(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
12 February 2004 (12.02.2004)

PCT

(10) International Publication Number
WO 2004/013061 A1

(51) International Patent Classification[7]: C03C 3/06, 4/00

(21) International Application Number:
PCT/EP2003/007914

(22) International Filing Date: 19 July 2003 (19.07.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2002-223673 31 July 2002 (31.07.2002) JP

(71) Applicants *(for all designated States except US)*: **HERAEUS QUARZGLAS GMBH & CO. KG** [DE/DE]; Quartzstrasse 8, 63450 Hanau (DE). **SHIN-ETSU QUARTZ PRODUCTS CO., LTD.** [JP/JP]; Shinjuku San-Ei Bldg. 22-2, 1-chome Nishi-Shinjuku, Shinjuku-ku, Tokyo 160-0023 (JP).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **FUJINOKI, Akira** [JP/JP]; 1-6-12, Midorigaoka-nishi, Koriyama-shi, Fukushima 963-0701 (JP). **NISHIMURA, Hiroyuki** [JP/JP]; 6-201-8, Kaisei, Koriyama-shi, Fukushima 963-8851 (JP). **YOSHIDA, Kunio** [JP/JP]; 18-8, Kayashima-minami-machi, Neyagawa-shi, Osaka 572-0825 (JP).

(74) Agent: **KÜHN, Hans-Christian**; Heraeus Holding GmbH, Patent Department, Heraeusstrasse 12-14, 63450 Hanau (DE).

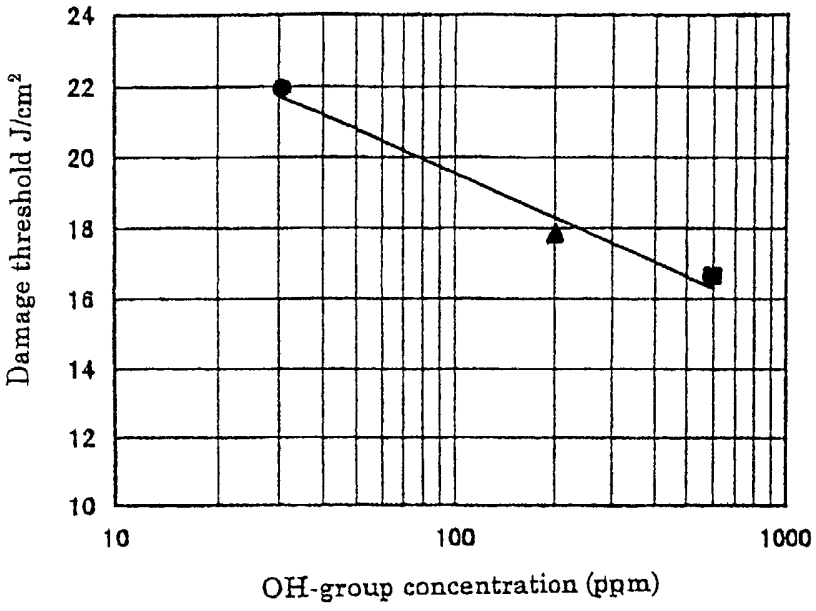
(81) Designated State *(national)*: US.

(84) Designated States *(regional)*: European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: SYNTHETIC QUARTZ GLASS OPTICAL MATERIAL FOR YAG LASER WITH HIGHER HARMONIC



(57) Abstract: It is an object of the present invention to provide synthetic quartz glass optical materials suitable for use in YAG of higher order harmonics. The damage threshold value in J/cm^2 (energy density at which cracks occur generated by irradiation) is to be considered when synthetic quartz glass material is irradiated with YAG laser of third or higher order harmonics with single pulses or continuously. Regarding a synthetic quartz glass optical material in use for the optical parts constituting the prism and lens used in a laser beam machine, this invention provides a synthetic quartz glass material suitably used for the YAG laser with the third or higher order of harmonic, choosing the following conditions: OH group concentration is in the range of ≥1 to ≤300ppm; contained hydrogen molecule concentration is in the range of ≥2 x 10^{18} to ≥2 x 10^{19} molecules/cm^3; transmittance of ultraviolet rays at 245nm of wavelength is 99.9% or more; and the fictive temperature is in the range of ≥880 to ≤990°C.

WO 2004/013061 A1

Synthetic Quartz Glass Optical Material for YAG Laser with Higher Harmonic

Technical Field of the Invention

The present invention relates to a synthetic quartz glass optical material for use in optical members such as prisms and lenses equipped in a laser-beam processing machine, and it relates to a synthetic quartz glass optical material suitably used for the YAG laser with the third or higher order harmonics.

Prior Art

For laser processing such as cutting or perforation of ceramics and metals using laser beams of high power output, carbon dioxide gas laser has been mainly used heretofore. However, with increasing fineness in processing, laser radiations with shorter wavelength are being used. Moreover, in case laser radiations with longer wavelength are used, deterioration due to the heat generated from processed parts was sometimes found to be problematic, and recently, more ultraviolet (UV)-emitting lasers are put into use. Furthermore, processing of plastics is now possible by use of UV lasers.

As the light source of UV laser-beam processing machines, in addition to those employing the higher order harmonics of YAG, known in the art are excimer lasers, for instance, XeCl (308 nm in wavelength) and KrF (248 nm in wavelength). These excimer lasers have advantages as such that they are capable of generating radiations of extremely high power output, and that they enable processing while minimizing damage attributed to heat.

However, most of them are used in large equipment assembled in a large scale production line, because of the facts as such that the apparatuses are expensive, and that complicated installation is necessary for the assurance of safety and for piping and the like, due to the use of corrosive gases such as chlorine and fluorine. Since YAG laser emitting higher order harmonics is a solid laser, the apparatus can be more simplified as compared with excimer lasers, and requires no gas piping and the like. Accordingly, YAG laser of higher order harmonics is prevailing as a simple apparatus. Moreover, as compared with the excimer lasers above, YAG laser of higher order is also characterized by its low photon cost, and the improvement in wave transformation device makes the laser promising.

YAG laser has its fundamental wavelength at 1064 nm, but the second order harmonics (532 nm), third order harmonics (355 nm), fourth order harmonics (266 nm), fifth order harmonics (212.8 nm) and the like are being used in processing after wave transformation. At present, mainly used are the second and third order harmonics, but in view of higher processing efficiency and smaller deterioration on processing, UV radiations are preferred, and the use of fourth order harmonics is now under consideration for practical use. Preference to fifth order harmonics and to shorter wavelengths is under way.

Higher order harmonics of YAG lasers are also characterized by that their pulse widths can be extremely shortened. At present, radiations with pulse widths ranging from nanoseconds (10^{-9} second) to picoseconds (10^{-12} second) are being used, but it is believed that radiations with pulse widths in the order of femtoseconds (10^{-15} second) will be used in future. By employing light with such short pulse widths, the influence of heat can be eliminated. Thus, in addition to the use of shorter wavelengths, the use of shorter pulses is an important tendency in the art.

Concerning the optical members for use in beam shaping and control of radiations in processing machines using YAG lasers, ordinary optical glasses

are sufficient for the fundamentals, however, for the second or higher harmonics, synthetic quartz glass is mainly employed from the viewpoint of durability and transmittance against damages. Such synthetic quartz glasses used in KrF excimer lasers with shorter wavelength have been believed usable as they are, however, problems have been found to occur for the optics used in YAG lasers with the third or higher order harmonics.

In case synthetic quartz glass used in KrF excimer lasers is used as it is in the optics of YAG lasers of third or higher order harmonics, there occurs a problem of causing failures such as the generation of sudden cracks and the like on a quartz glass before generating damages such as the emission of fluorescent light or a change in transmittance. Such cracks suddenly occurring on the optical members not only give damages impossible for repair on optical members such as lenses, but also make the entire apparatus suffer damage due to the generation of an intense scattered light, or is dangerous because, for instance, the scattered light entering human eyes damages the cornea.

In general, the damage generating on the quartz glass (optical damage) due to exposure to ultraviolet (UV) radiations having high energy is a defect denoted as E' center (E-prime center). Since E' centers generate through the destruction of S-O-Si bonds constituting the skeleton of quartz glass by the intense UV radiation and are characterized by a structure having lone pair electron remaining in the Si orbital, they are generally expressed by Si• (dot) and the like, where "•, dot" represents lone pair electron. Since the E' center has an intense optical absorption at 215 nm, an absorption band having a peak at 215 nm is observed on a quartz glass suffering damages by the irradiation of an excimer laser and the like. However, on measuring the UV transmittance characteristics of synthetic quartz glass suffering the generation of cracks attributed to third or fourth order harmonics of YAG, no absorption bands assigned to E' centers were found at the wavelength of 215 nm. In view of such cases, the mechanism of generating cracks in quartz glasses by the higher

order harmonics of YAG was found different from the mechanism of generating optical damages on quartz glasses by excimer lasers.

Problems that the Invention is to Solve

In the light of the aforementioned problems, the present inventors extensively conducted studies to develop synthetic quartz glass optical materials suitable for use in YAG of higher order harmonics. Furthermore, it has been found that it is possible to obtain a synthetic quartz glass material safely applicable to YAG laser with the third or higher order harmonics by considering the damage threshold value in case YAG of higher order harmonics is irradiated in single pulses and the damage threshold value in case YAG of higher order harmonics is irradiated continuously. When the YAG laser with the third harmonic with the pulse duration in the range of $\geqq$3n to $\leqq$5n seconds is irradiated by single pulse, damage threshold value should be 17 J/cm^2 or more, and when the YAG laser with the fourth harmonic with the pulse duration in the range of $\geqq$3n to $\leqq$5n seconds is irradiated by single pulse, damage threshold value should be 7 J/cm^2 or more. The present invention has been accomplished based on these findings. And when the YAG laser with the third harmonic with the pulse duration in the range of $\geqq$3n to $\leqq$5n seconds is irradiated by 12000 pulses continuously, the damage threshold value should be 11 J/cm^2 or more, and when the YAG laser with the fourth harmonic with the pulse duration in the range of $\geqq$3n to $\leqq$5n seconds is irradiated by 12000 pulses continuously, damage threshold value should be 2.5 J/cm^2 or more.

As a result, optimal ranges were found for OH group concentration, hydrogen molecule concentration, and fictive temperature to be followed by the synthetic quartz glass.

Means for Solving the Problems

In order to solve the problems above, the synthetic quartz glass optical material of the invention which is used in YAG lasers with higher harmonics is a synthetic quartz glass optical material for use in YAG lasers with the third or

higher order harmonics, characterized by that it has an OH group concentration in a range of 1 ppm or higher but not higher than 300 ppm, contains hydrogen molecules at a concentration of 2×10^{18} molecules/cm^3 or higher but not higher than 2×10^{19} molecules/cm^3, has a transmittance of 99.9 % or higher for ultraviolet radiation 245 nm in wavelength, and has a fictive temperature in a range of 880°C or higher but not higher than 990°C.

The concentration of chlorine contained in the synthetic quartz glass optical material above is not particularly limited, but it is preferably 20 ppm or lower.

The synthetic quartz glass optical material above is used suitably for YAG lasers with higher order harmonics in the range of from the third to the fifth harmonics.

In the synthetic quartz glass optical material above, in case single pulse of YAG laser of the third order harmonics is irradiated at a pulse width of 3 ns (10^{-9} second) or longer but not longer than 5 ns, the damage threshold value is 17 J/cm^2 or higher, and in case single pulse of YAG laser of the fourth order harmonics is irradiated at a pulse width of 3 ns or longer but not longer than 5 ns, the damage threshold value is 7 J/cm^2 or higher.

In the synthetic quartz glass optical material above, in case YAG laser of the third order harmonics is irradiated continuously for 12000 pulses at a pulse width of 3 ns or longer but not longer than 5 ns, the damage threshold value is 11 J/cm^2 or higher, and in case YAG laser of the fourth order harmonics is irradiated continuously for 12000 pulses at a pulse width of 3 ns or longer but not longer than 5 ns, the damage threshold value is 2.5 J/cm^2 or higher.

The synthetic quartz glass optical material above can be favorably used for YAG lasers emitting third harmonics with an energy density of 11 J/cm^2 or lower, a pulse width of 3 ps (10^{-12} second) or longer but not longer than 5ns, and at an oscillation frequency of 10 Hz or higher but not higher than 20 KHz.

The synthetic quartz glass optical material above can be favorably used for YAG lasers emitting fourth harmonics with an energy density of 2.5 J/cm^2 or lower, a pulse width of 3 ps or longer but not longer than 5ns, and at an oscillation frequency of 10 Hz or higher but not higher than 20 KHz.

Mode for Carrying Out the Invention

Modes for carrying the present invention are explained below, but it should be understood that these embodiments are shown only for examples and that various modifications are possible so long as they do not depart from the technological concept and idea of the present invention.

The synthetic quartz glass optical material for YAG lasers with higher order harmonics according to the present invention should be used with the OH group concentration ranging of 1 ppm or higher but 300 ppm or lower. Concerning the relation between the OH group concentration and the threshold value of laser damage, the damage threshold value increases with lowering OH group concentration. However, in case the OH group concentration is too low, for instance, in case it becomes lower than 1 ppm, defects of oxygen defective type tend to develop, and is therefore not preferred. Since the quantity of the defects of oxygen defective type is expressed by the UV transmittance for the radiation 245 nm in wavelength, it is sufficient if this value is 99.9% or higher. However, by taking the likelihood of generating oxygen defects, the OH group concentration is 1 ppm or higher, and preferably, 5 ppm or higher. In case the OH group concentration exceeds 300 ppm, on the other hand, the damage threshold value becomes relatively too high, the upper limit of the OH group concentration is preferably 300 ppm or lower, and more preferably, 50 ppm or lower.

In the present invention, the concentration of hydrogen molecules is in a range of from 2×10^{18} molecules/cm^3 or higher but not higher than 2×10^{19} molecules/cm^3, and preferably, in a range of from 4×10^{18} molecules/cm^3 or

higher but not higher than 8×10^{18} molecules/cm^3. Concerning the damage threshold value, it is necessary that the hydrogen molecule concentration is 2×10^{18} molecules/cm^3 or higher. However, the effect seems to be saturated at concentrations of 1×10^{19} molecules/cm^3 or higher. In case hydrogen molecules are incorporated at high concentration, a hydrogen treatment at pressures as high as 100 atm or higher is necessary in order to maintain hydrogen molecules at high concentration, and there occur problems concerning safety, or there generate industrial disadvantages such as that the quartz glass show high birefringence (e.g., that the birefringence exceeds 5 nm/cm) due to the treatment of quartz glass under atmosphere of high pressure.

With respect to fictive temperature, it is set in a range of 880°C or higher but not higher than 990°C. In order to set the fictive temperature to lower than 880°C, cooling at a considerably low rate (for instance, 0.5 °C/hour) is necessary, and this leads to problems such as the generation of drop in transmittance ascribed to the contamination from the furnace.

Examples

The present invention is explained in further detail below by making reference to Examples, but it should be understood that these embodiments are simply given as examples, and are by no way limiting the invention.

Examples 1 to 3

A porous quartz glass body (soot body) was obtained by introducing high purity silicon tetrachloride in an oxyhydrogen flame, and by then depositing the fine silica powder thus obtained by flame hydrolysis on a rotating base body. The soot body was heated under He atmosphere at 1150°C for 20 hours to accelerate the sintering of fine silica particles to uniformly increase the density thereof, and was then vitrified to obtain a transparent glass body by further heating it at 1500°C for 10 hours in vacuum furnace at 0.01 hPa (hecto Pascals) or lower to prepare about 2.5 kg of transparent quartz glass ingot 70 mm in

diameter and 300 mm in length.

The thus obtained synthetic quartz glass ingot was homogenized along one direction by zone melting method described below. More specifically, after welding support tubes of synthetic quartz to both ends of the ingot, the ingot was clamped with a lathe by the supports, and a melting zone was formed by heating a part of the ingot using an oxyhydrogen burner. Then, while applying differential rotary movement to both chucks of the lathe to stir inside the melting zone, the burner was moved to homogenize the entire ingot. After homogenization, the ingot was shaped into a barrel type, cut from the support tubes, and set inside a graphite mold 170 mm in inner diameter and 100 mm in height to heat the whole mold at 1800°C to obtain a quartz glass mold body 170 mm in diameter and 40 mm in thickness.

In order to remove the contaminated part, the quartz glass mold body was cut for a thickness of 5 mm from the outer peripheral portion that was brought into contact with graphite. Thus was obtained a mold body 160 mm in outer diameter and 30 mm in thickness, which was held for 20 hours at 1150°C in atmospheric furnace, and then gradually cooled to 600°C at a rate of 2°C per hour. The power source of the furnace was cut at that moment to cool the molding to room temperature (mold body (1)).

On performing purity analysis on the thus obtained synthetic quartz glass mold body by means of ICP mass spectrometer, it was found to contain 10 ppb in total of alkali metal elements of Na, Li, and K, 5 ppb or less in total of alkaline earth elements of Mg and Ca, and 5 ppb or less in total of other metallic elements of Fe, Cu, Ni, Ti, and Cr.

Four quartz glass disks each 60 mm in diameter and 30 mm in thickness were cut out from the synthetic quartz glass mold body, and hydrogen doping was performed on three of them by placing one each under high pressure

atmosphere of hydrogen at 20 atm (Example 1), 40 atm (Example 2), and 60 atm (Example 3), respectively, and heating them at 400°C for 3 weeks.

Comparative Example 1

Furthermore, the fourth quartz glass disk cut out from the mold body (1) above was subjected to hydrogen doping in a manner similar to Example 1, except for changing the hydrogen pressure to 2 atm.

Example 4

A porous quartz glass body (soot body) was obtained by introducing high purity silicon tetrachloride in an oxyhydrogen flame, and by then depositing the fine silica powder thus obtained by flame hydrolysis on a rotating base body. The soot body was vitrified by heating under He atmosphere at 1500°C for 10 hours to obtain about 2.5 kg of transparent quartz glass ingot 70 mm in diameter and 300 mm in length. After performing homogenization in one direction by zone melting in a manner similar to that described in Examples 1 to 3, the ingot was set inside a graphite mold 170 mm in inner diameter and 100 mm in height to heat the whole mold at 1800°C. Thus was obtained a quartz glass mold body 170 mm in diameter and 40 mm in thickness.

In order to remove the contaminated part, the quartz glass mold body was cut for a thickness of 5 mm from the outer peripheral portion that was brought into contact with graphite. Thus was obtained a mold body 160 mm in outer diameter and 30 mm in thickness, which was held for 20 hours at 1150°C in atmospheric furnace, and then gradually cooled to 600°C at a rate of 2°C per hour. The power source of the furnace was cut at that moment to cool the molding to room temperature (mold body (2)). Three quartz glass disks each 60 mm in diameter and 30 mm in thickness were cut out from the synthetic quartz glass mold body, and hydrogen doping was performed on one of them by placing it in a furnace maintained under high pressure atmosphere of hydrogen at 40 atm at a temperature of 400°C for 3 weeks.

Comparative Example 2

Another quartz glass disk cut out from the mold body (2) was held at 1150°C in the atmosphere for 20 hours, and was cooled to 600°C at a rate of 20°C per hour. The power source of the furnace was cut at that moment to cool the molding to room temperature. The quartz glass disk was then placed in a furnace maintained under high pressure atmosphere of hydrogen at 40 atm at a temperature of 400°C for 3 weeks to perform hydrogen doping.

Comparative Example 3

A porous quartz glass body (soot body) was obtained by introducing high purity silicon tetrachloride in an oxyhydrogen flame, and by then depositing the fine silica powder thus obtained by flame hydrolysis on a rotating base body. The soot body was subjected to dehydration treatment by heating it at 800°C for 20 hours under a mixed gaseous atmosphere containing 10 vol% of chlorine and 90 vol% He, and was vitrified by heating under He atmosphere at 1500°C for 10 hours to obtain about 2.5 kg of transparent quartz glass ingot 70 mm in diameter and 300 mm in length. After performing homogenization in one direction on the thus obtained synthetic quartz glass ingot by zone melting in a manner similar to that described in Examples 1 to 3, the ingot was set inside a graphite mold 170 mm in inner diameter and 100 mm in height to heat the whole mold at 1800°C. Thus was obtained a quartz glass mold body 170 mm in diameter and 40 mm in thickness.

In order to prevent contamination from occurring, the quartz glass mold body was cut for a thickness of 5 mm from the outer peripheral portion that was brought into contact with graphite. Thus was obtained a mold body 160 mm in outer diameter and 30 mm in thickness, which was held at 1150°C for 20 hours in atmospheric furnace, and then gradually cooled to 600°C at a rate of 2°C per hour. The power source of the furnace was cut at that moment to cool the molding to room temperature (mold body (3)). A quartz glass disk 60 mm in diameter and 30 mm in thickness was cut out from the synthetic quartz glass

mold body, and hydrogen doping was performed on one of them by placing it in a furnace maintained under high pressure atmosphere of hydrogen at 40 atm at a temperature of 400°C for 3 weeks.

Comparative Example 4

An about 2.5 kg of transparent quartz glass ingot 70 mm in diameter and 300 mm in length was obtained by introducing high purity silicon tetrachloride in an oxyhydrogen flame, and by then depositing while melting the fine silica powder obtained by flame hydrolysis on a rotating base body. Thus was obtained. After performing homogenization in one direction on the thus obtained synthetic quartz glass ingot by zone melting in a manner similar to that described in Examples 1 to 3, the ingot was set inside a graphite mold 170 mm in inner diameter and 100 mm in height to heat the whole mold at 1800°C. Thus was obtained a quartz glass mold body 170 mm in diameter and 40 mm in thickness.

In order to prevent contamination from occurring, the quartz glass mold body was cut for a thickness of 5 mm from the outer peripheral portion that was brought into contact with graphite. Thus was obtained a mold body 160 mm in outer diameter and 30 mm in thickness, which was held at 1150°C for 20 hours in atmospheric furnace, and was then gradually cooled to 600°C at a rate of 2°C per hour. The power source of the furnace was cut at that moment to cool the molding to room temperature (mold body (4)). A quartz glass disk 60 mm in diameter and 30 mm in thickness was cut out from the synthetic quartz glass mold body, and hydrogen doping was performed on one of them by placing it in a furnace maintained under high pressure atmosphere of hydrogen at 40 atm at a temperature of 400°C for 3 weeks.

The OH group concentration, hydrogen molecule concentration, chlorine concentration, fictive temperature, and transmittance for UV radiation 245 nm in wavelength for the synthetic quartz glass bodies thus obtained are given in Table 1. Measurements were made on the OH group concentration by infrared

spectroscopy, hydrogen molecule concentration by laser Raman spectroscopy, chlorine concentration by fluorescent X-ray analysis, fictive temperature by laser Raman spectroscopy, and UV transmittance by ultraviolet spectroscopy.

Table 1

	OH group concentration	Hydrogen molecule concentration	Chlorine concentration	Fictive temperature	Transmittance for radiation 245 nm in wavelength
Example 1	30 ppm	4×10^{18} mole/cm^3	8 ppm	940°C	99.9 %
Example 2	30 ppm	8×10^{18} mole/cm^3	8 ppm	940°C	99.9 %
Example 3	30 ppm	1.2×10^{19} mole/cm^3	8 ppm	940°C	99.9 %
Example 4	200 ppm	8×10^{18} mole/cm^3	5 ppm	930°C	99.9 %
Comparative Example 1	30 ppm	4×10^{17} mole/cm^3	8 ppm	940°C	99.9 %
Comparative Example 2	200 ppm	8×10^{18} mole/cm^3	5 ppm	1010°C	99.9 %
Comparative Example 3	0 ppm	8×10^{18} mole/cm^3	200 ppm	950°C	98.2 %
Comparative Example 4	600 ppm	1×10^{19} mole/cm^3	80 ppm	910°C	99.9 %

Laser Damage Test

Irradiation test using higher order harmonics of YAG laser was performed on the specimens prepared above. Schematically drawn explanatory drawing of the YAG laser damage test apparatus is shown in Fig. 2. Referring to Fig. 2, the damage test on quartz glass using higher order harmonics of YAG laser comprises converting fundamentals irradiated from YAG laser 10 into the third or fourth order harmonics using two wavelength transformation devices 12, 14, and then irradiating the transformed laser radiation to the quartz glass sample 18 in such a manner that it may be focused inside the quartz glass by using a lens 16 having relatively short focus with F = 300.

In this manner, the damage (the generation of cracks) of quartz glass is detected by the photo acoustic change caused by the irradiation. The reason why laser radiation is irradiated at a relatively short focus is that, in case irradiation is performed at a relatively long focus, or in an afocal system, self-conversion generates internally due to thermal lens effect as to make the calculation of energy density difficult. Thus, by using a short focus lens, self-conversion is avoided, and more accurate calculation of the irradiated energy density is made possible. The change in transmittance of the quartz glass is detected by photo acoustic measurement. This comprises sensing a part of the optical energy absorbed by the quartz glass sample in case laser radiation passes the sample, which is converted to acoustic energy, by means of an AE sensor (acoustic emission sensor) 20, then converting it to electric energy, and the voltage signal amplified with an amplifier 22 is observed with an oscilloscope 24 as voltage waveform. In case damage occurs on the quartz glass sample, an extremely large acoustic energy different from the ordinary state generates as to show the generation of damage at high sensitivity. After irradiation, the cracks generated on the quartz glass can be observed under the microscope.

1) Damage threshold value by irradiating third order harmonics in single pulse

Third order harmonics of YAG was irradiated in single pulses to each of the samples, and the energy density at which fine cracks generate on the quartz glass was measured. The results are given in Table 2 and Fig. 1. The damage threshold value in the table shows the energy density per pulse in J/cm^2 unit, at which cracks generated on the quartz glass by irradiation.

Table 2

Sample	Damage threshold value in J/cm^2
Example 1	17.7
Example 2	21.9
Example 3	18.9
Example 4	17.8
Comparative Example 1	15.5
Comparative Example 2	16.9
Comparative Example 3	14.0
Comparative Example 4	16.6

As shown in Table 2, favorable results for damage threshold values of 17.7 J/cm^2 or higher were obtained in Examples 1 to 4 on irradiating the third order harmonics in single pulses. However, the damage threshold values for Comparative Examples 1 to 4 were 16.9 J/cm^2 or lower. Figure 1 is a graph showing the relation between OH group concentration and the damage threshold values for Example 2 (value with a ●), Example 4 (value with a ▲) and Comparative Example 4 (value with a ■), together with primary regression line. Referring to Fig. 1, in Comparative Example 4 (with OH group concentration of 600 ppm), the damage threshold value was found to be relatively too high as compared with those of Example 2 (with OH group concentration of 30 ppm) and Example 4 (with OH group concentration of 200 ppm).

2) Damage threshold value by irradiating fourth order harmonics in single pulse

Fourth order harmonics of YAG was irradiated in single pulses to each of the samples, and the energy density at which fine cracks generate on the quartz glass was measured. The results are given in Table 3.

Table 3

Sample	Damage threshold value in J/cm^2
Example 1	8.1
Example 2	8.8
Example 3	8.6
Example 4	7.7
Comparative Example 1	5.8
Comparative Example 2	6.9
Comparative Example 3	5.1
Comparative Example 4	6.8

As shown in Table 3, favorable results of damage threshold values of 7.7 J/cm^2 or higher were obtained in Examples 1 to 4 on irradiating the fourth order harmonics in single pulses. However, the damage threshold values for Comparative Examples 1 to 4 were 6.9 J/cm^2 or lower.

3) Damage threshold value by continuously irradiating third order harmonics

Third order harmonics of YAG was irradiated for 12000 pulses at a frequency of 10 Hz to each of the samples, and the energy density at which fine cracks generate on the quartz glass was measured. The results are given in Table 4.

Table 4

Sample	Damage threshold value in J/cm^2
Example 1	12.2
Example 2	13.0
Example 3	12.7
Example 4	11.9
Comparative Example 1	8.7
Comparative Example 2	10.1
Comparative Example 3	8.2
Comparative Example 4	10.8

As shown in Table 4, favorable results for damage threshold values of 11.9 J/cm^2 or higher were obtained in Examples 1 to 4 on continuously irradiating the third order harmonics. However, the damage threshold values for Comparative Examples 1 to 4 were 10.8 J/cm^2 or lower.

3) Damage threshold value by continuously irradiating fourth order harmonics

Fourth order harmonics of YAG was irradiated for 12000 pulses at a frequency of 10 Hz to each of the samples, and the energy density at which fine cracks generate on the quartz glass was measured. The results are given in Table 5.

Table 5

Sample	Damage threshold value in J/cm^2
Example 1	2.9
Example 2	3.7
Example 3	3.2
Example 4	3.0
Comparative Example 1	1.6
Comparative Example 2	1.6
Comparative Example 3	1.5
Comparative Example 4	2.1

As shown in Table 5, favorable results of damage threshold values of 2.9 J/cm^2 or higher were obtained in Examples 1 to 4 on continuously irradiating the fourth order harmonics. However, the damage threshold values for Comparative Examples 1 to 4 were 2.1 J/cm^2 or lower.

4) Long term irradiation test using the third harmonics

Continuous irradiation of the third order harmonics of YAG laser was performed by irradiating the samples of Example 1 and Comparative Example 1 each with

10,000,000 pulses at a frequency of 1 kHz, at an energy density of 14 J/cm^2, and at a pulse width of 4.5 ns. As a result, no change was observed on the sample of Example 1, but cracks were found to generate on the sample of Comparative Example 1 on irradiating about 10,000 pulses after initiation of the irradiation as to make further irradiation impossible.

5) Long term irradiation test using the fourth harmonics

Continuous irradiation of the fourth order harmonics of YAG laser was performed by irradiating the samples of Example 1 and Comparative Example 1 each with 10,000,000 pulses at a frequency of 500 Hz, at an energy density of 2 J/cm^2, and at a pulse width of 4 ns. As a result, no change was observed on the sample of Example 1, but cracks were found to generate on the sample of Comparative Example 1 on irradiating about 8,000 pulses after initiation of the irradiation as to make further irradiation impossible.

Effect of the Invention

As described above, in the synthetic quartz glass optical materials for use as optical members such as those constituting prisms and lenses of a laser-beam processing machine, the present invention provides a synthetic quartz glass optical material suitable for use in higher order harmonics of the third order or higher of YAG laser.

Brief Description of the Drawings:

Fig.1: This drawing is a graph that shows the correlation of the OH group concentration in Example 2 and 4, and Comparison Example 4, with the damage threshold value due to the single pulse irradiation of the YAG laser with third harmonic.

Fig.2: This drawing is a rough illustration of a YAG laser damage testing apparatus.

Explanation of the Reference Numbers

10: YAG laser

12, 14: Wave transformation device

16: Lens

18: Sample

20: AE (acoustic emission) sensor

22: Amplifier

24: Oscilloscope

Claims

1. A synthetic quartz glass optical material used for the YAG laser with the third or higher order of harmonic, and especially, a synthetic quartz glass optical material for the YAG laser with higher harmonic characterized by OH group concentration in the range of ≧1 to ≦300ppm, contained hydrogen molecule concentration in the range of ≧2×10^{18} to ≦2×10^{19} molecules/cm^3, transmittance of ultraviolet rays at 245nm of wavelength with 99.9% or more, and fictive temperature in the range of ≧880 to ≦990℃.

2. A synthetic quartz glass optical material for the YAG laser with higher harmonic as claimed in Claim 1, characterized in that chloride concentration contained in the aforesaid synthetic quartz glass optical material is 20ppm or less.

3. A synthetic quartz glass optical material for the YAG laser with higher harmonic as claimed in Claim 1 or Claim 2, characterized in that the aforesaid higher harmonic of YAG laser is the third, fourth or fifth order.

Fig. 1

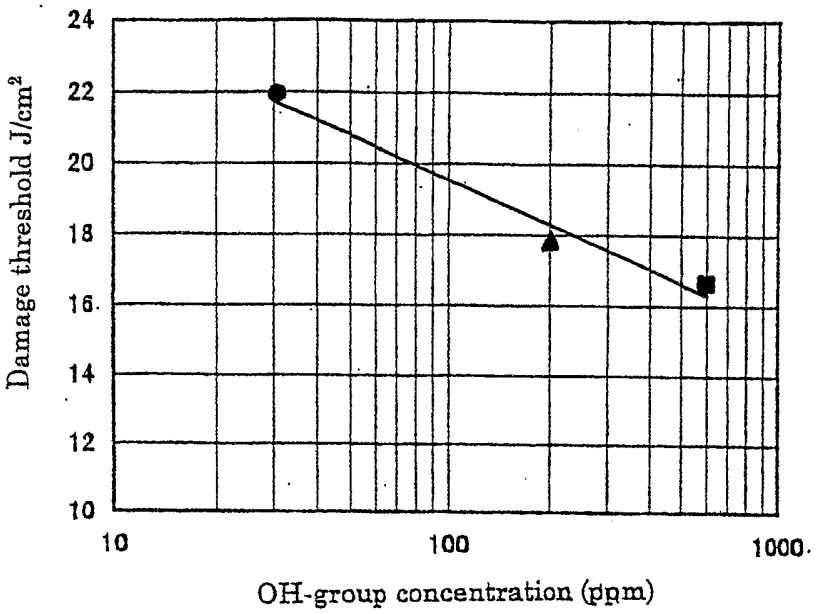
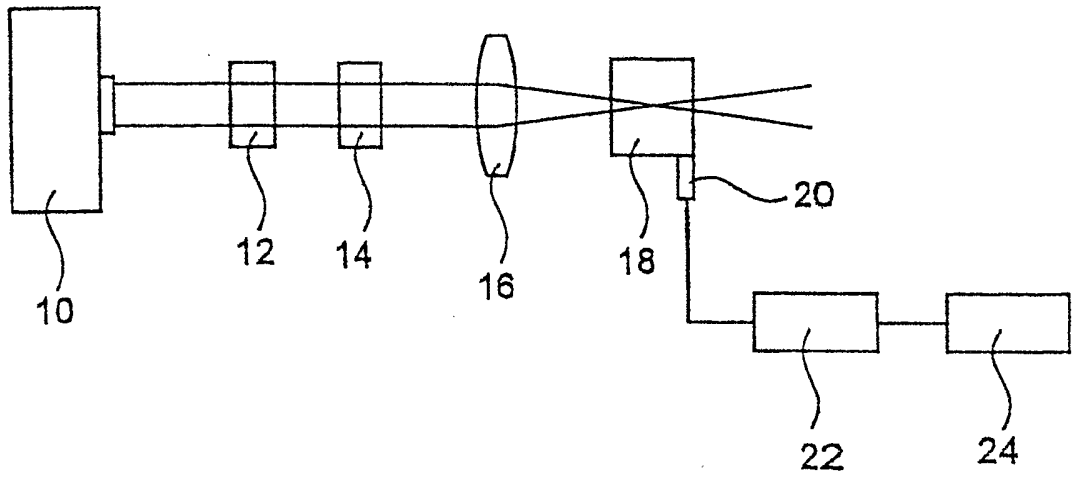

Damage threshold J/cm²
24
22
20
18
16
14
12
10
10
100
1000
OH-group concentration (ppm)

Fig. 2



INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/07914

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C03C3/06 C03C4/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C03C C03B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 143 676 A (OHASHI NORIO ET AL) 7 November 2000 (2000-11-07) column 3, line 33 - line 45 column 4, line 59 - line 67 column 7, line 21 - line 36; examples	1-3
X	US 5 325 230 A (FABIAN HEINZ ET AL) 28 June 1994 (1994-06-28) column 23, line 39 - line 66; claims; examples 12-14,18-20	1-3
X	EP 1 061 052 A (ASAHI GLASS CO LTD) 20 December 2000 (2000-12-20) claims; examples 14-16	1-3

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 October 2003	21/10/2003

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Van Bommel, L

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/07914

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 483 752 A (HERAEUS QUARZGLAS ;SHINETSU QUARTZ PROD (JP)) 6 May 1992 (1992-05-06) claims; example 2	1-3
X	PATENT ABSTRACTS OF JAPAN vol. 2002, no. 07, 3 July 2002 (2002-07-03) & JP 2002 087833 A (SUMITOMO METAL IND LTD), 27 March 2002 (2002-03-27) abstract; examples	1-3
A	WO 97 16382 A (HERAEUS QUARZGLAS ;FUJINOKI AKIRA (JP); MORI TOSHIKI (JP); NISHIMU) 9 May 1997 (1997-05-09) claims	1-3

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/07914

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 6143676	A	07-11-2000	JP	3403317 B2	06-05-2003
			JP	10324538 A	08-12-1998
			JP	11060264 A	02-03-1999
			DE	69816758 D1	04-09-2003
			EP	0917523 A1	26-05-1999
			WO	9852879 A1	26-11-1998
US 5325230	A	28-06-1994	AT	116448 T	15-01-1995
			DE	69015453 D1	09-02-1995
			DE	69015453 T2	01-06-1995
			EP	0401845 A2	12-12-1990
			JP	3088742 A	15-04-1991
			JP	6053593 B	20-07-1994
			US	5086352 A	04-02-1992
			JP	3109233 A	09-05-1991
			JP	6027013 B	13-04-1994
			JP	3101282 A	26-04-1991
			JP	6048734 B	22-06-1994
			JP	1898031 C	23-01-1995
			JP	3088743 A	15-04-1991
			JP	6027014 B	13-04-1994
EP 1061052	A	20-12-2000	AT	246154 T	15-08-2003
			DE	69909983 D1	04-09-2003
			EP	1061052 A1	20-12-2000
			WO	9938814 A1	05-08-1999
			US	2003051507 A1	20-03-2003
EP 0483752	A	06-05-1992	JP	4164833 A	10-06-1992
			JP	8025764 B	13-03-1996
			JP	4164834 A	10-06-1992
			JP	8025765 B	13-03-1996
			JP	4224130 A	13-08-1992
			JP	8000711 B	10-01-1996
			JP	4224131 A	13-08-1992
			JP	8000712 B	10-01-1996
			AT	135669 T	15-04-1996
			DE	69118101 D1	25-04-1996
			DE	69118101 T2	19-09-1996
			EP	0483752 A2	06-05-1992
			US	5410428 A	25-04-1995
			JP	2782131 B2	30-07-1998
			JP	5043267 A	23-02-1993
JP 2002087833	A	27-03-2002	NONE		
WO 9716382	A	09-05-1997	JP	9124337 A	13-05-1997
			WO	9716382 A1	09-05-1997