Optical Properties of sapphire

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Abstract:

Sapphire (single crystal aluminum oxide) is a material commonly used in optical, electronic and chemical applications due to its material properties.

Sapphire is usually used for optical applications due to its ability to transmit from the Ultra Violet (UV) wavelengths into the mid Infra-red (IR) wavelengths. The transmission characteristics of the material is determined by various factors, however the impurities content seems to play a significant role. These impurities can either come from the growth process or from the starting raw material (commonly called crackle).

We studied the effect of impurities of the starting raw material with specific interest in hydrogen's effect on the optical properties (absorption, transmission) of sapphire crystals grown by different growth techniques.

We have characterized these growth techniques into two categories:

A) Large Thermal Gradient Method: (Czochralski (Cz), Edge Defined Film Fed Growth (EFG) or Stepanov)
B.) Low Thermal Gradient Methods (Kyropoulos, Heat Exchange Method (HEM))

We used the following starting raw materials ("crackle"):

a. Vernuil crystals produced by different manufacturers
b. High purity aluminum oxide powder
c. High Purity Densified Alumina (EMT HPDA^{R}) produced by EMT, Inc thru their proprietary patented technology.

Through Nuclear Magnetic Resonance (NMR) analytical techniques, it was found that the hydrogen concentration is very high in Vernuil crystals or in aluminum oxide powder. Consequently, sapphire crystals grown using Vernuil starting material or aluminum oxide powder also have a very high Hydrogen content.

Utilizing the same NMR analytical techniques, EMT HPDA^{R} starting material showed very low Hydrogen concentration. Thus, sapphire crystals grown from EMT HPDA^{R} starting material has a very low Hydrogen content.

It was found that optical properties in sapphire crystals grown using EMT HPDA^{R} starting material are more uniform and have higher transmission than in sapphire crystals grown using as starting material aluminum oxide powder or Vernuil crystals.

Keywords: sapphire crystals, transmission, absorption, impurities, Nuclear Magnetic Resonance, Hydrogen,

Introduction

In the last few years, sapphire has become the material of choice in manufacturing blue LD and LED devices [1] and also its ability to be successfully used in the semiconductor industry as a wafer for silicon deposition to produce SOS (silicon on sapphire) [2,3]. This has caused explosive growth in the sapphire industry and has initiated efforts to understand the material science controlling its optical properties such as transmission, luminescence, etc.

Common knowledge has been that higher purity material yields greater and more consistent UV transmission with negligible solarization [4,5]. While this has always been understood, the mechanism for this effect has been theorized

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but never fully tested due to insufficient testing capability on the “as grown” finished boule. Furthermore, the IR transmission portion of sapphire spectrum has never been significantly explored to gain an understanding of what controls the transmission characteristics in this spectral range [6,7].

The best way to control the purity of sapphire had been to control the purity of the starting material. However, the control of the starting or “raw” material used to make sapphire has been limited. Traditionally, the raw material of choice has been the “by-product” of the “flame fusion” or Vernuil process typically called “crackle” [8]. This technique has improved due to the growing demand but the process of making crackle is problematic due to the “flame processing”. This process involves oxygen – hydrogen flame, causing possibility of contamination by hydrogen in grown crystals.

An alternative starting material has been aluminum oxide powder itself. However, while starting with a powder yields reasonable quality boules, the effort and reasonably poor sized boules make this process un-economical. Also, it is well known that aluminum oxide powder is a very hydroscopic material and it’s possible to absorb very large quantity of water.

Emerging Material Technologies, Inc (EMT) has developed and patented a method for the preparation of raw material in which alumina powder goes through high temperature (> 10, 000 ^{o}C) plasma in which it melts with the following crystallization into a densified product. In this process, no hydrogen is used and the traces of water that might come from the starting aluminum oxide powder is vaporized together with other impurities. This allows for production of High Purity Densified Alumina (EMT HPDA^{R}) with the purity of 99.999%.

Several analytical techniques have been developed in the past that are able to measure impurities level in sapphire to ppm limits [9,10]. The most commonly used method is Glow Discharge Mass Spectrometry (GDMS) with resolution of up to 0.01 ppm for the most elements of periodical table, excluding certain elements such as: hydrogen, carbon, and nitrogen. Hydrogen concentration has been measured using traditional IR absorption methods [11]. This method works well for materials such as fused silica and fused quartz. Hydrogen concentration in these materials reach from several ppm to several thousand ppm and it can easily and reliably be detected by IR absorption method.

One would expect that Vernuil grown sapphire would have very high hydrogen concentration due to the growth process that evolves hydrogen-oxygen flame. But surprisingly it was reported by many researchers that hydrogen concentration in Vernuil grown sapphire measured by method of IR absorption reaches only couple of ppm [12,13]. The same low level of hydrogen concentration was also found in the naturally formed corundum crystals [14].

The Nuclear Magnetic Resonance (NMR) method has been known for a long time but was only recently successfully applied to measure low concentration of hydrogen in nominally anhydrous minerals [15]. In this work, we applied for the first time NMR method, together with the traditional IR absorption method to sapphire crystals grown by different growth techniques and utilizing different starting materials .

The crystal growth methods might be divided into 2 groups determined by the thermal gradient at solid/liquid interface [16]. Large Thermal Gradient Methods (HTGM) used to grow crystals are the Czochralski process, Edge Defined Film Fed Growth (EFG) / Stepanov method and Horizontally Directed Solidification Method (Bagdasarov method). In these methods the thermal gradient at the solid /liquid interface is reaching up to 100 ^{o}C per cm.
Low Thermal Gradient Methods (LTGM) to grow crystals are the Heat Exchange Method (HEM) and Kyropolus process. In these methods thermal gradient at solid/liquid interface is reaching up to 1-2 ^{o}C per cm. Both groups of crystal growth methods are currently applied to grow sapphire crystals.

Sapphire samples for measurements were made using sapphire crystals grown by HTGM and LTGM methods utilizing different raw materials:

a.) Vernuil crystals
b.) alumina powder
c.) EMT HPDA^{R}.

We also determined the level of impurities using Glow Discharge Mass spectrometry (GDMS). Transmission and absorption data were measured in all sapphire samples over the range of 200 nm up to 7000 nm.

It is theorized that the transmission characteristics of sapphire are controlled by its growth technique AND starting raw material impurity content [5,6,17]. These impurities control solarization and transmission characteristics throughout the entire spectral region. By controlling and verifying the impurity content (including hydrogen content) of the starting raw material, low impurity content sapphire crystals can be grown and verified.

We found out that hydrogen content plays a critical role in controlling impurities, the lower the hydrogen impurity content the better the transmission characteristics of the material throughout the transmission spectrum!

Experimental Procedure

Sapphire crystals studied in this work were grown by both HTGM and LTGM using three different starting raw materials.

1.) The first source was "crackle" produced from the flame fusion or Vernuil process in which starting aluminum oxide powder was high purity material produced by Sasol North America-Ceralox division, or Spolchene, Inc.

2.) The second source was from aluminum oxide powder from Sasol North America-Ceralox division.

3.) The third was from EMT HPDA^{R} in which the starting raw material was Sasol North America-Ceralox division aluminum oxide powder.

Samples were processed into randomly oriented polished sapphire windows of approximately .500" diameter x 10 mm thick.

All samples were analyzed using Glow discharge mass spectroscopy method (GDMS).
The content of Hydrogen in all samples was measured using:

A) Nuclear Magnetic resonance (NMR) measurements of hydrogen (^{1}H) were done using Brinkler model. Hydrogen proton concentration was determined by integral intensity of the obtained peaks. Crystal of natural muscovite with hydrogen content of 40000 ppm was used as standard.

B.) IR transmission spectra were measured using IR Bruker spectrometer. IR spectrum was recorded with resolution of 6 cm^{-1}. Initially, the spectrum without sapphire samples was recorded. Then transmission spectrum with the sample was recorded. Transmission of the sapphire samples were determined by dividing the spectrum obtained with the sample against the spectrum obtained without sample using Bruker Optics Software.

Results and Discussion

Results of impurities concentrations measurements including hydrogen are presented in table 1. As can be seen from this table starting materials and grown crystals demonstrate very low impurities concentration excluding hydrogen, Total impurities concentration not considering hydrogen is reaching only couple of ppm. In contrary hydrogen concentration in Vernuil crystals, alumina powder and corresponding sapphire crystals grown by different methods show very large hydrogen concentration reaching thousands of ppm when measured using NMR method. One can see that hydrogen concentration measured on the same samples but using method of IR absorption show very low hydrogen concentration. Hydrogen concentration measured using IR absorption method is in agreement with previously reported results for hydrogen content in sapphire crystals measured by the same method of IR absorption [12-14]. NMR method should be considered as a direct method to measure quantity of hydrogen protons regardless of the position that hydrogen atom can occupy in aluminum oxide lattice. In contrary, IR absorption method can be considered as an indirect method to measure hydrogen content. Probably for aluminum oxide (sapphire) IR absorption method is an inappropriate method to determine real hydrogen concentration and more reliable results are obtained using NMR method or any other direct methods.

Hydrogen concentration in EMT HPDA^R starting material and crystals grown utilizing starting material is very low and in orders of magnitude lower then hydrogen concentration for sapphire crystals grown by the same methods but with Vernuil starting material (table 1).

Table 1.
The impurity content of the sapphire samples measured by GDMS, IR and NMR methods

Sample	**1**	**2**	**3**		**4**	**5**	**6**		**7**	**8**		**9**	**10**
	Starting material				**HTGM 1**				**LTGM 2**			**LTGM 3**	
	ppm	**ppm**	**ppm**		**ppm**	**ppm**	**ppm**		**ppm**	**ppm**		**ppm**	**ppm**
Na	**4**	**<0.05**	**<0.05**		**1**	**<0.05**	**<0.05**		**<0.05**	**<0.05**		**<0.05**	**<0.05**
Mg	**2**	**0.1**	**<0.05**		**0.5**	**<0.05**	**0.2**		**0.1**	**<0.05**		**0.1**	**<0.05**
Si	**5**	**<0.5**	**<0.5**		**<0.5**	**<0.5**	**<0.5**		**<0.5**	**<0.5**		**<0.5**	**<0.5**
K	**2**	**0.5**	**0.1**		**0.5**	**<0.05**	**<0.05**		**<0.05**	**<0.05**		**<0.05**	**<0.05**
Ca	**3**	**0.1**	**0.2**		**0.9**	**0.9**	**0.6**		**0.6**	**0.5**		**0.8**	**0.6**
Ti	**<0.1**	**<0.1**	**<0.1**		**<0.1**	**<0.1**	**<0.1**		**<0.1**	**<0.1**		**<0.1**	**<0.1**
Cr	**<0.1**	**<0.04**	**<0.04**		**<0.04**	**0.4**	**0.7**		**<0.04**	**<0.04**		**<0.04**	**<0.04**
Mn	**0.1**	**<0.05**	**<0.05**		**0.07**	**<0.05**	**<0.05**		**<0.05**	**<0.05**		**<0.05**	**<0.05**
Fe	**0.1**	**0.02**	**0.2**		**1**	**0.1**	**2**		**1**	**0.09**		**1**	**0.02**
Co	**0.1**	**<0.05**	**<0.05**		**<0.05**	**<0.05**	**<0.05**		**<0.05**	**<0.05**		**<0.05**	**<0.05**
Ni	**0.2**	**0.2**	**<0.1**		**0.5**	**<0.1**	**0.3**		**0.2**	**<0.1**		**0.3**	**<0.1**
Cu	**0.05**	**0.1**	**0.1**		**1**	**0.2**	**0.2**		**1**	**0.3**		**1**	**0.3**
Zn	**0.4**	**0.3**	**<0.2**		**1**	**1**	**0.9**		**<0.2**	**<0.2**		**0.7**	**0.5**
Total	**16.9**	**1.5**	**0.6**		**6.7**	**2.6**	**4.9**		**2.9**	**0.89**		**3.9**	**1.42**
H by IR	**N/A**	**2.3**	**N/A**		**<0.2**	**0.3**	**0.3**		**<0.2**	**<0.2**		**12**	**<0.2**
H by NMR	**97000**	**1100**	**23**		**2560**	**919**	**243**		**635**	**355**		**807**	**410**
Sample history													
1. Aluminum oxide powder ,SPA gamma, produced by Sasol North America													
2. Vernuil crystal													
3. EMT HPDA^R													
4. sapphire grown by HTGM from Vernuil starting material, middle part of the crystal													
5. sapphire grown by HTGH from Vernuil starting material, bottom part of the crystal													
6. sapphire grown by HTGM from EMT HPDA^R starting material, middle part of the crystal													
7. sapphire grown by LGTM from Vernuil starting material, middle part of the crystal													
8. sapphire grown by LTGM from EMT HPDA^R starting material, middle part of the crystal													
9. sapphire grown by LTGM from Vernuil material, middle part of the crystal													
10. sapphire grown by LTGM from EMT HPDA^R material, middle part of the crystal													

Typical NMR spectrum for hydrogen atoms are presented in fig.1. The peaks in these figures are very broad ranging in interval of chemical shift from 150 ppm to -150 ppm. Wide peaks signify that hydrogen atoms have strong H-H dipolar coupling forming H_2O, CH_2, CH-CH, CH_3, etc bonds. Unfortunately we were not able to measure carbon and nitrogen concentrations as they cannot be measured by GDMS.

The central narrow line in the NMR spectrum represents uncompensated hydrogen atoms and absorbed water. The integral intensity of this line is very low and does not make a large contribution into total integral intensity of the NMR spectrum

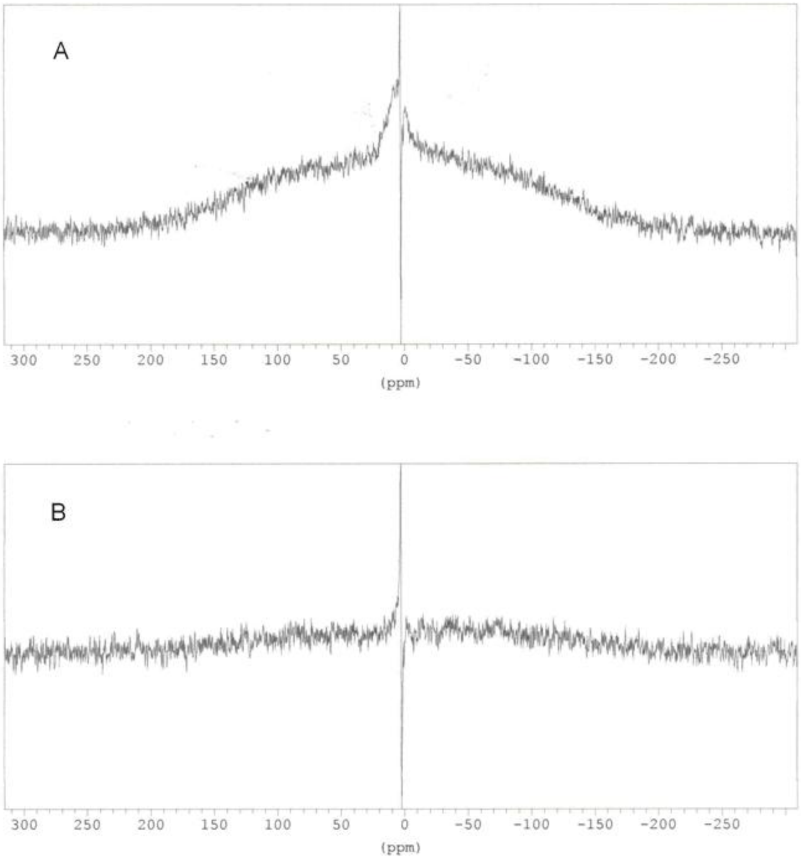


Fig.1 NMR spectrum for ^{1}H sapphire crystals grown from different starting materials
A: sapphire grown from Vernuil crackles, hydrogen concentration 2560 ppm
B: sapphire grown from EMT HPDA^R , hydrogen concentration 243 ppm

On fig 2, 3 we present the result of IR absorption measurements in sapphire samples grown by different methods. As can be seen from these figures, Vernuil crystals and sapphire crystals grown using Vernuil crackles show significant absorption in the range of 3600-2800 cm^{-1} (2500-3500 nm). In Vernuil crystals these peaks are narrow that according to [12, 13] can be attributed to OH groups that are related to cations in valence state +4 (Si, Ti, etc). Sapphire crystals grown from Vernuil starting material in addition demonstrate wide absorption with peak at 3020 nm that according to [12,13] can be attributed to OH groups that are related to cations in valence state +2 (Ca, Mg, Mn, etc).

No significant absorption was observed in sapphire crystals grown by the same methods but from EMT HPDA^R starting material (fig.3).

Hydrogen concentration calculated from these absorption data for sapphire samples is orders of magnitude lower than obtained from direct NMR measurement. It shows that IR absorption method does not provide correct information if applied for sapphire crystals.

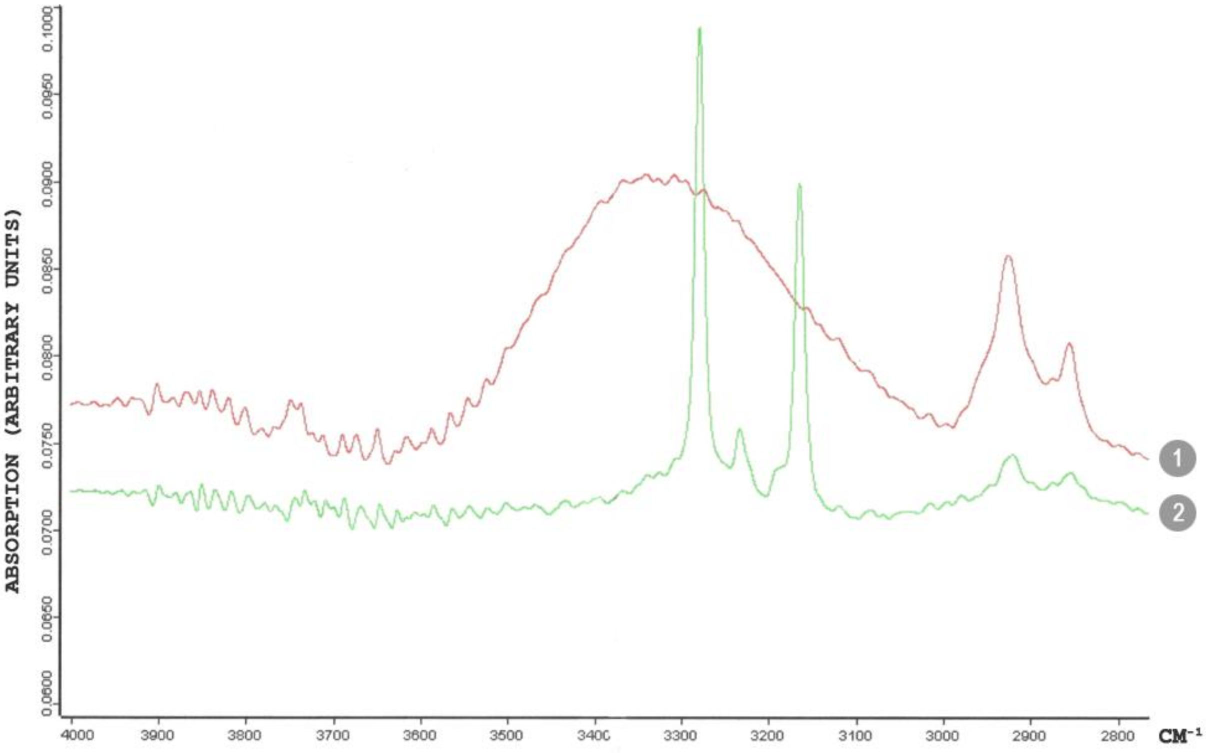


Figure. 2

1 (Red): sapphire crystal grown by LTGM using Vernuil starting material, hydrogen concentration measured by IR method - 12 ppm

2 (Green): Vernuil grown sapphire crystal, hydrogen concentration measured by IR method - 2.3 ppm

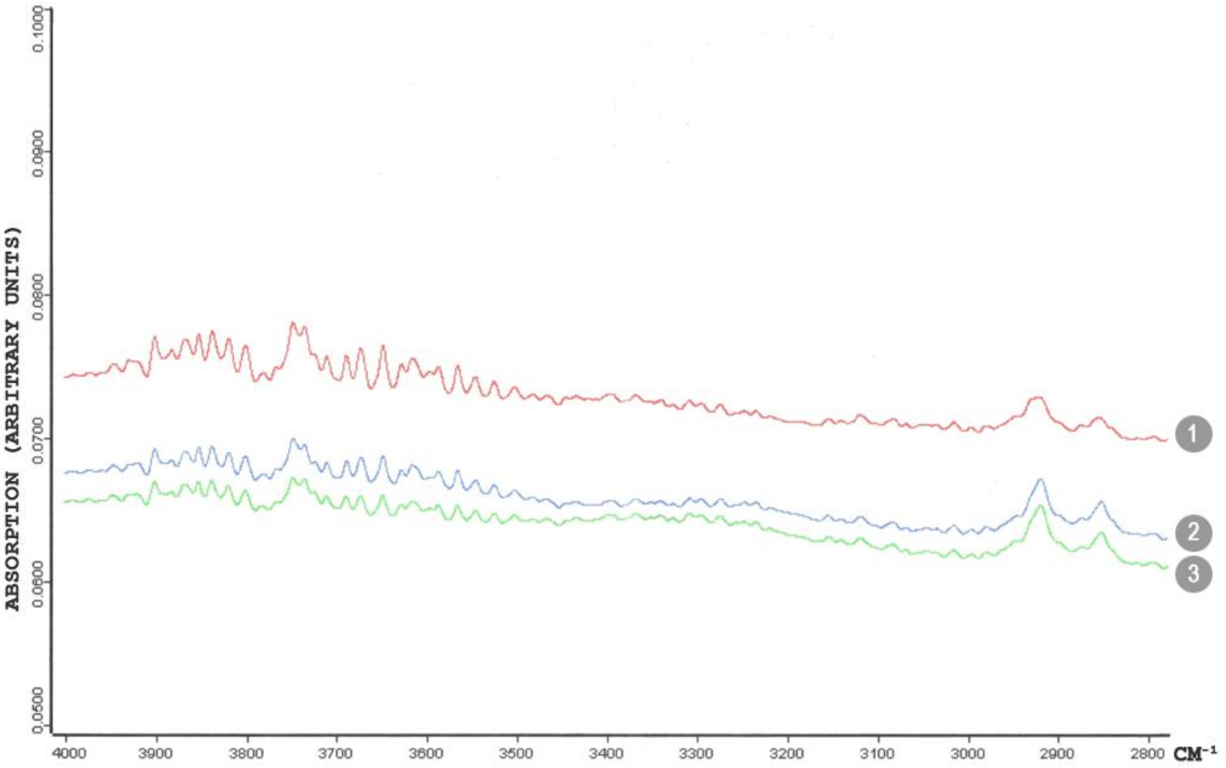
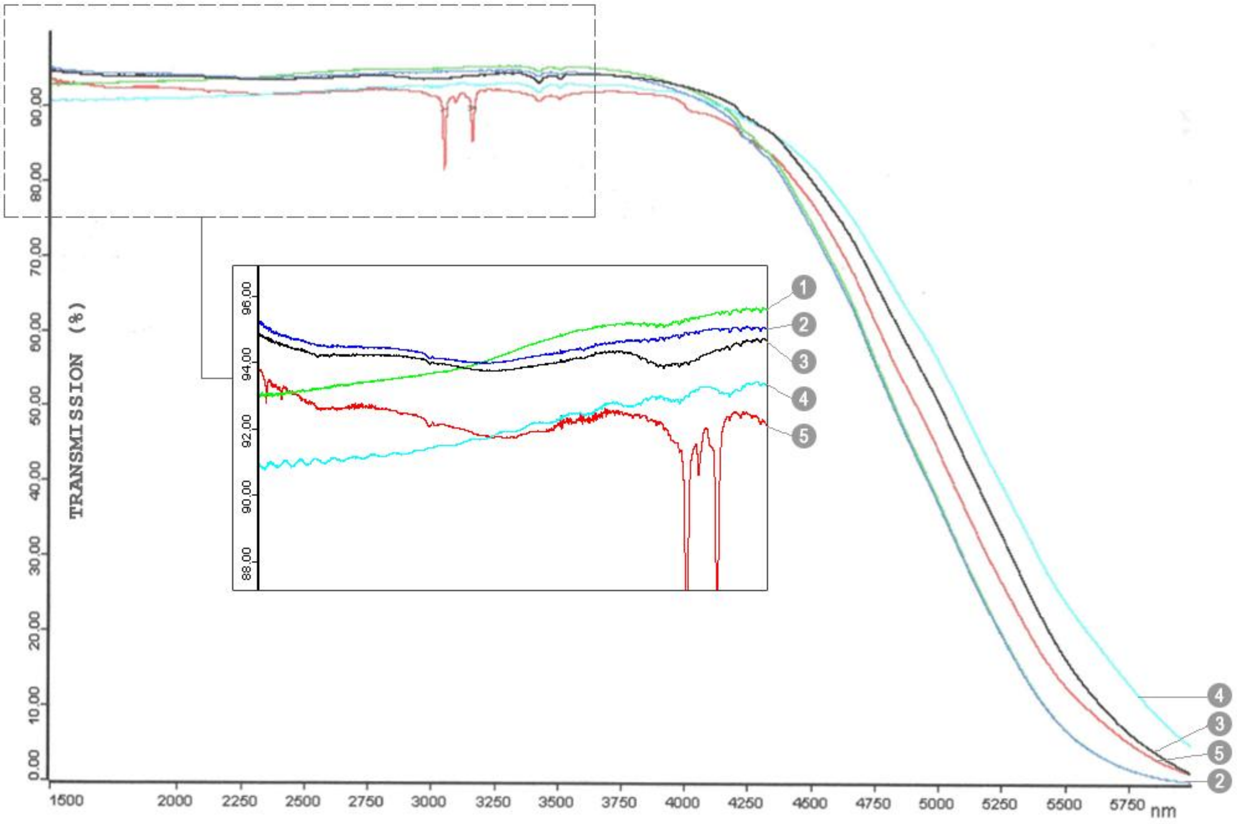


Figure. 3

IR absorption sapphire crystal grown from EMT HPDA^R starting material:
1(red) - grown by HTGM method, **2**(blue), **3**(green) -grown by LTGM method, samples cut from different parts of the same crystal
Hydrogen concentration measured by IR method < 0.2 ppm

On fig 4 and 5 we represent IR transmission data for sapphire samples grown by one of the LTGM but with the different starting materials – Vernuil (Fig.4) and EMT HPDA^R (Fig.5). As can be seen from fig. 4 there is significant variation in transmission for sapphire samples cut from different parts of the crystal boule when Vernuil grown crackle is the starting material. This variation in transmission can reach up to 10 -15% especially in the infrared region. Transmission data for the sapphire samples grown by the same method and utilizing the same growth furnaces but grown from EMT HPDA^R starting material demonstrated uniformity throughout the crystal (fig.5). Similar observations were made in all groups of crystals grown by LTGM or HTGM methods. Sapphire crystals grown from Vernuil starting material or aluminum oxide powder demonstrated significant variation in transmission throughout the crystal whereas crystals grown using EMT HPDA^R starting material show no variation.
Additionally, crystals grown from EMT HPDA^R starting material always demonstrated higher transmission compared to crystals grown utilizing Vernuil crackles or alumina powder.

The precise physical mechanism by which absorption in the IR range occurs is not completely understood. It is known [7] that impurities might produce absorption in sapphire crystals leading to decrease in transmission in IR range. In comparing trace elements concentrations in sapphire crystals grown by different methods and utilizing different starting materials (table 1) one might conclude that there is only one significant difference in impurity concentration- hydrogen concentration measured by NMR method. The difference in hydrogen concentration of sapphire crystals and starting materials can reach orders of magnitude. The lowest hydrogen concentration is in EMT HPDA^R starting material (20-30 ppm) and sapphire crystals grown from EMT HPDA^R starting material. In Vernuil crystals and sapphire crystals grown from Vernuil starting material, the hydrogen concentration is reaching about 1000 ppm. It is unclear how hydrogen might effect on transmission properties of sapphire and more investigation is required.



<u>**Figure. 4**</u>

IR transmission of the samples from different parts of a crystal grown by a LTGM with Vernuil crackle as the starting material.

<u>**Note:**</u> **5**(red) is a Vernuil crystal itself

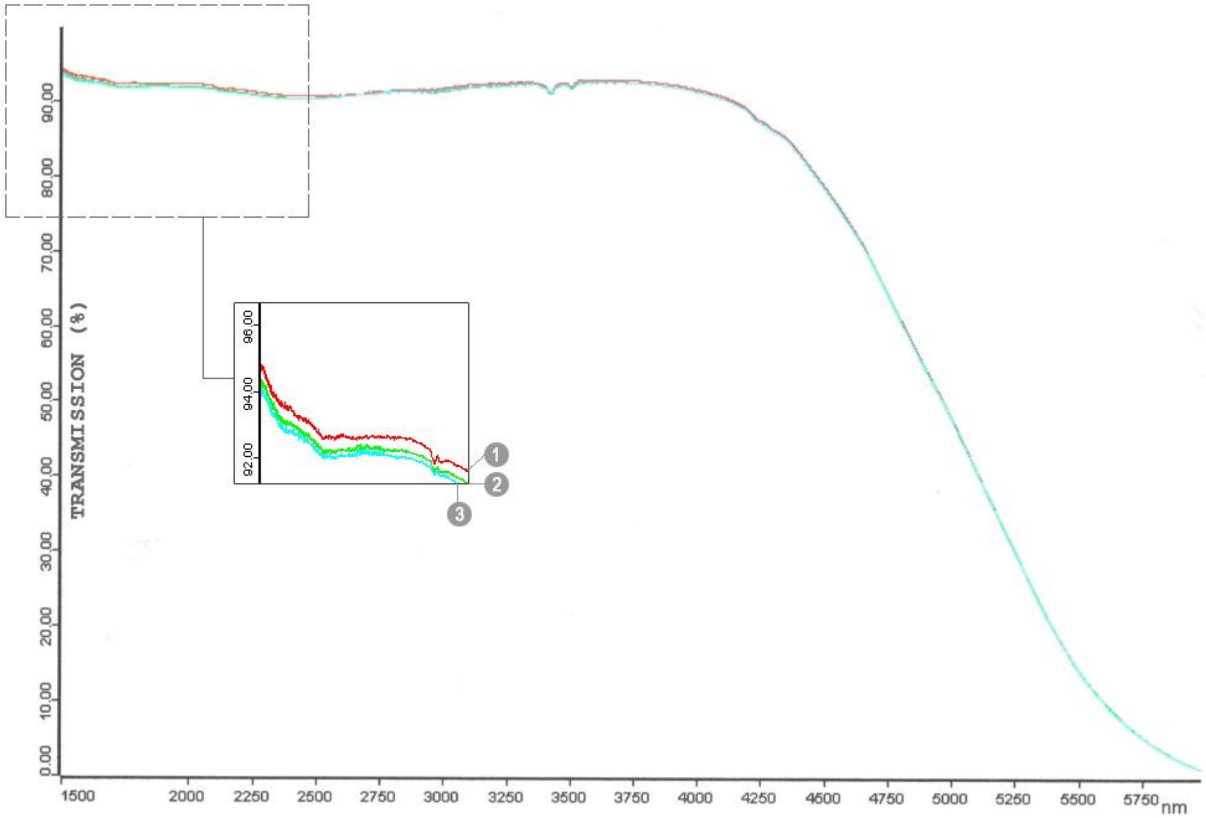


Figure 5

IR transmission of sapphire crystals grown by LTGM with EMT HPDA^R starting material.

Samples were taken from different locations

1(red): top part of the crystal,

2(green): middle part of the crystal,

3 (blue): bottom part of the crystal

We also studied UV transmission from 200 nm in all selected samples (fig 6-8). It's known [5, 17] that absorption in the UV range can be caused by impurities. The transmission data shows there is not significant absorption in all samples regardless of starting material confirming that impurities level except hydrogen is very low in all samples. However, the transmission in sapphire crystals grown from EMT HPDA^R starting material is higher and more uniform than from crystals grown from Vernuil crackles or alumina powder (Fig.8). Once again, we would like to emphasize that the hydrogen concentration is significantly different in these groups of crystals. Hydrogen does not easily evaporate from the grown crystals regardless it is Large Thermal Gradient Method or Low thermal Gradient method.

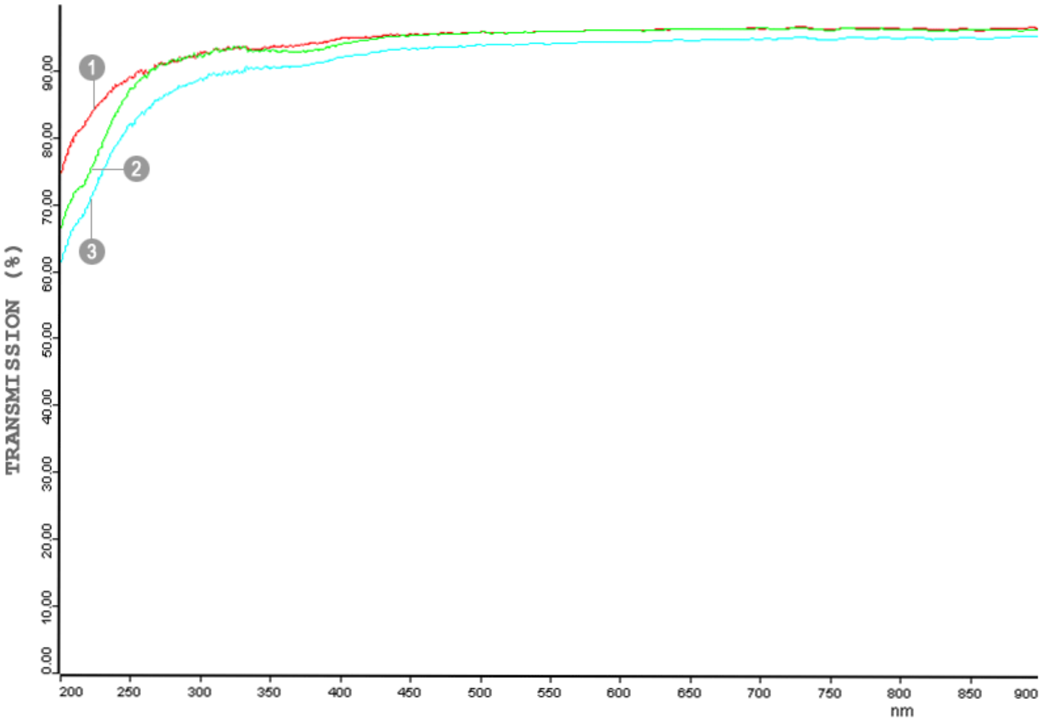


Figure 6

UV transmission of sapphire crystals grown by LTGM with Vernuil starting material

This graph shows variability in the ultraviolet region based upon geographic location within the boule.

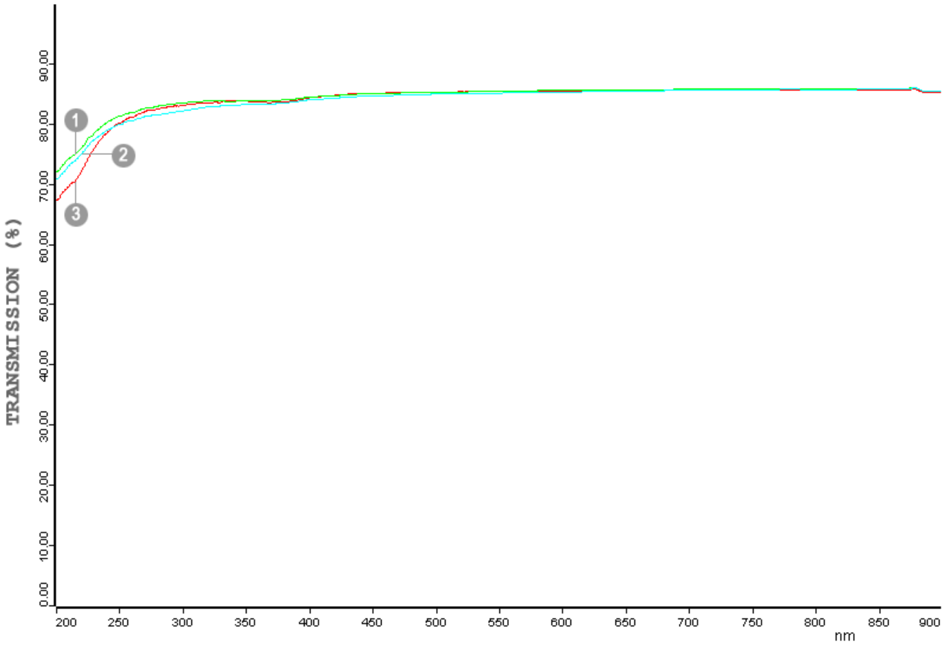


Figure 7

UV transmission of sapphire crystals grown by LTGM with EMT HPDA^R starting material

This graph shows consistent UV transmission regardless of sample location within the crystal

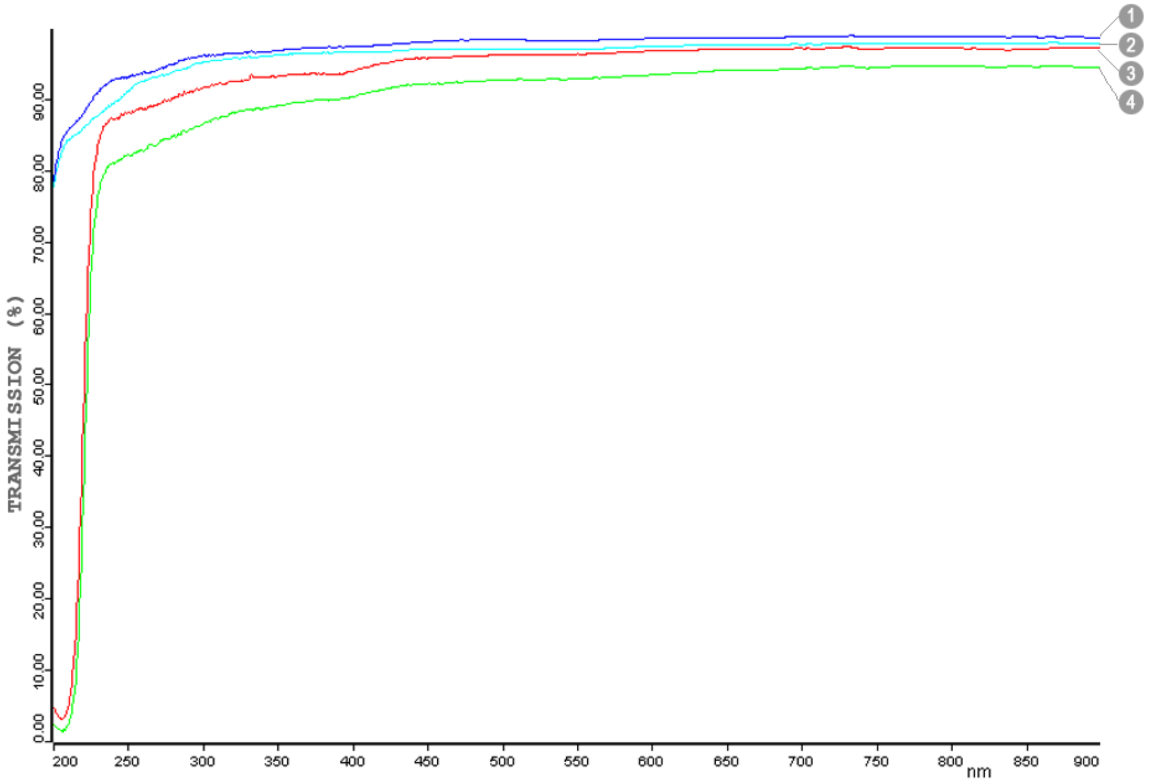


Figure 8

UV transmission of sapphire crystals grown by HTGM with different starting materials.
Red (3), green (4), light blue (2) – Vernuil starting material, samples taken from different parts of the crystal
Dark blue (1) - EMT HPDA^{R} starting material

Conclusions

The Hydrogen concentration in sapphire is much higher than was considered in previous works where only IR methods were applied. Furthermore, IR absorption methods do not reflect real hydrogen concentration in sapphire crystals.

NMR methods can be successfully used to determine hydrogen content in sapphire crystals and raw material.

It was shown that hydrogen concentration in sapphire crystals grown by the Vernuil process and sapphire crystals grown from Vernuil “charge” is very high (up to thousands ppm). This high hydrogen concentration is due to the nature of the Vernuil growth process which involves hydrogen. The hydrogen in this starting material is not removed in subsequent HTGM or LTGM crystal growth processes.

EMT HPDA^{R} starting material and sapphire crystals grown from EMT HPDA^{R} starting material have very low hydrogen concentration that is confirmed by NMR analyses.

Sapphire crystals grown from Vernuil starting material or aluminum oxide powder show lower transmission from the UV to IR compared to crystal grown utilizing EMT HPDA^{R} starting material.

Crystals grown from Vernuil starting material are not uniform in transmission throughout the boule whereas sapphire crystals grown from EMT HPDA^{R} material have excellent transmission uniformity.

Based on the data, Hydrogen concentration is the only impurity which has varied amongst the samples tested. Therefore, hydrogen content is theorized to cause the transmission properties deterioration shown.

Hydrogen concentration in sapphire crystals grown from Vernuil starting material varies throughout the crystal. The wide hydrogen proton (H^{+1}) NMR spectrum suggests that hydrogen is forming some additional bonds with other impurities including: carbon and nitrogen suggesting that hydrogen serves as charge compensator to the impurities with the charge different than the charge of aluminum or oxygen that forms the sapphire lattice.

Further investigation is required in order to determine the role of hydrogen impurity concentration on the optical properties of sapphire, and new analytical techniques need to be used to determine the hydrogen content

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