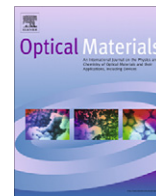




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Sapphire: Relation between luminescence of starting materials and luminescence of single crystals

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ABSTRACT

A relation between photoluminescence (PL) characteristics of different starting materials used for crystal growth and un-doped sapphire single crystals manufactured using various methods of crystal growth (Kyropolus, HEM, Czochralski, and EFG) was found. The crystals grown using the Verneuil starting material exhibited significant PL when any method of crystal growth was used. On the contrary, sapphire samples grown by the same technologies wherein the starting material was EMT HPDA^R revealed very low PL (HPDA^R is produced by EMT, Inc., with proprietary and patented technology.)

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1. Introduction

The PL of Ti- (Ti-sapphire) and Cr- (ruby) doped sapphire (aluminum oxide single crystal) have been studied repeatedly since these materials are used as laser elements [1–3]. An un-doped sapphire is the best and the most economical substrate to deposit a GaN based compound producing blue light in LED devices, but ‘parasite’ yellow–red luminescence arises in this case [4]. The PL of a sapphire substrate due to its intense illumination by the light produced by the GaN structure might be the reason for this emission. We studied here the PL properties of both extra pure un-doped sapphire crystals grown using various methods of crystal growth and starting material that were used to grow sapphire crystals.

2. Experimental

The crystals were grown by both the Low Thermal Gradient Methods (LTGM) – Kyropolus (Kyr) process and the Heat Exchange Method (HEM) and the Large Thermal Gradient Methods (HTGM) – the Czochralski (Cz) process and the Edge Defined Film Fed Growth (EFG) using different starting raw materials (“crackles”). The first source was a “crackle” produced from the Verneuil (Ver) process in which the starting Al₂O₃ powder was produced by Sasol North America-Ceralox division (SNAC) (Ver1) or Spolchene, Inc. (Ver2). The Al₂O₃ powder from SNAC was the second source. The third source was from EMT HPDA^R in which the starting raw material was Al₂O₃ from SNAC. The following system was used to mark the studied samples: (a) the crystal growth method, (b) the ingot

part where the sample was cut from (t – top, m – middle, b – bottom), and (c) the type of starting materials. When the studied crystals were grown by different manufacturers using the same method, we identified the samples by numbers 1, 2, etc. The numbers were given to the sample according to the increasing integral intensity of red PL (600–850 nm) (TRI – Total Red Intensity).

Impurities concentrations were analyzed using the Glow Discharge Mass Spectroscopy method (GDMS). The Nuclear Magnetic Resonance (NMR) and the IR absorption analysis were performed to determine the hydrogen concentration in the samples.

The PL was excited using laser radiation with excitation wavelengths $\lambda_{\text{ex}} = 473$. The density of the radiation power was near 0.4 W/cm². The radiation from a DKSL-1000 xenon lamp was also used for recording the spectra of excitation. Standard spectral equipment was used for measurement of the PL characteristics.

3. Experimental results and discussion

A short wavelength band (SB: 450–650 nm) and a red wide band (RWB: 600–850 nm with maximum position $\lambda_m = 725$ nm) were observed in the PL spectra of various starting raw materials at room temperature (RT) (Fig. 1). Besides, a narrow peak of low intensity was observed at $\lambda_m \sim 694$ nm for some of the samples. On the contrary, the PL of the studied crystals revealed only RWB and a narrow line (Fig. 2). The narrow line is a doublet whose components are shifted into a short wavelength region and there is a redistribution of intensity between them at the temperature decreasing from RT to 77 K (Fig. 2, Insert a).

The TRI, integral intensity of RWB (RWI) and the narrow line (RLI) vary in wide limits from one sample to another and there is no correlation between the RWI and RLI values. The samples can

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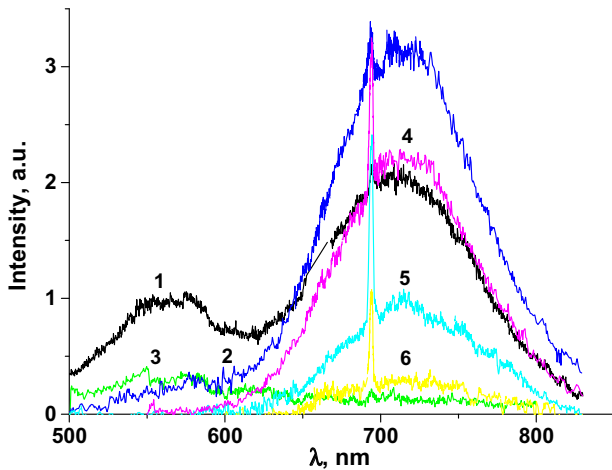


Fig. 1. PL spectra of different Vernuil (1, 2), HPDA^R (3) starting materials and crystals grown from them (4–6). Samples: #10 (Ver1) (1), #14 (Ver2) (2), #1 HPDA^R (3) and #11 (Kyr2/Ver2) (4), #7 (Kyr1-m/Ver1) (5), #3 (Kyr1-m/HPDA^R) (6).

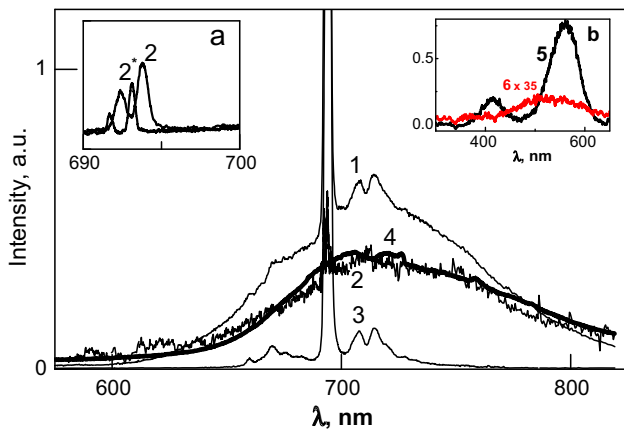


Fig. 2. PL spectra of un-doped (1–3) and Ti³⁺ ions-doped (4) sapphire crystals at 300 (1–4) and 77 K (2). The curve 4 intensity is reduced at many times to fit curve 1. Inset b. Spectra of PL excitation monitored at R – line (5) and RWB luminescence (6); RT; Samples: #23 (Cz1-m/Ver2) (1, 5, 6), #21 (EFG1/Ver2) (2) and #17 (Cz1/HPDA^R) (3).

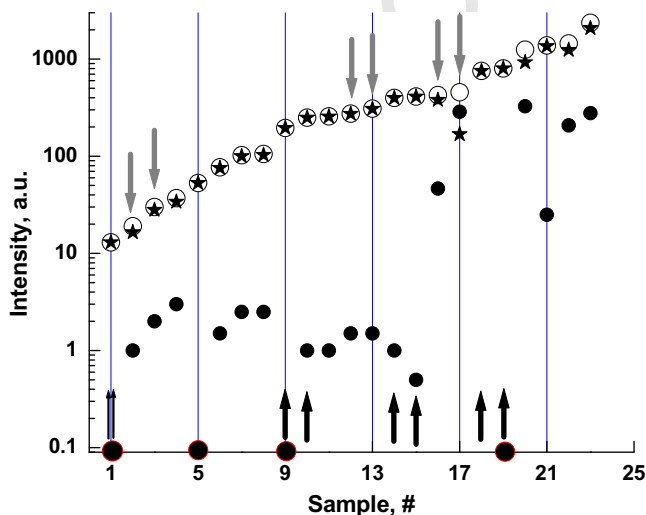


Fig. 3. Total Red Intensity (TRI - ○), integral intensity of Red Wide Band (RWI - *) and R - line luminescence intensity (RLI - ●) versus the number of samples.

be provisionally divided into 3 groups (SETs) in an increasing TRI order regarding three linear regions of TRI and RWI dependences on the sample number (Fig. 3).

The excitation spectra of the narrow line and RWB are also different. The excitation spectrum of the narrow line consists of two wide bands ($\lambda_m \approx 415$ and 517 nm) and the excitation spectrum of RWB exhibits a new band with $\lambda_m \approx 500$ nm (Fig. 2, Insert b).

Concentrations of impurity elements such as Na (<0.05), K (<0.05), Ti (<0.1), Si (<0.5), Mn (<0.05) and Co (<0.05) were below the detection limit of the GDMS in all samples. The total concentration of the measured multi-valence impurity metals was very low in all the studied samples, from ~1 to ~4 ppm. The hydrogen concentration in samples measured by the NMR method varied from tens to thousands of ppm (Table 1).

The PL and excitation properties allow us to do conclusion about the various nature of SB, RWB, and the narrow line. The disappearing SB in the spectra of single crystals is in agreement with the assumption that SB components are caused by PL of uncontrolled impurities or microprecipitates [5]. We should also point out here that the SB PL of the EMT HPDA^R material is practically absent. (This sample (#1) and other starting materials are marked with arrows directed up in Fig. 3.)

The narrow line undoubtedly is caused by the ${}^2E \rightarrow {}^4A_2$ radiation transition in Cr³⁺ ions (R-line luminescence), while the origin of the RWB is still under question. These could be: (1) manifestation of R-line vibronic sidebands, however, the details of a fine vibronic structure are observed in the background of RWB, so they cannot determine just this band (Fig. 2) [1,2]; (2) the ${}^4T_2 \rightarrow {}^4A_2$ electron-vibronic transition in Cr³⁺ ions [6–8], but the ${}^4T_2 \rightarrow {}^4A_2$ type PL becomes significant only at $T > 500$ C for ruby crystals [1–3]. (3) The PL of the Ti³⁺ ions in crystals is characterized by a similar wide band [1–3,9]. We measured a PL spectrum of the Al₂O₃-Ti³⁺ crystal where the Ti³⁺ concentration was 800–900 ppm (Fig. 2, curve 4). The Ti³⁺ concentration can be estimated as ~1–10 ppm, respectively for samples #13 and #23, assuming RWB caused only by the Ti³⁺ ions emission. These values exceed significantly the Ti³⁺ concentration (<0.1). Therefore, the Ti³⁺ ions emission cannot determine the red PL of an un-doped sapphire are insufficiently argued [10,11].

The RWI and RLI dependences on the number of samples reflect the role of the crystal growth method together with the impact of the starting material. In fact, the SET1 and SET2 groups of samples represent starting materials and crystals fabricated by various manufacturers using LTGM when samples were cut from various parts of the crystal ingot, and SET3 (the samples from #16 to #23) are the Vernuil starting materials (#18, 19) and the crystals grown by HTGM (#16 is EFG/HPDA^R, #21 is EFG1/Ver2; #17 is Cz1/HPDA^R, while #20, 22, and 23 are Cz1-t/Ver2, Cz1-b/Ver2, and Cz1-m/Ver2, respectively.) The TRI, RWI and RLI values are lesser for the samples grown using LTGM comparing with the data for the crystals grown by HTGM, and especially with regard to the Czochralski process. Then, the crystals grown using EMT HPDA^R materials are characterized by lower RWI values for each SET of samples. (These samples are marked with arrows directed down in Fig. 3.) The next samples in the region of each SET possess much higher RWI values and these crystals were grown using Vernuil starting materials (Fig. 3). It can be stated that the content of the Cr³⁺ ions in the EMT HPDA^R material is negligible as we were not able to detect any R-line luminescence there. As for the Ver2 starting material the Cr³⁺ content can be estimated using the RLI value. If its value (5 a.u., sample #18, e.g.) is compared with the RLI for crystals grown from this “crackle” (samples #21, 23) it has to be concluded that the concentration of the Cr³⁺ luminescence centers (LC) in a grown single crystal exceeds its content in the starting materials. Hence, the question arises about the reason for such changes. We did not find

Table 1
Impurity concentrations (ppm).

Sample, #	1	3	16	10	8	22
Impurity	HPDA ^R	Kyr1-m/HPDA ^R	Cz1-m/HPDA ^R	Ver1	Kyr1-m/Ver1	Cz1-m/Ver1
Ca	0.2	0.5	0.1	0.6	0.6	0.9
Mg	<0.05	<0.05	0.1	0.2	0.1	< 0.05
Zn	<0.2	<0.2	0.3	0.9	<0.2	< 0.2
Cu	<0.05	0.3	0.1	<0.05	1.0	2.0
Cr	<0.04	<0.04	0.7	<0.04	<0.04	0.1
Fe	0.2	0.09	2.0	0.02	1.0	0.2
Ni	<0.1	<0.1	0.3	0.2	0.2	< 0.1
H	23	355	243	1100	635	2560

any correlation between the RWI and RLI values and the concentrations of multi-valence elements. However, the only significant difference between both various starting materials and crystals grown from them is the hydrogen concentration (Table 1).

Traditionally, the raw material of choice has been the “by-product” of the “flame fusion” or the Vernuil process (“crackle”). This process involves oxygen–hydrogen flame and one can expect that Vernuil sapphire would have a very high hydrogen concentration due to the peculiarity of the process, but it was reported early that hydrogen concentration in Vernuil sapphire was reaching only a couple of ppm [12]. Our NMR measurements have shown that the hydrogen concentration in the Vernuil starting material and crystals grown from them is reaching thousands of ppm (Table 1).

Emerging Material Technologies, Inc (EMT) has developed and patented a method for the preparation of raw materials in which alumina powder is going through plasma (the temperature of which can achieve above 10,000 °C) with the following crystallization. In this process, no hydrogen is used and the traces of water that might come from the starting aluminum oxide powder are simply vaporized together with other impurities. The hydrogen concentration measured by NMR on the HPDA^R material and the crystal grown using the HPDA^R material is very low and in order of magnitude lower than the hydrogen concentration for sapphire crystals grown by the same methods but with Vernuil starting materials (Table 1). Hydrogen atoms can facilitate transformation of LC from an passive charge state into charge state that is active in red PL. Another mechanism is that hydrogen effects the probabilities of radiation transition in LC. However, the described experimental data are insufficient to reliably discuss the physical mechanisms of hydrogen influence on the PL properties of an undoped sapphire.

4. Conclusions

The red photoluminescence (PL) of extra pure sapphire single crystals grown utilizing standard starting materials such as “crackles” prepared by the Vernuil method and a sapphire grown using

High Purity Densified Alumina (HPDA^R) was measured. The PL was excited with light which had the energy quanta smaller than the sapphire band gap energy. The red PL is a superposition of both the narrow line (R-lines) peaked near 694 nm related to ²E_g → ⁴A₂ transition in chromium ions Cr³⁺ replacing Al³⁺ ions of the sapphire matrix and wide band luminescence in the region of 600–850 nm. The origin of the red wide band luminescence has not been established yet.

Crystals grown using the Vernuil starting material exhibited significant PL. On the contrary, very low PL existed in the sapphire samples grown by the same technologies but wherein the starting material was EMT HPDA^R.

The hydrogen concentration in the Vernuil starting materials and sapphire crystals grown using Vernuil starting material was very high reaching thousands of ppm. The hydrogen concentration in HPDA^R and crystals grown using the HPDA^R starting material was lower in terms of the order of magnitude. A direct correlation between the hydrogen concentration and intensity of the red wide band luminescence was observed.

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