Crystal

Titanium

Color center

Luminescence

ABSTRACT

Undoped and Ti-doped sapphires crystals were grown under stationary stable regime. The effect of growth parameters on the formation of color center is evaluated by absorption and luminescence measurements. The grown crystals with pulling rate less than 5 mm/h presents less F^+ center, therefore demonstrates a better crystal quality.

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1. Introduction

Sapphire crystals have tremendous physical properties, hardness, optical transmission, thermal and chemical resistance, lattice parameter, biocompatibility. It is used for numerous applications: wafer for micro-electronics or LED, windows, watch and cellular phone glasses, optic fibers and wave guides for surgery. It is nowadays the most strategic crystal for a ultra-fast laser technology [1,2]. In particular, Ti-sapphire has allowed the production of the shortest pulses ever produced from a laser oscillator and it is currently developed as amplifier for several petawatt level laser systems [3–5]. Pure sapphire is clear and colorless. Defects such bubbles can strongly affect the optical performances and crystal coloration [6–9]. Depending on the purity and the dopant type, sapphire has a variety of colors. The red color of ruby comes from Cr^{3+} in corundum, which gives rise to electronic transitions that absorb visible light. The impurities can be the direct reason of color, or they can chemically interact together to cause color or to modify the contrast (saturation) of color. So, the sapphire color is considered as one of the important criteria which is a key factor in the beauty and jewelry. In contrary, the presences of color centers are to avoid in crystal for laser application. Unfortunately, it is difficult to grow sapphire crystal with the wanted color. The starting charges, dopants concentration, atmosphere and the growth technology are of great importance to obtain the wanted color with the best optical performances. We present the growth of undoped and Ti-doped

sapphire by a Czochralski (Cz) technique. We describe the crystal growth process to obtain homogeneous and uniform crystals. The presence of color center in undoped sapphire is presented and discussed as a function of the grown parameters. During the growth of Ti-doped sapphire, Ti^{3+} and Ti^{4+} with intrinsic absorption around 532 nm and 253 nm corresponding to pink color in the visible region were observed. This pink color can be colorless if Ti^{3+} is converted to Ti^{4+} under specific annealing treatment.

2. Experimental

2.1. Sapphire crystal growth by Czochralski technique

The starting raw materials were alumina and high purity TiO_2 (rutile) powders. Alumina ($Al_2O_3-\alpha$) is produced by RSA Le Rubis [10] company in good agreement with JSPDS file no. 46-1212 of at least 99.99% purity. Sometimes sapphire and Ti-sapphire crackle were also used as starting charge for crystal growth. Czochralski (Cz) crystal growth technique was used to grow the crystals [7]. A 60 mm-diameter iridium crucible was inductively heated and automatic controlled diameter based on the time derivative of the crystal weight is used for all the growth process. In addition, to control melt decomposition and material evaporating from the charge, the weight of the crucible including charge were followed during all the experimental procedure. To avoid oxidation or other damages of crucible and crystallization, high vacuum was carried out and appropriate pressure of argon (1 bar) is used during the whole growth process. Typical sapphire and Ti-sapphire crystals weighted 250–400 g and were

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approximately 28–35 mm in diameter and 90–110 mm-long (Fig. 1). The other growth parameters were shown in Table 1.

2.2. Characterizations

The absorption spectrum of the samples was measured by a Perkin-Elmer UV-vis-NIR spectrometer operating between 200 and 3200 nm, with a slit of 2 nm resolutions.

The measurements were performed using an EQ-99 broadband Laser-Driven Light Source (LDLS) from Energetic coupled with a Jobin Yvon Gemini 180 monochromator as excitation source. The luminescence is collected with a UV fiber to a Jobin Yvon Triax 320 monochromator and detected by a Jobin Yvon 3000 V CCD camera. This setup allows obtaining excitation emission amplitude map of the sample luminescence.

3. Results

3.1. Absorption spectra on sapphires

The sapphire crystals grown by the Cz method were cut into wafers perpendicular to growth direction (a axis), and optically polished. The thickness of the samples is 2 mm, Fig. 2 shows the



Fig. 1. (a) Undoped sapphire and (b) Ti (0.17at%)-doped sapphire.

Table 1
Cz technique growth parameters of sapphire crystals.

Number of sample	Orientation	Pulling rate (mm/h)	Rotation rate (rpm)
Sample 1	A[11 $\bar{2}$ 0]	3	8
Sample 2	A[11 $\bar{2}$ 0]	5	8
Sample 3	A[11 $\bar{2}$ 0]	3	10
Sample 4	A[11 $\bar{2}$ 0]	2.5	16
Sample 5*	R[10 $\bar{1}$ 2]	1.5	8
Sample 6*	A[11 $\bar{2}$ 0]	2.5	8

* The sample 5 and sample 6 are doped with 0.10 and 0.17 atom% of Ti³⁺ respectively.

absorption spectra realized on the samples. In Fig. 2a, the absorption spectra are few modified with the increase of the rotation rate. Only with a rotation rate of 16 rpm, a slight increase of the absorption around 200 nm appears which may be attributed to F centers [11,12]. In Fig. 2b, the absorption spectrum of the sample 2 growing with high pulling rate presents two absorptions bands around 255 nm and 310 nm. These two absorption bands are attributed to F⁺ centers [11,12]. Fig. 3 shows the absorption spectra of Ti doped sapphire crystals. The spectra present two overlapping broad bands peaking around 490 and 525 nm, which correspond to two phonon side bands of the same Ti³⁺ optical transition from level ²T₂ to level ²E but split into two sublevels according to the Jahn–Teller effect [13].

3.2. Photoluminescence spectra on sapphire

In Fig. 4 the excitation–emission amplitude maps in the excitation range 190–300 nm of sample 1 and sample 2 are reported. In Fig. 4a it is possible to observe two different emissions of sample 1: one centered on 330 nm for excitation at 260 nm; and a second one centered on 430 nm for excitation at 220 nm. The emission at 330 nm is attributed to F⁺ centers [11,14]. The weak emission around 425 nm should be attributed to the F color centers. The maximum emission of F centers in sapphire is normally around 413 nm for excitation at 205 nm [11,14], unfortunately the excitation lamp of the experimental setup emit to low energy on this area to record correctly this luminescence.

In Fig. 4b, for an excitation at 230 nm a strong emission around 430 nm is observed on the sample 2. This emission is well known in Ti-doped sapphire [15–19]. The excitation wavelength corresponds to an absorption band of F⁺ centers and the emission corresponds to Ti⁴⁺ emission band. So, this emission is usually attributed to Ti⁴⁺ emission after energy transfer from F⁺ centers [16]. With the increasing of the growth rate, sample 2 presents a big amount of

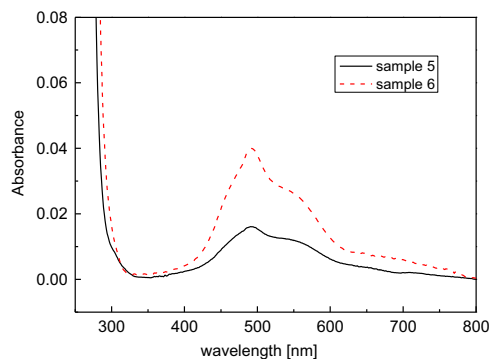


Fig. 3. Absorption spectra of the Ti-doped sapphire crystals sample 5 and 6 (see Table 1).

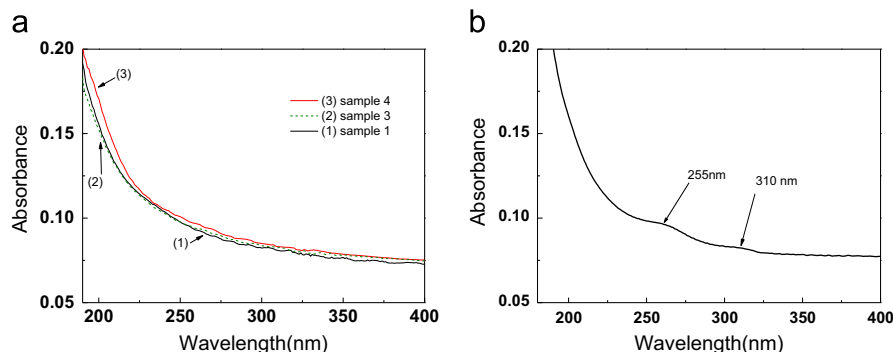


Fig. 2. Absorption spectra of the grown sapphire crystals by the Cz technique in (left) sample 1, sample 3, sample 4; and in (right) sample 2.

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